DEPARTMENT OF THE INTERIOR
HUBERT WORK, Secretary
BUREAU OF MINES
H. FOSTER BAIN, Director

ANALYTICAL METHODS FOR CERTAIN METALS
INCLUDING
CERIUM, THORIUM, MOLYBDENUM,
TUNGSTEN, RADIUM, URANIUM,
VANADIUM, TITANIUM,
AND ZIRCONIUM

BY
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PREFACE.

The rare metals are becoming increasingly important to our industries. Rare-metal alloys have properties which indicate that we are only on the threshold of the possibilities of their utilization, not only in making nonferrous alloys, but also as special steels. Not only are their uses broadening rapidly, but the metals are affecting our industries in other ways. The oxides and some salts are used as pigments; others have medicinal value. The pure metals are made into filaments for incandescent lamps, and targets for X-ray tubes. By their efficient use in alloys, the weight of automobiles is reduced, and the wear and tear on tires and roads is thus minimized; in machine shops they help to give greater efficiency to tools and reduce production costs. Their development has marked a milestone in the progress of civilization.

There has been considerable uncertainty regarding analytical methods for the rare metals. A great deal has been published, but the weak and the strong points of the various methods have not been investigated as carefully as is needed.

The Bureau of Mines at its Rare Metals station in Colorado necessarily had to do a great deal of analytical work in connection with the metals covered by this bulletin, which aims to give the results of the experience so acquired. No claim for much originality is made, although some published methods given have been modified, and some new ones have been developed by members of the staff. The principal methods available were studied critically, and it is to be hoped that the work will assist those interested in analytical work in connection with the metals named.
CONTENTS.

Preface................................................................. III

Part I.—Methods for quantitative separation and estimation of the alloy metals when associated with one another, by J. E. Conley......................................................... 1
  Introduction....................................................... 1
  Determination of tungsten in the presence of one or more of the other alloy metals. ...................................................... 2
    Estimation of tungsten and molybdenum........................................ 2
    Determination of tungsten, vanadium, and titanium........................ 3
    Estimation of tungsten, vanadium, and molybdenum (chromium and nickel)..................................................................... 4
  Determination of molybdenum in the presence of the other rare metals... 5
    Estimation of molybdenum, vanadium, chromium, and nickel in steel. 5
    Simultaneous estimation of molybdenum and vanadium..................... 6
  Simultaneous estimation of vanadium and other rare metals................. 6
    Vanadium and tungsten.............................................. 6
    Vanadium and molybdenum............................................ 6
    Vanadium and uranium................................................ 6
    Vanadium, uranium, and zirconium..................................... 6
    Determination of zirconium........................................... 7
    Determination of uranium and vanadium.................................... 7
    Estimation of vanadium and uranium..................................... 8
    Simultaneous estimation of vanadium and titanium......................... 8
    Estimation of uranium and vanadium..................................... 8
  Estimation of titanium in the presence of the other rare metals.......... 8
    Titanium and tungsten.............................................. 8
    Titanium and vanadium.............................................. 9
    Titanium, zirconium, and iron........................................ 9
  Systematic analysis for the alloy metals tungsten, molybdenum, uranium, vanadium, titanium, and zirconium.............................. 10
    Decomposition of steel.............................................. 10

Procedure in analysis................................................ 11
  1. Separation of silicon and tungsten from other elements... 11
  2. Treatment of residue containing W and Si.......................... 11
  3. Separation of tungsten from silicon................................ 11
  5. Treatment of solution containing iron, aluminum, molybdenum, zirconium, titanium, uranium, vanadium, chromium, arsenic, and phosphorus.......................................................... 11
  6. Precipitate containing a small quantity of iron, with all the aluminum, zirconium, titanium, molybdenum, uranium, vanadium, chromium, arsenic, and phosphorus.......................................................... 12
  7. Reprecipitation of iron, titanium, and zirconium.................. 12
  10. Iron precipitate containing titanium and zirconium................. 13

Decomposition of ores and solution of sample.......................... 13
VI

CONTENTS.

Part I.—Methods for quantitative separation, etc.—Continued.

Decomposition of ores and solution of sample—Continued. Page.

11. Acid decomposition for materials high in silica but yielding their metals to this treatment. ............................. 13
12. Ignited residue containing silica and tungsten, with small amounts of the other elements. ................................. 14
13. Main filtrate containing iron, aluminum, molybdenum, uranium, vanadium, zirconium, arsenic, phosphorus, and chromium. ......................................... 14
14. Solution of materials low in silica which do not respond to acid decomposition. ............................................. 14
15. Carbonate solution containing aluminum, tungsten, molybdenum, vanadium, uranium, chromium, phosphorus, arsenic, and silica. ........................................ 15
16. Residue from carbonate fusion of ore containing aluminum, iron, zirconium, titanium, and silica. ............................. 15
20. Hydrochloric acid solution of aluminum, molybdenum, uranium, vanadium, chromium, phosphorus, and arsenic. ...................... 15
21. Sodium carbonate-hydroxide solution containing aluminum, uranium, vanadium, molybdenum, arsenic, phosphorus, and chromium ........................................... 15
22. Filtrate containing uranium, vanadium, chromium, arsenic, and molybdenum. .................................................. 16
23. Acetic acid solution containing uranium. ......................... 16
24. Precipitate containing the lead salts of vanadium, molybdenum, arsenic, and chromium. ...................................... 17
25. Separation of arsenic and molybdenum in the precipitate of their sulphides. .................................................. 17
26. H₂S solution containing vanadium and chromium .............. 18
27. Estimation of chromium ............................................. 18

Bibliography on the quantitative separation and estimation of alloy metals. 18

Part II.—Cerium and thorium, by J. P. Bonardi. 19

Introduction .................................................................... 19

Cerium ........................................................................... 19

Thorium .......................................................................... 20

Method of decomposition and solution of the rare earths from minerals and other products ........................................... 20

Decomposition .................................................................. 20

Solution and precipitation of cerium, thorium, and the rare earths 21

Chemical properties of cerium and thorium ......................... 23

Properties and compounds of cerium .................................. 23
Properties and compounds of thorium .................................. 24

Qualitative detection of cerium ........................................ 26

Qualitative detection of cerium ........................................ 26

By means of hydrogen peroxide .................................... 26
By means of ammoniacal silver nitrate .............................. 27
By means of tartaric acid and hydrogen peroxide ............... 27
By means of lead peroxide and nitric acid ......................... 27
By means of bromine on the precipitated rare-earth hydroxides 27
CONTENTS.

Part II.—Cerium and thorium, by J. P. Bonardi—Continued.

Qualitative detection of cerium and thorium—Continued.

<table>
<thead>
<tr>
<th>Qualitative detection of thorium</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>By means of hydrogen peroxide</td>
<td>28</td>
</tr>
<tr>
<td>By means of sebacic acid</td>
<td>28</td>
</tr>
<tr>
<td>By means of sodium thiosulphate</td>
<td>28</td>
</tr>
<tr>
<td>By means of potassium iodate</td>
<td>28</td>
</tr>
<tr>
<td>By means of pyrophosphate</td>
<td>29</td>
</tr>
<tr>
<td>Radioactivity (electroscopic) and spectrum (spectroscopic) examination</td>
<td>29</td>
</tr>
</tbody>
</table>

Quantitative separation of cerium and thorium.

<table>
<thead>
<tr>
<th>Separation of cerium and thorium from the common metal bases, and from titanium and zirconium</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Separation of thorium from cerium and the rare earths</td>
<td>30</td>
</tr>
<tr>
<td>By means of hydrogen peroxide</td>
<td>31</td>
</tr>
<tr>
<td>By means of sodium thiosulphate</td>
<td>31</td>
</tr>
<tr>
<td>By means of potassium iodate from strong nitric acid solution</td>
<td>33</td>
</tr>
<tr>
<td>By means of pyrophosphate</td>
<td>34</td>
</tr>
<tr>
<td>By means of sebacic acid</td>
<td>34</td>
</tr>
<tr>
<td>Separation of cerium from cerium and other rare earths</td>
<td>35</td>
</tr>
<tr>
<td>Separation of cerium by means of alkali sulphates</td>
<td>35</td>
</tr>
<tr>
<td>Qualitative testing of the completeness of the separation by means of the absorption spectra</td>
<td>36</td>
</tr>
<tr>
<td>Separation of cerium and thorium from the rare earths by means of potassium iodate</td>
<td>37</td>
</tr>
<tr>
<td>Separation of cerium from the rare earths by means of potassium permanganate</td>
<td>37</td>
</tr>
<tr>
<td>Separation of cerium by the bromate method</td>
<td>38</td>
</tr>
<tr>
<td>Separation of cerium by treating the suspended precipitated hydroxides with bromine or chlorine gas</td>
<td>38</td>
</tr>
<tr>
<td>Treatment with an ice-cold solution of sodium peroxide</td>
<td>39</td>
</tr>
<tr>
<td>Treatment with lead dioxide or bismuth tetroxide</td>
<td>39</td>
</tr>
<tr>
<td>Treatment with persulphate</td>
<td>39</td>
</tr>
<tr>
<td>Treatment with cuprous oxide</td>
<td>40</td>
</tr>
<tr>
<td>Separation of thorium from the rare earths and from cerium by means of hypophosphates</td>
<td>40</td>
</tr>
<tr>
<td>Separation of cerium and thorium from titanium and zirconium by means of fluorides and double fluorides</td>
<td>40</td>
</tr>
<tr>
<td>Separation of cerium and yttrium earths from thorium by means of sulphite</td>
<td>41</td>
</tr>
<tr>
<td>Separation of thorium from the cerium and yttrium earths by means of the solubility of the double oxalate of thorium</td>
<td>41</td>
</tr>
<tr>
<td>Separation of thorium from the cerium earths by the carbonate method</td>
<td>42</td>
</tr>
</tbody>
</table>

Quantitative determination of cerium.

<table>
<thead>
<tr>
<th>Gravimetric determination</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Precipitation with oxalic acid, ignition to the dioxide, and weighing</td>
<td>42</td>
</tr>
<tr>
<td>Precipitation with potassium iodate, conversion to oxalate, ignition, and weighing</td>
<td>43</td>
</tr>
<tr>
<td>Volumetric determination</td>
<td>43</td>
</tr>
<tr>
<td>Iodometric method</td>
<td>44</td>
</tr>
<tr>
<td>Ferricyanide and permanganate method</td>
<td>44</td>
</tr>
</tbody>
</table>
CONTENTS.

Part II.—Cerium and thorium, by J. P. Bonardi—Continued.
Quantitative determination of cerium—Continued.

Volumetric determination—Continued. ........................................ Page
Hydrogen peroxide and permanganate method ......................... 45
Alkaline permanganate method ............................................. 46
Sodium bismuthate—permanganate method ............................... 47
Procedure for analysis ..................................................... 48
Selected methods .................................................................. 49
Lindsay Light Co.'s method for determination of cerium ........... 49
Reagents needed .................................................................. 49
Procedure when iron and titanium are present ....................... 49
When iron and titanium are absent ..................................... 50
Treatment of the sulphate .................................................... 50
Colorimetric determination of cerium ..................................... 50
Quantitative analysis for thorium .......................................... 51
Volumetric method for determining thorium ............................ 51
Gravimetric methods for determining thorium ......................... 52
Determination of thorium by precipitation of a thorium salt from
a neutral solution .............................................................. 52
Sodium thiosulphate method ................................................ 53
Analysis of monazite sand. Method used by Welsbach Co. ....... 53
Hydrogen peroxide method .................................................. 55
Potassium azoimide method .................................................. 56
Sebacic acid method ............................................................ 56
Lead carbonate method ........................................................ 56
Metanitrobenzoic acid method .............................................. 57
Fumaric acid method ........................................................... 58
Ammonium oxalate method ................................................... 60
Determination of thorium by precipitation of a thorium salt from
mineral acid solution .......................................................... 61
Precipitation of thorium by potassium iodate in nitric acid
solution ............................................................................. 61
Precipitation by sodium hypophosphate in hydrochloric acid
solution .............................................................................. 62
Precipitation of thorium by sodium pyrophosphate in hydro-
chloric or sulphuric acid solution ........................................ 63
Determination of thorium in monazite sand by Lindsay
Light Co. ............................................................................ 63
Reagents needed ................................................................... 64
Decomposition of the sand .................................................... 64
Analysis of the solution ....................................................... 64

Selected bibliography on the qualitative and quantitative chemistry of
cerium and thorium ............................................................ 66

Part III.—Molybdenum, by J. P. Bonardi ................................. 71
Introduction ........................................................................ 71
Qualitative tests ................................................................. 72
Method 1 ............................................................................. 72
Method 2 ............................................................................. 73
Method 3 ............................................................................. 73
Method 4 ............................................................................. 73
Method 5 ............................................................................. 73
Method of decomposition of ores, alloys, steels, and the general products
of molybdenum .................................................................... 74
Crushing samples for analysis ................................................ 74
Solution of sample ................................................................ 74
CONTENTS.

Method of decomposition of ores, etc.—Continued.
Solution of sample—Continued. ........................................ 74
Decomposition by acid .................................................. 74
Decomposition by fusion ............................................... 76
Alkaline leaching methods ............................................ 76
Quantitative separation of molybdenum from the group elements .. 77
Group position of molybdenum ...................................... 77
Separation of molybdenum from the members of Group I—Silver, lead, and mercury ......................................................... 78
Separation of molybdenum from the members of Group II—Division A, lead, mercury, bismuth, copper, and cadmium; Division B, arsenic, antimony, tin, and tungsten not taken out in Group I . . . 78
Separation of molybdenum from the members of Group III—Aluminum, chromium, iron, zinc, nickel, cobalt, manganese, zirconium, titanium, and the rare earths ........................................ 80
Separation of molybdenum from the members of Group IV and Group V—The alkaline earths and fixed alkalies including magnesium .............................................................. 81
General conclusion of the separation of molybdenum from the group elements and the rare metals ........................................... 81
Review of quantitative methods in general use ......................... 81
Abstracts of above methods, with comments .......................... 82
Method 1. Precipitation as the sulphide ............................ 82
   a. In cold dilute acid solution without pressure .................. 82
   b. By saturating a cold solution, slightly acid with hydrochloric or sulphuric acid, with hydrogen sulphide and heating in a pressure flask .................................................. 83
   c. Interfering elements connected with the sulphide precipitation method in acid solutions .................................................. 84
   d. Precipitation of molybdenum by saturating an alkaline solution with hydrogen sulphide, acidifying with either hydrochloric or sulphuric acid, and heating in a pressure flask . . . 84
   e. Precipitation from an alkaline solution by coagulation of molybdenum sulphide in an acid solution without pressure .... 85
   f. Conclusions concerning the sulphide methods ................. 86
Method 2. Precipitation as mercuric molybdate ..................... 86
Method 3. Precipitation as lead molybdate ......................... 87
Method 4. Titration with lead acetate ................................ 88
Method 5. Titration with potassium permanganate .................. 89
Method 6. Titration with methylene blue ............................ 91
Method 7. Titration with ferric chloride after reduction with titanium chloride ......................................................... 91
Method 8. Iodometric method .......................................... 92
Method 9. Titration with potassium iodate ......................... 93
Method 10. Colorimetric method ...................................... 93
Method 11. Determination of molybdenum by volatilization ....... 94
   a. In a current of carbon tetrachloride vapor .................... 94
   b. In a current of dry hydrochloric acid gas ...................... 94
Method 12. Liberated iodine from a molybdic solution precipitated as silver iodide ...................................................... 94
Method 13. Acidimetric method ...................................... 94
Method 14. Electrolytic method ..................................... 94
Two accurate methods of determining molybdenum .................. 95
 CONTENTS.


Gravimetric determination of molybdenum by precipitating and weighing as lead molybdate ........................................... 96
Gist of method ........................................................................... 96
Procedure for decomposition of sample by acids ....................... 96
Procedure for decomposition of sample by fusion method ......... 97
Further preparation of the solution .......................................... 98
Precipitation ............................................................................. 98
Comments on process. Procedure in presence of interfering elements. 99
Removal of lead ......................................................................... 99
Effect and removal of phosphorus, arsenic, and antimony ......... 100
Effect and removal of chromium ............................................... 101
Separation of molybdenum from large amounts of iron .......... 101
Effect of sulphuric acid on the precipitation of molybdenum by lead acetate ................................................................. 102
Experiments of Bonardi and Barrett ......................................... 102
Schoeller and Powell method .................................................... 103
Brearley method ....................................................................... 104
Effect and removal of barium, strontium, and calcium .......... 104
Influence of the rare metals uranium, zirconium, titanium, tungsten, and vanadium and any rare-earth metals occurring with molybdenum ................................................................. 105
Separation of tungsten from molybdenum ............................... 105
Separation of vanadium from molybdenum ............................. 107
Conclusions on the gravimetric method ................................. 108

Volumetric (potassium permanganate) method for determining molybdenum .............................................................. 109
Gist of method ........................................................................... 110
Procedure for acid decomposition ............................................ 110
Interfering elements .................................................................. 110
Removal of copper, arsenic, tin, and antimony ....................... 111
Removal of chromium, vanadium, and tungsten from molybdenum ................................................................. 111
Decomposition by fusion ............................................................. 111
Procedure ................................................................................ 111
Comments on the fusion decomposition method ..................... 112
Jones reductor ............................................................................ 113
Titration ..................................................................................... 115
Normality of potassium permanganate ..................................... 115
Effect of blank ........................................................................... 115
Results of first set of experiments ............................................. 116
Results of standardization ........................................................ 117
Results of second set of experiments ........................................ 117
Comments on results ................................................................. 117
Precaution against a fading end point ....................................... 118
Precautions for high-grade ore ............................................... 119
Stage of reduction of the molybdenum solution ...................... 119
Limit of accuracy ....................................................................... 120
Information for analysts ........................................................... 120
Conclusions on the volumetric method ..................................... 121
Appendix .................................................................................. 121
Analytical method used by the Bureau of Standards ............... 121
Determination of molybdenum in alloys ................................. 122
CONTENTS.


Appendix—Continued.

Analytical method used by the Bureau of Standards—Continued. Page.

Determination of molybdenum in wulfenite and molybdenite. 122
1. Method of solution of wulfenite. 122
2. Method of solution of molybdenite. 122
3. Method of analysis. 122

Preparation and standardization of solutions. 125
Ferric phosphate solution. 125
Potassium permanganate, approximately 0.1 N. 125

Bibliography on the qualitative and quantitative chemistry of molybdenum. 125

Part IV.—Tungsten, by C. W. Davis. 131

Introduction. 131

Solution or decomposition of ores and metals containing tungsten. 132
General solubility. 132
Ores and minerals. 132
Tungsten powder. 134
Ferrotungsten. 134
Tungsten steel. 134
Tungsten-chromium steel. 135
Tungsten-molybdenum steel. 135
Tungsten-nickel steel. 135
Tungsten-molybdenum-nickel steel. 135
Tungsten bronzes. 136
Slag (from manufacture of tungsten steels). 136

Qualitative analysis. 136

Detection of tungsten. 136
Detection in general. 136
Characteristic reactions. 137

Separation of tungsten from the elements found or associated with it in ores or commercial alloys. 139
General separations. 139
Arsenic and phosphorus. 139
Silica. 140
Tin. 140
Molybdenum. 141
Vanadium. 142
Titanium. 142
Chromium. 142
Miscellaneous. 142

Quantitative analysis. 143

Proposed methods for determination of tungsten. 143
General. 143

Gravimetric methods. 143
Precipitation of tungsten as tungsten acid. 143
Precipitation of tungsten as mercurous tungstate. 144
Precipitation of tungsten as tungstesates of other metals. 144
Precipitation of tungsten with organic reagents. 144
Miscellaneous. 145

Volumetric methods. 145
Colorimetric methods. 146

New methods. 146
Part IV.—Tungsten, by C. W. Davis—Continued.

Quantitative analysis—Continued.

<table>
<thead>
<tr>
<th>Proposed methods for determination of tungsten—Continued.</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ores and slags--------------------------------------------</td>
<td>147</td>
</tr>
<tr>
<td>Gravimetric methods----------------------------------------</td>
<td>147</td>
</tr>
<tr>
<td>Precipitation of tungsten as tungstic acid</td>
<td>147</td>
</tr>
<tr>
<td>Precipitation of tungsten as mercurous tungstate</td>
<td>149</td>
</tr>
<tr>
<td>Precipitation of tungsten with organic reagents</td>
<td>150</td>
</tr>
<tr>
<td>Specific gravity methods</td>
<td>150</td>
</tr>
<tr>
<td>Steel, metallic tungsten, and alloys</td>
<td>151</td>
</tr>
<tr>
<td>Gravimetric methods----------------------------------------</td>
<td>151</td>
</tr>
<tr>
<td>Precipitation of tungsten as tungstic acid</td>
<td>151</td>
</tr>
<tr>
<td>Precipitation of tungsten as mercurous tungstate</td>
<td>155</td>
</tr>
<tr>
<td>Volumetric methods-----------------------------------------</td>
<td>155</td>
</tr>
<tr>
<td>Selected methods-------------------------------------------</td>
<td>156</td>
</tr>
<tr>
<td>General</td>
<td>156</td>
</tr>
<tr>
<td>Ores and slags---------------------------------------------</td>
<td>156</td>
</tr>
<tr>
<td>Ammonia solution of tungstic acid</td>
<td>156</td>
</tr>
<tr>
<td>Résumé of process</td>
<td>156</td>
</tr>
<tr>
<td>Reactions involved</td>
<td>157</td>
</tr>
<tr>
<td>Method of procedure</td>
<td>157</td>
</tr>
<tr>
<td>Notes on the method</td>
<td>160</td>
</tr>
<tr>
<td>Hydrofluoric difference method</td>
<td>162</td>
</tr>
<tr>
<td>Résumé of process</td>
<td>162</td>
</tr>
<tr>
<td>Reactions involved</td>
<td>162</td>
</tr>
<tr>
<td>Method of procedure</td>
<td>162</td>
</tr>
<tr>
<td>Low's method</td>
<td>162</td>
</tr>
<tr>
<td>Résumé of process</td>
<td>162</td>
</tr>
<tr>
<td>Reactions involved</td>
<td>162</td>
</tr>
<tr>
<td>Method of procedure</td>
<td>163</td>
</tr>
<tr>
<td>Notes and remarks</td>
<td>163</td>
</tr>
<tr>
<td>Steels and alloys</td>
<td>164</td>
</tr>
<tr>
<td>Tungsten powder, ferrotungsten, ferrotungsten alloys and all</td>
<td></td>
</tr>
<tr>
<td>low-tungsten steels when tungsten only is required</td>
<td>164</td>
</tr>
<tr>
<td>Johnson's method</td>
<td>164</td>
</tr>
<tr>
<td>Rapid method</td>
<td>165</td>
</tr>
<tr>
<td>Tungsten steels</td>
<td>166</td>
</tr>
<tr>
<td>Method of Lord and Demorest</td>
<td>166</td>
</tr>
</tbody>
</table>

Part V.—Radium, by S. C. Lind                              | 173  |

Introduction                                               | 173  |
Use of electroscope in detecting radioactivity             | 174  |
Electrosopes for radium measurement                        | 174  |
Use of the open alpha-ray chamber for the examination of ores, tailings, and other solid materials | 178  |
Use of interchangeable electroscope in the emanation method | 178  |
Calibration of emanation electroscope                       | 180  |
Accessories for electroscope                               | 181  |
Methods of measurement                                     | 182  |
1. Alpha-ray method for solids                             | 182  |
   Rate of discharge                                        | 182  |
   Sources of error                                         | 182  |
   Comment on method                                        | 183  |

Methods of measurement—Continued.

<table>
<thead>
<tr>
<th>Procedure for radium in solution or in a soluble form</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2. Gamma-ray method of measuring radium</td>
<td>184</td>
</tr>
<tr>
<td>3. Emanation method of measuring radium</td>
<td>185</td>
</tr>
<tr>
<td>Recommended methods</td>
<td>186</td>
</tr>
<tr>
<td>Démanation</td>
<td>187</td>
</tr>
<tr>
<td>1. Solutions containing barium in large excess of the radium</td>
<td>189</td>
</tr>
<tr>
<td>2. Solutions containing little or no barium</td>
<td>189</td>
</tr>
<tr>
<td>3. Solutions containing no barium but an excess of barium precipitant, such as sulphate or carbonate</td>
<td>189</td>
</tr>
<tr>
<td>Procedure for liquids of the third class</td>
<td>190</td>
</tr>
</tbody>
</table>

- **Fusion methods** | 190  |
- **Carbonate method** | 190  |
- **Direct-fusion method** | 191  |
- **Bisulphate-fusion method** | 192  |

Method and apparatus for boiling off and transferring emanation from a solution.

- **Choice of method** | 193  |
  - Pitchblende | 195  |
  - Carnotite | 195  |
  - Carnotite residues or tailings | 196  |
  - Acid filtrates from ore extraction | 196  |
  - Barium (radium) sulphates and sulphides | 197  |
  - Filtrates with excess of sulphate or carbonate | 197  |
  - Barium (radium) chloride (or bromide) liquors or crystals | 197  |

Bibliography on radium | 197  |

# Part VI.—Uranium, by C. W. Davis

- Introduction | 199  |
- Method of decomposition or solution of uranium ores and metals | 200  |
- Solubility | 200  |

## Qualitative analysis

- Detection of uranium | 201  |
  - Radioactive method | 201  |
  - Chemical method | 202  |
  - Characteristic reactions | 202  |

- Separation of uranium from the elements found or associated with it in ores or commercial alloys | 203  |
  - General separations | 203  |
  - Alkalies and alkali earths | 204  |
  - Iron, aluminum, nickel, etc | 204  |
  - Beryllium, chromium, and zirconium | 205  |
  - Phosphorus and arsenic | 206  |
  - Molybdenum and tungsten | 206  |
  - Vanadium | 207  |
  - Miscellaneous | 208  |

- Quantitative analysis | 208  |
- Methods proposed for the determination of uranium | 208  |
  - General | 208  |
    - Gravimetric determination | 208  |
      1. Precipitation as ammonium or sodium uranate | 208  |
      2. Precipitation as uranium phosphate | 208  |
      3. Precipitation as the sulphide | 209  |
      4. Electrolytic precipitation | 209  |
      5. Miscellaneous precipitations | 210  |
    - Volumetric determination | 211  |
    - Colorimetric determination | 214  |
Part VI.—Uranium, by C. W. Davis—Continued.
Quantitative analysis—Continued.

Methods proposed for the determination of uranium—Continued.  

<table>
<thead>
<tr>
<th>Method</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ores</td>
<td>214</td>
</tr>
<tr>
<td>Gravimetric determination</td>
<td>214</td>
</tr>
<tr>
<td>Volumetric determination</td>
<td>218</td>
</tr>
<tr>
<td>Colorimetric determination</td>
<td>220</td>
</tr>
<tr>
<td>Radioactive method for ores</td>
<td>220</td>
</tr>
<tr>
<td>Metals</td>
<td>221</td>
</tr>
<tr>
<td>New methods</td>
<td>223</td>
</tr>
<tr>
<td>Selected methods</td>
<td>223</td>
</tr>
<tr>
<td>General</td>
<td>223</td>
</tr>
<tr>
<td>Ores</td>
<td>224</td>
</tr>
<tr>
<td>Bureau of Mines method</td>
<td>224</td>
</tr>
<tr>
<td>Résumé of method</td>
<td>224</td>
</tr>
<tr>
<td>Reactions involved</td>
<td>224</td>
</tr>
<tr>
<td>Method of procedure</td>
<td>225</td>
</tr>
<tr>
<td>Notes on Ledoux’s method</td>
<td>226</td>
</tr>
<tr>
<td>Remarks</td>
<td>227</td>
</tr>
<tr>
<td>Volumetric method for carnotite and vanadiferous uranium ores</td>
<td>227</td>
</tr>
<tr>
<td>Résumé of process</td>
<td>227</td>
</tr>
<tr>
<td>Reactions involved</td>
<td>227</td>
</tr>
<tr>
<td>Method of procedure</td>
<td>228</td>
</tr>
<tr>
<td>Notes on volumetric method</td>
<td>229</td>
</tr>
<tr>
<td>Remarks</td>
<td>229</td>
</tr>
<tr>
<td>Scholl’s rapid method</td>
<td>230</td>
</tr>
<tr>
<td>Résumé of process</td>
<td>230</td>
</tr>
<tr>
<td>Reactions involved</td>
<td>230</td>
</tr>
<tr>
<td>Method of procedure</td>
<td>230</td>
</tr>
<tr>
<td>Notes on the Scholl method</td>
<td>230</td>
</tr>
<tr>
<td>Remarks</td>
<td>230</td>
</tr>
<tr>
<td>Ferrouranium and alloy steels</td>
<td>231</td>
</tr>
<tr>
<td>Method of Kelley, Myers, and Illingsworth</td>
<td>231</td>
</tr>
<tr>
<td>Résumé of process</td>
<td>231</td>
</tr>
<tr>
<td>Reactions involved</td>
<td>232</td>
</tr>
<tr>
<td>Method of procedure</td>
<td>232</td>
</tr>
<tr>
<td>Notes on the method of Kelley, Myers, and Illingsworth</td>
<td>233</td>
</tr>
<tr>
<td>Remarks</td>
<td>233</td>
</tr>
</tbody>
</table>

Selected bibliography of uranium analyses.  

Part VII.—Vanadium, by J. E. Conley.  

Introduction.  

Methods of solution of ores and alloys.  

<table>
<thead>
<tr>
<th>Method</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Decomposition of ores</td>
<td>241</td>
</tr>
<tr>
<td>Treatment with mineral acids</td>
<td>241</td>
</tr>
<tr>
<td>Treatment by fusion</td>
<td>242</td>
</tr>
<tr>
<td>Decomposition of alloys</td>
<td>243</td>
</tr>
<tr>
<td>Iron and steel</td>
<td>243</td>
</tr>
<tr>
<td>Ferrovanadium</td>
<td>243</td>
</tr>
<tr>
<td>Vanadium bronzes</td>
<td>243</td>
</tr>
</tbody>
</table>

Qualitative analysis.  

Detection of vanadium.  

<table>
<thead>
<tr>
<th>Method</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen peroxide</td>
<td>244</td>
</tr>
<tr>
<td>Detection in rocks and minerals</td>
<td>244</td>
</tr>
<tr>
<td>Detection in iron and steel</td>
<td>244</td>
</tr>
</tbody>
</table>
CONTENTS

Part VII.—Vanadium, by J. E. Conley—Continued.

Qualitative analysis—Continued. ........................................... 246
Separation of vanadium from the common elements .................. 246
General comment .................................................. 246
Separation from iron ................................................ 246
Separation from iron and aluminum ................................. 247
Separation of vanadium from chromium ............................ 247
Separation from arsenic and antimony .............................. 248
Separation from $P_2O_5$ .......................................... 248
Separation from silica .............................................. 249
Separation of $V_2O_5$ from barium, calcium, zinc, and lead .... 249
Separation of vanadium from the alkalies .......................... 250
Separation of vanadium from the rare metals found or associated with it in ores or commercial alloys .... 250
Separation of vanadium from uranium ................................ 250
Separation of vanadium from molybdenum .......................... 250
Separation of vanadium from tungsten ............................ 251
Separation of vanadium from zirconium and titanium ............. 251
Quantitative analysis .................................................. 251
Methods for the gravimetric determination of vanadium .......... 251
Determination by mercurous nitrate method ........................ 251
Determination of vanadium as ammonium vanadate ............... 252
Lead acetate method .............................................. 252
Miscellaneous gravimetric methods .................................. 253
Estimation as barium pyrovanadate ................................ 253
Estimation as manganese vanadate ................................ 253
Volumetric methods for the quantitative determination of vanadium .......................................... 254
Titration by means of potassium permanganate ................. 254
Methods of reducing vanadium solution ............................ 255
Use of the Jones reductor in the estimation of vanadium ....... 256
Titration of vanadium by means of ferrous sulphate ............. 256
Electrometric determination ......................................... 257
Iodometric titration of vanadium .................................. 257
Titration of vanadium by means of potassium ferricyanide ..... 259
Titration of vanadium by means of titanium chloride ........... 259
Miscellaneous volumetric methods .................................. 260
Colorimetric methods .................................................. 261
Electrolytic determination of vanadium ............................ 262
Special methods of analysis for ores, slags, and other products ............................................. 262
Methods for the analysis of carnotite ores for estimation of uranium and vanadium .................. 262
Volumetric method of Ledoux ...................................... 262
Method of Ledoux and Low ....................................... 263
Method of Blair .................................................. 263
Vanadium ores containing chromium ................................ 263
Vanadiferous sandstones ............................................ 264
Vanadium in iron ores, rocks, and slags .......................... 265
Materials low in silica .......................................... 265
Materials high in silica .......................................... 265
Analysis of vanadium metal and alloys .......................... 266
Vanadium metal .................................................. 266
Vanadium steel and iron .......................................... 266
Ferrous sulphate method for steel ................................ 266
HCl method for iron and steel .................................... 268


**CONTENTS.**

**Part VII.**—Vanadium, by J. E. Conley—Continued.

**Quantitative analysis—Continued.**

**Analysis of vanadium metal and alloys—Continued.**

<table>
<thead>
<tr>
<th>Vanadium steel and iron—Continued.</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Colorimetric method for steel.</td>
<td>268</td>
</tr>
<tr>
<td>Method for Cr-V steel.</td>
<td>268</td>
</tr>
<tr>
<td>Electrometric determination of vanadium in iron and steel</td>
<td>269</td>
</tr>
<tr>
<td>Gravimetric methods for estimation of vanadium in iron and steel</td>
<td>270</td>
</tr>
</tbody>
</table>

| Estimation of vanadium in ferrovanadium | 270 |
| Selected methods for the analysis of materials containing vanadium | 270 |
| Methods for the determination of vanadium in ores | 270 |

| Method of Ledoux | 271 |
| Résumé of method | 271 |
| Procedure in analysis | 271 |
| Notes on the Ledoux method | 272 |
| Calculations and factors | 273 |

**Rapid method for ores—reduction with HCl** | 273 |
| Résumé of method | 273 |
| Procedure in analysis | 273 |
| Factors | 274 |
| Notes on the HCl reduction method | 274 |

| Selected methods for the estimation of vanadium in iron, steel, and ferrovanadium | 275 |

| Method of Johnson | 275 |
| Résumé of method | 275 |
| Procedure in analysis | 275 |
| Procedure for vanadium only | 276 |
| Procedure for simultaneous estimation of chromium | 276 |

| HCl reduction method for determination of vanadium in iron and steel | 276 |
| Procedure in analysis | 276 |
| Notes on method | 277 |

**Bibliography on vanadium** | 278 |

**Part VIII.**—Titanium and zirconium, by J. W. Marden | 281

**Introduction** | 281

| Titanium | 281 |
| Introduction | 281 |
| Method of solution of ores and alloys | 283 |
| Treatment with acids | 283 |
| Treatment by fusion | 283 |
| Sodium carbonate and potassium carbonate mixture | 283 |
| Sodium hydroxide and sodium carbonate | 283 |
| Sodium hydroxide and sodium peroxide | 283 |
| Sodium or potassium bisulphate | 284 |
| Potassium bifluoride | 284 |
| Sodium carbonate and borax | 284 |
| Fusions recommended | 284 |

**Qualitative analysis** | 284 |
| Detection of titanium | 284 |
| Separation of titanium from other elements | 285 |

**Quantitative analysis for titanium** | 286

**Gravimetric methods** | 286 |
| Separation of titanium by alkali acetates | 286 |
| Preparation of the sample | 286 |
| Oxides | 286 |
CONTENTS.

Part VIII.—Titanium and zirconium, by J. W. Marden—Continued.

Titanium—Continued.

Quantitative analysis for titanium—Continued.

Gravimetric methods—Continued.

Separation of titanium by alkali acetates—Continued.

Precipitation of iron........................................................................... 286
Precipitation of TiO₂............................................................................. 287
Precipitation of titanium with sodium thiosulphate or
SO₂ analysis of ferro-alloy................................................................. 287
Plain titanium steel............................................................................. 288
Insoluble ferrotitanium....................................................................... 289
SO₂ method of separation................................................................... 289

Volumetric methods............................................................................ 290
Colorimetric method with H₂O₂............................................................ 290
Determination by titration.................................................................... 290
Preparation of the sample................................................................... 291
Volumetric method by reduction of titanium and titration
with a ferric salt.................................................................................. 291
Determination of titanium in ferrocobaltic titanium......................... 291
Determination of titanium when interfering elements are
present..................................................................................................... 292
Colorimetric determination of titanium with thymol.......................... 292
Titration with methylene blue............................................................... 293
Volumetric method for estimating titanium and iron......................... 294

Methods of analysis selected for ores and alloys.............................. 294
Preparation of sample.......................................................................... 294
Method of solution and separation of silica......................................... 294
Separation of titanium from interfering elements by means of
phenyl hydrazine.................................................................................. 295
H₂O₂ method for determining small amounts of titanium in
the phenyl hydrazine precipitate......................................................... 296

Preparation of standard TiO₂ solutions.............................................. 296
1. From K₂TiF₆..................................................................................... 296
2. By direct precipitation........................................................................ 297
Methylene-blue method of titration...................................................... 298

Bibliography on titanium................................................................. 299

Zirconium............................................................................................. 301

Introduction......................................................................................... 301
Method of solution of ores and alloys................................................ 301
Treatment with acids.......................................................................... 301
Treatment by fusion............................................................................ 302
Sodium carbonate or sodium potassium carbonate mixture.............. 302
Sodium hydroxide and sodium peroxide.......................................... 302
Sodium hydroxide and sodium carbonate......................................... 302
Sodium or potassium bisulphate.......................................................... 303
Fluoride fusions.................................................................................. 303
Sodium carbonate and borax............................................................... 303
Fusion recommended for solution of ores.......................................... 303

Qualitative analysis............................................................................ 304
Detection of zirconium......................................................................... 304
Separation of zirconium from the other elements.............................. 305
Quantitative determination of zirconium............................................ 306
Insoluble compounds of zirconium...................................................... 306

111533°—23——2
XVIII

CONTENTS.

Part VIII.—Titanium and zirconium, by J. W. Marden—Continued.
Zirconium—Continued.
Insoluble compounds of zirconium—Continued. 306

<table>
<thead>
<tr>
<th>Method</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methods based on the precipitation of zirconium as hydrated oxide</td>
<td>306</td>
</tr>
<tr>
<td>Precipitation by ammonia</td>
<td>307</td>
</tr>
<tr>
<td>Precipitation by phenylhydrazine</td>
<td>307</td>
</tr>
<tr>
<td>Precipitation by sodium iodate</td>
<td>307</td>
</tr>
<tr>
<td>Precipitation by sodium thiosulphate</td>
<td>308</td>
</tr>
<tr>
<td>Precipitation by sulphur dioxide</td>
<td>308</td>
</tr>
<tr>
<td>Methods based on the precipitation of zirconium as phosphate</td>
<td>308</td>
</tr>
<tr>
<td>Methods based on the precipitation of zirconium by cupferron</td>
<td>309</td>
</tr>
<tr>
<td>Methods based on the precipitation of zirconium by selenious acid</td>
<td>310</td>
</tr>
<tr>
<td>Miscellaneous methods largely of historical interest</td>
<td>310</td>
</tr>
<tr>
<td>Recommended method for the analysis of zirconium ores</td>
<td>311</td>
</tr>
<tr>
<td>Procedure</td>
<td>312</td>
</tr>
<tr>
<td>Determination of titanium in portion 1</td>
<td>314</td>
</tr>
<tr>
<td>Determination of the rare earths in portion 2</td>
<td>315</td>
</tr>
<tr>
<td>Recommended method for analysis of zirconium steel</td>
<td>315</td>
</tr>
<tr>
<td>Procedure</td>
<td>315</td>
</tr>
<tr>
<td>Determination of aluminum</td>
<td>317</td>
</tr>
<tr>
<td>Determination of zirconium and titanium</td>
<td>317</td>
</tr>
<tr>
<td>Bibliography on zirconium</td>
<td>318</td>
</tr>
<tr>
<td>Index</td>
<td>321</td>
</tr>
</tbody>
</table>

-----------------------------

ILLUSTRATIONS.

-----------------------------

PLATE I. A, Alpha-ray electroscope; B, Gamma-ray electroscope.................... 178

FIGURE 1. Cross section of electroscope.................................................. 176
2. Cross section of ammeter insulation..................................................... 177
3. Fusion boat sealed in glass................................................................. 190
4. Apparatus for boiling off radium emanation......................................... 194
PART I.—METHODS FOR QUANTITATIVE SEPARATION AND ESTIMATION OF THE ALLOY METALS WHEN ASSOCIATED WITH ONE ANOTHER.

By J. E. Conley.

INTRODUCTION.

This chapter indicates the methods of determining several of the alloy metals when occurring together in the same sample. Most materials seldom contain more than two or three of these elements, but considerable time may be saved if determinations can be combined.

Certain steels and alloys frequently contain a number of the rare elements, and the increasing use of these alloys has made necessary the devising of methods for their simultaneous estimation or quantitative separation. Sometimes the most satisfactory methods of analysis are such that the estimation of more than one or two of the rare elements in the same sample becomes more cumbersome and time consuming than analyses of separate samples of material. This section of the bulletin will not attempt to replace those methods by others less satisfactory, but to outline methods that may prove of some use when the combined estimation of a number of the rare metals is required.

Details of the analyses and separations are not given here, as they have been covered more fully in the other chapters. Wherever possible, reference is made to the particular chapter.

The same scheme has been employed for the table for the estimation and separation of the elements. Only sufficient directions have been given to outline the method of procedure, actual conditions for the separations being presented on other pages.
DETERMINATION OF TUNGSTEN IN THE PRESENCE OF ONE OR MORE OF THE OTHER ALLOY METALS.

In analyzing materials containing tungsten associated with other alloy metals, little difficulty is encountered in removing the tungsten. Most methods for analyzing any of these other metals can be modified so as first to separate out the tungsten as the oxide, then to determine by suitable methods the elements desired in the filtrate.

Separation of tungsten from the rare elements therefore becomes a simple procedure, but its separation from some of the common elements, such as phosphorus, tin, and silica, is actually a more complicated operation.

The actual instances in which the determination of tungsten must be made in the presence of molybdenum, uranium, vanadium, titanium, and zirconium are usually few, and are largely confined to analyses of special steels. There are, however, a few exceptions, particularly some of the rarer minerals. In the light of these facts, most of the information on the estimation of tungsten to be given here will be largely restricted to the literature on the simultaneous estimation of tungsten and other alloy metals.

ESTIMATION OF TUNGSTEN AND MOLYBDENUM.

The estimation of tungsten and molybdenum in the same sample presents little or no difficulty. Analyses that call for the simultaneous estimation of these two elements most frequently concern iron and steels.

Auchy (1) separates his W in the usual manner by dissolving the steel in HNO₃ and HCl, and evaporating to dryness. The Fe is separated by NaOH, and the Mo determined in the filtrate by reduction with Zn and titration with KMnO₄; 0.8-gram samples of the steel are dissolved in HNO₃ and taken to dryness; 25 c. c. of concentrated HCl is added and the precipitated WO₃ is filtered off. The filtrate is fumed with 10 c. c. of 1:3 H₂SO₄, cooled, and diluted to 50 to 60 c. c., and poured into a 5 per cent solution of NaOH. The Fe is filtered off, and a portion of the filtrate acidified with H₂SO₄, reduced with Zn, and the Mo titrated with standard permanganate.

Mennicke (7) outlines the method of Bazin for the simultaneous estimation of W and Mo in steel, which is essentially as follows: A sample of the steel, 5 to 20 grams, is dissolved in 100 c. c. of concentrated HNO₃ and evaporated to dryness. The residue is heated with 100 c. c. of 1.19 HCl until a large part of the HCl has been

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1 Figures in parentheses refer to items in the bibliography, p. 18.
expelled. The solution, after dilution, is filtered, and the residue on the filter is retained to determine the tungsten. The filtrate is diluted to 1,000 c. c., warmed to 30° C., and H₂S passed through the solution for one hour. The solution is allowed to stand for 12 hours and then filtered. The precipitate of MoS₂ is washed with a dilute HCl solution of H₂S. The filtrate is then evaporated to half its volume and H₂S again passed through. Any precipitate formed is added to the first precipitate obtained and treated with a warm solution of (NH₄)₂S and filtered from insoluble material. The Mo is eventually precipitated from the (NH₄)₂S solution by means of dilute 1.124 HCl and the excess H₂S removed by boiling. The precipitate is finally filtered through a tared filter and dried to constant weight. A known portion of the dried precipitate is then taken and heated in a current of hydrogen at a red heat to constant weight and weighed as MoS₂.

Evidently the method is rather long and tedious, but should give accurate results.

DETERMINATION OF TUNGSTEN, VANADIUM, AND TITANIUM.

Tungsten, vanadium, and titanium, when present together in a metal or ore, may be separated and estimated as done by Fenner (5). A mineral containing W, V, and Ti, particularly with large quantities of Fe and SiO₂, when fused with sodium peroxide and leached with water, will yield its W to the filtrate; but the Ti remains in the residue, as does a large portion of the V, if originally present in quantities less than 0.5 per cent; hence, although W may be separated from T₄ by this method, V tends to be held up in the residue.

To determine the V and Ti as well as W, the following procedure may be used: The ore or metal is first treated with HF and H₂SO₄ to eliminate the bulk of the SiO₂. The residue from this treatment is ignited, then fused with several times its weight of sodium pyrosulphate, and the melt extracted with water that has been slightly acidified with a few drops of H₂SO₄. This treatment extracts the V and Ti and leaves the W in the residue. The W is then separated from the remaining SiO₂ by solution in NH₄OH or by any of the known methods. (See chapter on Tungsten, p. 131.)

The V is determined in the filtrate by adding H₂O₂ to produce the well-known reddish-brown pervanadic acid, which is compared with a known standard vanadium solution. The effect of the yellow color of Ti produced under exactly similar conditions is destroyed by the addition of a small quantity of NH₄F or HF. Any color due to Fe is destroyed with phosphoric acid.

The Ti may be determined by separation with NaOH with subsequent colorimetric estimation. (See "Titanium," p. 281.)
ESTIMATION OF TUNGSTEN, VANADIUM, AND MOLYBDENUM
(CHROMIUM AND NICKEL).

Tungsten, molybdenum, and vanadium, when present together in a steel or other alloy, may be separated and estimated as outlined by Svenson (9). Two grams of a steel containing W, Mo, V, Cr, and Ni are dissolved in 50 c. c. of concentrated HCl, and warmed with the addition of 5 to 10 c. c. of HNO₃. The solution is evaporated to dryness, the dry residue dissolved in a small quantity of 1:5 HCl, and filtered. The residue on the filter is treated with HF to eliminate the SiO₂ and then weighed as WO₃. The filtrate is made strongly acid with HCl, and the Fe and Mo are extracted with ether as in the Rothe method.

The Ni and Cr remain in the aqueous layer in which they are estimated as follows: The ether present is destroyed by heating with KClO₃. The Cr is precipitated from the solution after dilution to 250 c. c. by the addition of 10 grams of NH₄Cl and an excess of NH₄OH. The nickel is determined in the filtrate by titration with KCN. The precipitate containing the Cr is redissolved in HCl, and the resulting solution heated with the addition of sodium-ammonium phosphate; then the Cr is again precipitated with NH₄OH. The precipitate is dissolved in 75 to 100 c. c. of 1:6 H₂SO₄, oxidized with KMnO₄, reduced with an excess of FeSO₄ solution, and titrated with standard KMnO₄ to determine the amount of Cr.

The Mo and V are estimated in a separate sample. Four grams of the steel are dissolved in HCl and HNO₃ and the precipitated WO₃ removed by filtration. The Fe, Ni, and Cr are removed by pouring into a 5 per cent solution of NaOH. The filtrate containing the Mo and V is made up to 500 c. c., and a one-half aliquot used for the determination of V and Mo. The aliquot is first acidified with dilute HCl and then made slightly alkaline with NH₄OH. Twenty grams of NH₄Cl is then added, and the V precipitated as manganese vanadate by the addition of manganese chloride. The Mo, which remains in the filtrate, is determined by nearly neutralizing the NH₄OH with HCl, precipitating by the addition of lead acetate and 50 c. c. of a concentrated ammonium acetate solution, and weighing as lead molybdate.

The precipitate of manganese vanadate is incinerated with the filter paper, and the ignited residue is dissolved in HCl. The resulting solution is then fumed with H₂SO₄ and the reduced V titrated with standard KMnO₄.

Materials containing W, V, and Mo may also be separated and estimated by the procedure of Zinberg (12).

A 1-gram sample of the steel is dissolved in 1:4 HCl with the final addition of a few cubic centimeters of HNO₃. The solution is evap-
orated to dryness and the precipitated W filtered off exactly as done by Bazin (7) and Svenson (9). The Mo is precipitated from the filtrate by H₂S under pressure, filtered, ignited, and weighed as the oxide. The filtrate from the Mo precipitation is first freed from excess H₂S by boiling, and is then poured into boiling 5 per cent NaOH. The resulting precipitate contains the Fe, Cr, and Ni, and is reserved for their estimation. The small quantity of Cr that passes into the filtrate is recovered by acidifying the solution with HNO₃ and evaporating to dryness after the addition of Ba(NO₃)₂ and alcohol, then reprecipitating with NH₄OH. The ammoniacal solution then contains the V, free from Cr. The V content is determined by making slightly acid with HNO₃ and precipitating as mercurous vanadate by the addition of mercurous nitrate. The precipitate of mercurous vanadate is finally ignited and weighed as vanadic oxide.

DETERMINATION OF MOLYBDENUM IN THE PRESENCE OF THE OTHER RARE METALS.

ESTIMATION OF MOLYBDENUM, VANADIUM, CHROMIUM, AND NICKEL IN STEEL.

A method for the separation and estimation of Mo, V, and Cr is given by Blair (2). A 2-gram sample of the steel is dissolved in HNO₃ with the addition of HCl. The solution is evaporated to dryness and redissolved in HCl, then treated with ether as outlined on page 4, to extract the Fe and Mo. The ether solution is evaporated nearly to dryness, 10 c. c. of strong H₂SO₄ added, and the heating continued to copious fumes. The solution is diluted and deoxidized with ammonium bisulphite and after expulsion of the excess SO₂ the Mo is precipitated under pressure with H₂S. The precipitated MoS₃ is filtered off, ignited, and weighed as MoO₃.

The aqueous extract from the ether separation contains the V, Ni, and Cr. The Ni and Cr are precipitated from the solution by pouring into a boiling solution of NaOH. The V, which passes into the filtrate, is precipitated as lead vanadate by first acidifying with HNO₃, then making slightly alkaline with NaOH, adding an excess of a 10 per cent solution of Pb(NO₃)₂ and sufficient acetic acid to make distinctly acid. The lead vanadate precipitate is then dissolved in HCl, fumed with H₂SO₄, and titrated with KMnO₄ according to the method of Campagne.

Another method for separating and estimating these elements is used by Pozzi-Escot (8). The mineral to be analyzed is dissolved in either HCl or HNO₃. An excess of a strongly alkaline solution of sodium hypobromite is then added to the acid solution, which has been brought to a boil. After boiling several minutes, the solution is filtered, and the precipitate, which now contains the Fe, Ni, and Co,
is reserved for their estimation. The filtrate contains the Cr, V, and Mo as their respective sodium salts.

The Fe precipitate is redissolved in a few cubic centimeters of dilute HCl and again precipitated to insure a quantitative separation of the Fe and Ni from the Cr, V, and Mo. The Fe is separated from the Ni by precipitation with NH₄OH.

The Cr is separated from the V and Mo by acidifying and reducing with alcohol, and subsequently precipitating with NH₄OH. The Mo and V are separated by precipitation of the latter with manganese chloride by the method of Carnot (3). (See p. 251.) The Mo remains in the filtrate, and may be estimated by any of the well-known methods outlined in the chapter on “Molybdenum,” pages 71–130.

**SIMULTANEOUS ESTIMATION OF MOLYBDENUM AND VANADIUM.**

When present together, Mo and V may be estimated by the method of Edgar given on pages 260 and 261; or by the method of Travers, on pages 91 and 260.

**SIMULTANEOUS ESTIMATION OF VANADIUM AND OTHER RARE METALS.**

**VANADIUM AND TUNGSTEN.**

For the estimation of V and W in the same sample of material, see section under “Tungsten,” in this part, page 3.

**VANADIUM AND MOLYBDENUM.**

Methods used for the simultaneous estimation of molybdenum and vanadium are given under the section of this part on “Molybdenum.” (See p. 5.)

**VANADIUM AND URANIUM.**

Methods that may be used for estimating uranium and vanadium in ores are outlined on pages 225 and 263.

**VANADIUM, URANIUM, AND ZIRCONIUM.**

A method suitable for simultaneous estimation of V, U, and Zr in steels has been developed by Johnson (6). The procedure considers each element separately, so that a special determination for each metal required would be necessary. Evidently, if the estimation of more than one element were required, these determinations could be made from one sample.

In order to combine these operations the procedure would be essentially as follows: A sample of suitable size, 2 to 4 grams, is dissolved in 50 c. c. of 1 : 3 H₂SO₄, heated to solution, and filtered. The insoluble carbides obtained on the filter are asched at a low red
heat, treated with 6 c. c. of HF plus 6 c. c. of 1:3 H₂SO₄, and the mixture heated to fumes of SO₃. The mixture is then diluted and filtered and added to the main filtrate. Any material obtained on the filter is reserved for further treatment.

The main filtrate is now treated with enough dilute 1:1 NH₄OH to produce a slight black precipitate, and 2 c. c. is added beyond this point. The U, V, and Zr are obtained in the precipitate, and the bulk of the Fe is retained in the filtrate. The precipitate is then dissolved in 50 c. c. of 1:1 HCl, and enough Na₂O₂ carefully added so that the solution is alkaline and the Fe has been precipitated. Five grams of Na₂CO₃ is then added, and the solution boiled. The Fe and Zr are found in the precipitate; the U and V in the filtrate. Solution, followed by a second peroxidation, is usually advisable to effect a quantitative separation.

The insoluble carbides reserved above are now washed into a beaker and treated with hot HNO₃ until the residue, which consists principally of WO₃, is bright yellow. The filtrate from this treatment is added to the filtrate from the peroxidation, which contains the uranium and vanadium.

**DETERMINATION OF ZIRCONIUM**

The Zr, which has been separated with the Fe by the Na₂O₂ and Na₂CO₃, is estimated as phosphate after precipitation from dilute H₂SO₄ solution. The procedure is as follows:

The Fe and Zr on the filter are dissolved in 30 c. c. of hot 1:3 H₂SO₄, diluted with 50 c. c. of water. Wash the filter paper about 40 times with dilute sulphuric wash. Add to the filtrate 20 c. c. of a saturated solution of Na₂HPO₄ (disodium phosphate); stir well. Add 1:1 ammonia slowly till a precipitate just starts to form. Zirconium phosphate comes down at this stage with very little iron, as the solution is still acid and most of the iron is in solution. The more zirconium with the sample the less ammonia it is necessary to add before a precipitate starts to form. After a few hours, preferably overnight, filter off the zirconium phosphate plus iron phosphate plus some silicon. Wash the phosphate with water 40 times. Burn it off in a weighed platinum crucible. Add about 10 drops of concentrated sulphuric acid and 10 c. c. HF. Evaporate just to SO₃ fumes. Transfer the insoluble residue into a beaker. The iron phosphate will be in solution as iron sulphate, while the zirconium phosphate is insoluble. Warm the solution for a while to redissolve the iron sulphate that may be separated out. Filter off the insoluble residue, wash it about 50 times with water and burn it off in the same platinum crucible. (Some of the zirconium may stick to the crucible and can not be transferred to the filter.) Burn it to a constant weight and weigh as zirconium phosphate, using the original weight of the crucible gotten just before the ZrPO₄ plus a little FePO₄ was burned in it. Multiply by 0.3838 to calculate to zirconium.

**DETERMINATION OF URANIUM AND VANADIUM.**

The U and V in the filtrate free from Fe may be separated and estimated in a variety of ways. The U may be precipitated as the phosphate and estimated as done by Johnson (see Part VI, p. 222);
and the V present in the filtrate from the U precipitation may be estimated by fuming with H₂SO₄ and reducing with FeSO₄ (see p. 256), SO₂ (p. 255), or by HCl (p. 255) and titration with standard KMnO₄. The U and V may also be separated and estimated as in the Ledoux method, as given under “Vanadium” (pp. 263 and 271).

**ESTIMATION OF VANADIUM AND URANIUM.**

For their simultaneous estimation in ores, see page 262, Part VII, and page 225, Part VI.

**SIMULTANEOUS ESTIMATION OF VANADIUM AND TITANIUM.**

When present in the same sample these metals may be estimated as outlined under “Tungsten,” page 3.

Small quantities of V and Ti mutually interfere with the colorimetric determination of each other by the use of H₂O₂. The color effect due to the Ti may be readily destroyed by the addition of NH₄F or HF as given by Fenner (5), and the quantity of V determined by direct comparison with the standard. The color effect due to the V in a mixture containing both V and Ti is not so easily overcome. Wright (11) gives a method for the estimation of V by reduction with an excess of FeSO₄ and titration with KMnO₄, then colorimetric estimation of the Ti after the addition of H₂O₂. To overcome the color effect of the V, he prepares a standard to contain the same quantity of V as the unknown. While this procedure may work satisfactorily for extremely minute quantities of V and Ti, unquestionably the difficulties increase with the increase in the V content. Under such circumstances, actual separation of the V and Ti is recommended. This separation may be accomplished as given under “Titanium,” page 285; and under “Vanadium,” page 251.

**ESTIMATION OF URANIUM AND VANADIUM.**

When together in a material, uranium and vanadium may be separated and satisfactorily estimated by a number of methods. The method of Ledoux, as given on page 263, has been extensively used to determine both of these elements. The method of Blair, page 263, the method of Finn, page 250, and the method of Campbell and Griffin, page 212, have been developed for this purpose.

Johnson (6) (see under “Estimation of V, Zr, and U,” p. 6) gives a method which may be used for estimating uranium and vanadium in iron and steels.

**ESTIMATION OF TITANIUM IN THE PRESENCE OF THE OTHER RARE METALS.**

**TITANIUM AND TUNGSTEN.**

The separation of Ti from W presents little difficulty, so that both may be easily determined in the same sample.
Fusions with alkalies, followed by water leach of the melt, offer a simple method for the separation. The W is obtained in the filtrate, while the Ti remains in the residue. In the fusion with sodium or potassium pyrosulphate the conditions are reversed, in that the W remains in the insoluble residue as WO₃, and the Ti passes into the filtrate as the sulphate. This separation is best accomplished if a few drops of concentrated H₂SO₄ are added to the H₂O in which the pyrosulphate fusion is dissolved. This precaution assists in keeping the W in the insoluble portion.

Titanium may be determined as outlined under "Tungsten," page 3 (this part), and by the methods given on page 286.

TITANIUM AND VANADIUM.

For the simultaneous estimation of titanium and vanadium, see page 8, this part.

TITANIUM, ZIRCONIUM, AND IRON.

In the precipitation of Fe by the use of NH₄OH, Na₂CO₃, and Na₂O₂ or NaOH, a precipitate is obtained which carries all the Ti and Zr present in solution. For this reason, alkaline fusions present a convenient method for the separation of the Fe, Ti, and Zr from a large number of elements, particularly the rarer ones.

On the other hand, pyrosulphate fusions present a means of obtaining these three elements in solution. However, with considerable quantities of Ti or Zr, several fusions with pyrosulphate are required.

Dittrich and Pohl (4) use a method for the separation and estimation of Ti and Zr that is essentially as follows:

The material or precipitate containing these elements in the presence of Fe is put into solution by fusion with KHSO₄, with subsequent extraction with H₂O. The solution containing the Fe, Ti, and Zr as soluble sulphates is reduced by passing in a current of H₂S. A quantity of tartaric acid is then added to the solution, and then an excess of NH₄OH and NH₄HS. The Fe is precipitated as FeS, but the Ti and Zr are held in solution by the tartaric acid, which is then destroyed by warming the solution and adding a slightly acid solution of potassium persulphate. The Ti and Zr are then precipitated with NH₄OH, filtered, ignited, and weighed as the combined oxides ZrO₂ + TiO₂. The residue is then finally fused again with pyrosulphate, and the melt dissolved in water. The quantity of Ti is then determined colorimetrically by comparison with a known standard, and this quantity subtracted from the combined weight of oxides to determine the quantity of Zr. For other details of this separation, see page 286.

Travers (10) also determines Ti and Zr by weighing as their combined oxides, then colorimetric estimation of the Ti after solution
by fusion with $\text{K}_2\text{S}_2\text{O}_7$. The mineral containing Zr and Ti is fused with 10 times its weight of $\text{Na}_2\text{O}_2$ in a nickel crucible. The resulting melt is extracted with from 300 to 400 c. c. of water, and the residue on the filter washed with a 5 per cent solution of $\text{Na}_2\text{CO}_3$. By this treatment, the bulk of the Si and Al passes through into the filtrate, while the Fe, Ti, and Zr remain on the filter. The precipitate is rinsed back into a beaker, and the filter paper ignited, then added to the precipitate in the beaker. The mixture is treated with an excess of HCl, then heated, and an excess of NH$_4$OH added. The precipitate is filtered off, washed with NH$_4$Cl, then redissolved in HCl. The bulk of the excess of HCl is then neutralized with NH$_4$OH, and an excess of a 10 per cent solution of sodium thiosulphate is added. The mixture is boiled and filtered, and the precipitated hydroxides ignited in a porcelain crucible, and weighed as $\text{ZrO}_2 + \text{TiO}_2$. The small quantity of SiO$_2$ that generally contaminates this residue is expelled with HF and H$_2$SO$_4$ in the usual manner. To determine the quantity of Ti in the combined oxides, the residue is fused with $\text{K}_2\text{S}_2\text{O}_7$, dissolved in 10 per cent H$_2$SO$_4$, and determined colorimetrically after the addition of H$_2$O$_2$. (See Part VIII on "Titanium," p. 286, and "Zirconium," p. 306.)

SYSTEMATIC ANALYSIS FOR THE ALLOY METALS TUNGSTEN, MOLYBDENUM, URANIUM, VANADIUM, TITANIUM, AND ZIRCONIUM.

The scheme given in this section for the systematic analysis of materials containing W, Mo, U, V, Ti, and Zr has been so devised as to include the separation of Fe, Al, Cr, P, and As. These common elements have been included, owing principally to the fact that they largely constitute the chief interfering elements. They usually exist in considerable quantities with the alloy metals, so that their separation is of vital importance. Unless they are known definitely to be absent, the procedures for their separation should be followed. It is probably true that the gravimetric estimation of some of these common elements by the procedure outlined may be somewhat less satisfactory than by other methods, but if desired, the amount of these elements present may be determined as indicated.

The accompanying chart (see p. 18) is a brief of the methods described in this chapter.

DECOMPOSITION OF STEEL.

In the decomposition of steel containing any or all of the alloy metals, solution is made in 1:3 H$_2$SO$_4$. The SiO$_2$ is expelled in the usual manner with HF and H$_2$SO$_4$ and the residue is fused with $\text{K}_2\text{S}_2\text{O}_7$ to decompose the remaining carbides. The method is so devised as to permit the use of a large sample—from 5 to 10 grams.
of steel—to increase the quantities of the alloying elements for subsequent separation and estimation. Solution in \( H_2SO_4 \) places the elements in solution in the reduced state, a condition essential for the precipitation with ferrous iron as used by Johnson (6). Ammonia, carefully added to the reduced solution, precipitates the alloy metals with only a small part of the iron.

This separation is evidently suited for use only where the proportion of iron is large, and that of the alloy elements is relatively small, as is usual in special steels.

PROCEDURE IN ANALYSIS.

1. SEPARATION OF SILICON AND TUNGSTEN FROM OTHER ELEMENTS.

From 5 to 10 grams of the steel as filings or borings is dissolved in 50 c. c. of 1:3 \( H_2SO_4 \). After all evident action has ceased, the solution is diluted with warm water and filtered. The filtrate, which contains the bulk of the Fe, Al, Ti, Zr, Mo, U, V, As, P, and Cr, is reserved for treatment as in paragraph 5, and the residue, which contains the W and Si with traces of the other elements, is ignited in a platinum crucible and treated as in section 2, below.

2. TREATMENT OF RESIDUE CONTAINING W AND SI.

The ignited residue is fused with 2 grams of \( K_2SO_4 \), and extracted with water to which several drops of concentrated \( H_2SO_4 \) have been added. The solution is then filtered, and the filtrate (4) containing the traces of alloy elements is added to the original filtrate (5). The residue, which contains the W and Si, is ignited and treated as in paragraph 3.

3. SEPARATION OF TUNGSTEN FROM SILICON.

The SiO\(_2\) is expelled in the usual manner with 3 to 4 c. c. of HF and several drops of concentrated \( H_2SO_4 \), the residue being ignited and weighed directly as \( \text{WO}_3 \); or, better, dissolved in strong \( \text{NH}_4\text{OH} \) and filtered, then evaporated to dryness in a platinum crucible. The residue is again treated with HF and \( H_2SO_4 \), ignited, and weighed as \( \text{WO}_3 \). Precautions and procedure for the separation of Si and W are given under the estimation of W as \( \text{WO}_3 \), page 160.

4. See under 2, summary chart.

5. TREATMENT OF SOLUTION CONTAINING IRON, ALUMINUM, MOLYBDENUM, ZIRCONIUM, TITANIUM, URANIUM, VANADIUM, CHROMIUM, ARSENIC, AND PHOSPHORUS.

The solution containing Fe, with Al, Mo, Zr, Ti, U, V, Cr, As, and P, is diluted to about 250 c. c. and enough 1:1 \( \text{NH}_4\text{OH} \) (sp. gr. 0.9) is added to form a permanent black precipitate, then 2 c. c. added in excess; the solution is filtered immediately. The filtrate, which contains the bulk of the Fe as ferrous ammonium sulphate, is dis-
carded, and the precipitate carrying all of the alloy metals originally present is treated as in paragraph a or b below.

6. PRECIPITATE CONTAINING A SMALL QUANTITY OF IRON, WITH ALL THE ALUMINUM, ZIRCONIUM, TITANIUM, MOLYBDENUM, URANIUM, VANADIUM, CHROMIUM, ARSENIC, AND PHOSPHORUS.

The precipitate may be treated, in one of two ways, as outlined under a and b below:

a. The filter paper with the precipitate is placed in a 600 c. c. beaker, and dissolved in the least possible amount of 1:1 HNO₃. The solution is diluted to 250 c. c., and peroxidized by the careful addition of Na₂O₂ until the HNO₃ has been neutralized. From 3 to 4 grams excess of Na₂O₂ and 4 to 5 grams of Na₂CO₃ are then added, and the solution warmed to coagulate the Fe precipitate. The precipitate is filtered off and washed with a dilute (NH₄) NO₃ solution. To insure complete extraction of the V and U, a second precipitation, made in the same manner as the first, is recommended. Dilute HNO₃ should be used to dissolve the precipitate. The filtrates from the two precipitations are then combined and reserved for treatment as in paragraph 21. This filtrate now contains the Al, Mo, U, V, Cr, As, and P. The precipitate contains the Fe, Ti, and Zr, and is treated as outlined in paragraph 7.

b. If preferred, another method, which at this point separates the As and Mo from the other elements, may be used. To make this separation here, the precipitate obtained by adding NH₄OH to the solution of the steel is dissolved in the least possible quantity of dilute HCl. H₂S is then passed into the solution, which is placed in a pressure flask, and treated as given on page 79. The filtrate from this precipitate may then be heated to expel excess H₂S, and otherwise treated the same as given under a.

A large quantity of HCl should not be used because the use of lead precipitants should be eliminated as much as possible. The later precipitation of the other elements with lead acetate is more satisfactory, if only small quantities of chlorides and sulphates are present.

Method b is used when a separation of the Mo and V is desired. If a simultaneous estimation of these two metals is desired, method a should be used.

7. REPRECIPITATION OF IRON, TITANIUM, AND ZIRCONIUM.

The iron, titanium, and zirconium precipitate will always retain a part of the V with small quantities of P. To insure a quantitative separation a second precipitation is recommended. It is accomplished by placing the filter and contents in a beaker and treating with the least quantity of 1:1 HNO₃ required to dissolve the precipitate. The solution is then diluted, and the filter paper disintegrated with
a stirring rod. The second precipitation is made precisely as the first by the addition of Na₂O₂ and Na₂CO₃. The filtrate from this precipitation is combined with the original filtrate, and treated as outlined in section 21. The Fe precipitate containing the Zr and Ti is treated as outlined in section 10. See also page 9 and summary chart.

10. IRON PRECIPITATE CONTAINING TITANIUM AND ZIRCONIUM.

The precipitate is dissolved in dilute 1:5 H₂SO₄ and filtered. The filtrate is carefully washed with hot water. Insoluble material remaining on the filter is ignited and fused with two to three times its weight of K₂S₂O₇, extracted with water, and finally added to the main filtrate. A stream of H₂S is then passed into the filtrate to reduce the Fe. Tartaric acid, NH₄OH, and NH₄HS are added to precipitate the Fe, which is filtered off as the sulphide. The filtrate from this precipitation still contains the Zr and Ti. The solution is acidified with H₂SO₄, and sufficient potassium persulphate is added to destroy the tartaric acid. NH₄OH is then added to precipitate the Zr and Ti.

The combined precipitate of Zr and Ti is ignited in a platinum crucible, and weighed as TiO₂ + ZrO₂. The ignited precipitate is fused with from five to six times its weight of K₂S₂O₇ (with large quantities of Ti a second fusion is usually necessary) and extracted with water. The quantity of Ti is determined colorimetrically after the addition of H₂O₂. For this determination, see chapter on "Titanium," page 290.

DECOMPOSITION OF ORES AND SOLUTION OF SAMPLE.

To conform as closely as is practicable to the general method of separation and estimation of the alloy metals when found in ores, solution should when possible be made in acid. Decomposition by fusions for especially refractory samples is permissible, but doubtless is more applicable to materials low in silica.

11. ACID DECOMPOSITION FOR MATERIALS HIGH IN SILICA BUT YIELDING THEIR METALS TO THIS TREATMENT.

Dissolve 1 to 5 grams of the pulverized material, according to the proportion of metals present, in HCl, HNO₃, or aqua regia, if possible. Evaporate the sample to dryness on the water bath and treat the residue with 1:1 HNO₃, warm, and filter. The filtrate will contain the bulk of the Fe, Al, Mo, U, V, As, P, and Cr, with a considerable part of the Ti and Zr, and is treated as outlined in section 13. The insoluble material on the filter, which now contains the SiO₂ and all of the W present, with small portions of other metals, is ignited in a platinum crucible and treated as outlined in section 12.
12. IGNITED RESIDUE CONTAINING SILICA AND TUNGSTEN, WITH SMALL AMOUNTS OF THE OTHER ELEMENTS.

The ignited residue is treated with 4 to 5 c. c. of HF and 10 drops of concentrated $\text{H}_2\text{SO}_4$, and evaporated to dryness to remove the bulk of the $\text{SiO}_2$. The residue is then fused with four to five times its weight of $\text{K}_2\text{S}_2\text{O}_7$, never less than 1 to 2 grams. The melt is finally extracted with water to which a few drops of $\text{H}_2\text{SO}_4$ have been added, and then filtered. The filtrate will now contain the elements not extracted in the acid treatment, especially the remainder of the Ti and Zr with small quantities of Fe, etc. This filtrate is then treated with an excess of $\text{NH}_4\text{OH}$, warmed to coagulate the precipitate, and filtered. The precipitate is washed free from sulphates and then the filter and contents are placed in a beaker with 1:1 $\text{HNO}_3$ and warmed, and finally added to the main filtrate. (Sec. 13.)

The residue from the $\text{K}_2\text{S}_2\text{O}_7$ fusion contains the W with a small amount of $\text{SiO}_2$, and is treated as outlined in section 3 for steel.

13. MAIN FILTRATE CONTAINING IRON, ALUMINUM, MOLYBDENUM, URANIUM, VANADIUM, ZIRCONIUM, ARSENIC, PHOSPHORUS, AND CHROMIUM.

The main filtrate is treated with an excess of $\text{Na}_2\text{O}_2$ and $\text{Na}_2\text{CO}_3$ as outlined in section 5 for steel. A second solution and precipitation is recommended to effect clean separations. The filtrate will contain the Al, Mo, U, V, Cr, As, and P, and is treated as under section 21. The residue contains all of the Fe, Ti, and Zr, which are separated as in section 10.

The second optional method (b, sec. 5) for separating the As and Mo may similarly be applied here. This is accomplished by evaporating the solution to dryness and redissolving in 2 or 3 c. c. of concentrated $\text{HCl}$ by warming, then diluting and heating. $\text{H}_2\text{S}$ is then passed through the solution and the precautions as given on page 79 are applied to this separation.

DECOMPOSITION OF SAMPLE BY FUSION WITH SODIUM-POTASSIUM CARBONATE AND POTASSIUM NITRATE.

14. SOLUTION OF MATERIALS LOW IN SILICA WHICH DO NOT RESPOND TO ACID DECOMPOSITION.

From 1 to 2 grams of the finely pulverized material is thoroughly mixed and fused with five to six times its weight of a mixture of $\text{NaKCO}_3$ and $\text{KNO}_3$ (5:1). After a quiet fusion has been obtained for a half-hour, the melt is rolled up the sides of the crucible while cooling, or poured into another larger platinum dish to facilitate subsequent solution in water. After cooling, the melt and crucible are placed in a 400 c. c. beaker, and the melt is decomposed by boiling. When the melt has thoroughly disintegrated, the solution is filtered, and the residue is washed with hot water. The filtrate (sec. 15) will contain the bulk of the W, Mo, U, V, Cr, As, P, and
SiO₂. The residue (sec. 16) will contain the Al, Fe, Zr, Ti, and a part of the SiO₂.

18. CARBONATE SOLUTION CONTAINING ALUMINUM, TUNGSTEN, MOLYBDENUM, VANADIUM, URANIUM, CHROMIUM, PHOSPHORUS, ARSENIC, AND SILICA.

Acidify the solution with 1:1 HCl and evaporate to dryness. Moisten the residue with a few cubic centimeters of concentrated HCl and warm for several minutes, then dilute with warm water; filter when the residue has thoroughly disintegrated and everything is in solution except the SiO₂ and W. Then filter and wash carefully with dilute HCl. The residue (sec. 19) now contains the W and SiO₂, which are separated and estimated as under section 3 for steel. The filtrate contains the Al, Mo, U, V, Cr, P, and As, and is treated as outlined under section 20.

19. RESIDUE FROM CARBONATE FUSION OF ORE CONTAINING ALUMINUM, IRON, ZIRCONIUM, TITANIUM, AND SILICA.

Treat the residue and filter paper with 1:1 HCl and pour the solution and paper pulp into a warm 10 per cent solution of NaOH, warm, and filter. Wash the precipitate (sec. 17), which now contains the Fe, Zr, TiO₂, and some SiO₂, with warm water, then dry, and ignite in a platinum crucible and fuse with from four to five times its weight of K₂S₂O₇, and reserve for treatment as under section 10 for steel. The filtrate (sec. 18), which contains the Al and traces of the other elements occluded in the residue from the carbonate fusion, is added to the main filtrate and treated as under section 15.

See summary chart 17, 18, and 19.

20. HYDROCHLORIC ACID SOLUTION OF ALUMINUM, MOLYBDENUM, URANIUM, VANADIUM, CHROMIUM, PHOSPHORUS, AND ARSENIC.

The separation of Al, Mo, U, V, Cr, P, and As may be conducted exactly as under section 6 for steel. Either of the optional methods, a and b, may be used.

21. SODIUM CARBONATE-HYDROXIDE SOLUTION CONTAINING ALUMINUM, URANIUM, VANADIUM, MOLYBDENUM, ARSENIC, PHOSPHORUS, AND CHROMIUM.

The sodium carbonate-hydroxide solution represents the filtrate obtained from the Fe, Ti, and Zr precipitation by means of Na₂O₂ and Na₂CO₃. Al, U, V, P, and Cr, as well as Mo and As—if the latter two elements were not removed as indicated under b, section 6—may be present in this solution.

Precipitation of aluminum and phosphorus: The filtrate should be evaporated to 400 c. c. in order to decrease the quantity to be filtered. Then 1:1 HNO₃ is cautiously added until a cloudiness forms, showing the precipitation of the Al as hydroxide and phosphate. To insure complete precipitation of the P, at least 10 times as much Al as P should be present. If this excess of Al is not known to be
present, it is advisable to add a quantity of sodium aluminite (10 grams of Al dissolved in 50 grams of NaOH and diluted to 500 c. c.). If the quantity of Al in the material being analyzed is required, the quantity of sodium aluminite added should be known. The proper conditions for precipitation are insured by the use of turmeric paper. An alkalinity that does not turn the test paper to even a faint brown quickly is desirable. (See Johnson (6), p. 222.) After these conditions have been obtained, add 1 to 2 grams of \((\text{NH}_4)_2\text{CO}_3\) to assist in holding the U in solution. Allow the solution to stand at least two hours and filter off the Al and P.

The precipitate is ignited in a platinum crucible, and weighed as \(\text{Al}_2\text{O}_3 + \text{P}_2\text{O}_5\), then fused with \(\text{Na}_2\text{CO}_3\), extracted with an excess of dilute 1:1 HNO\(_3\), and the P determined by precipitation as ammonium phosphomolybdate. If the direct determination of the Al is preferred, the precipitate containing the Al and P may be used before ignition. This is done by dissolving in 1:1 HNO\(_3\) and precipitating the P with ammonium molybdate, then by adding NH\(_2\)OH to the filtrate from the P, filtering off the Al\(_2\)O\(_3\), igniting, and weighing.

22. FILTRATE CONTAINING URANIUM, VANADIUM, CHROMIUM, ARSENIC, AND MOLYBDENUM.

The filtrate from the Al precipitation should be treated with a slight excess of HNO\(_3\) and boiled to expel the CO\(_2\). Boiling should continue until the volume of the solution is not over 400 c. c. The excess of HNO\(_3\) is then just neutralized with 1:1 NH\(_4\)OH, and 2 c. c. of concentrated HNO\(_3\) added for each 100 c. c. of solution. From 15 to 20 c. c. of a 10 per cent solution of lead acetate is then added, and enough sodium acetate to replace the HNO\(_3\). The solution is then heated for one hour on the water bath and filtered. The precipitate contains the V, Cr, As, and Mo as their respective lead salts, and is treated as in section 24. The filtrate contains the U and is treated as outlined in section 23.

23. ACETIC ACID SOLUTION CONTAINING URANIUM.

The U in this filtrate is precipitated as ammonium uranate and after ignition is weighed as U\(_5\)O\(_8\). First, however, the bulk of the Pb, from the excess of lead acetate used to precipitate the V, is removed by adding 10 c. c. of concentrated H\(_2\)SO\(_4\) and filtering. The remainder of the Pb and all of the U are then precipitated as their sulphides, and redissolved in 1:2 HNO\(_3\); the remainder of the Pb is removed by fuming with 5 c. c. of concentrated H\(_2\)SO\(_4\). The U is then precipitated as ammonium uranate by the addition of NH\(_2\)OH, filtered, and ignited. The resulting residue of U\(_5\)O\(_8\) should be redissolved in HNO\(_3\) and tested for V with H\(_2\)O\(_2\) and for
Al, which may have been introduced from the chemicals used. For details and precautions in the estimation of the U, see under "Ura-
nium," page 224.

24. PRECIPITATE CONTAINING THE LEAD SALTS OF VANADIUM, MOLYBDENUM, ARSENIC, AND CHROMIUM.

The lead precipitate is dissolved in the least possible amount of HNO₃ by placing the filter-paper with its contents in a beaker and warming. The mixture is diluted and filtered, and the paper pulp on the filter is carefully washed with hot water.

The Pb present in the filtrate is removed by fuming with H₂SO₄. The solution is then filtered and reserved for further treatment; it may contain V, Mo, As, and Cr, which may be separated and estimated separately, or estimated simultaneously by several satisfac-
tory methods.

a. Separation of arsenic and molybdenum from chromium and vanadium.—Whenever only a small quantity of molybdenum is present with a much larger quantity of V, a separation and separate determination of each of these elements is desirable. The As and Mo are best separated by first passing in a stream of SO₂ gas, fol-
lowed by precipitation with H₂S under pressure. (See p. 79.) The mixture of As and Mo sulphides is treated as under section 25. The V and Cr remain in solution, and may be separated as given under section 26 or determined simultaneously as outlined under section 24, c.

b. Simultaneous estimation of molybdenum and vanadium.—As previously indicated, a satisfactory procedure may be used for the simultaneous estimation of Mo and V in the presence of As and Cr. Edgar gives a satisfactory method, described on pages 260 and 261.

c. Simultaneous estimation of vanadium and chromium.—The V and Cr may be determined in the presence of the Mo and As by the FeSO₄ method of Johnson, which has been given on page 256. The V alone may be estimated in this solution without removal of the As, Mo, or Cr, by reduction with SO₂ for necessary acidity in order not to reduce the Mo (see p. 255); or by reduction with HCl as in the HCl method given on page 255.

25. SEPARATION OF ARSENIC AND MOLYBDENUM IN THE PRECIPITATE OF THEIR SULPHIDES.

The precipitated sulphides should be dissolved in HNO₃ with the addition of KClO₃, heated to effect solution, and filtered. The solution is then made alkaline with NH₄OH and magnesia mixture is added as outlined on page 100. The precipitate of magnesium-
ammonium arsenate is filtered off, ignited, and weighed as pyro-
arseniate. The Mo remains in the filtrate, which should be made slightly acid with HNO₃. Lead acetate and ammonium acetate are
added, and the Mo determined as lead molybdate. For details of this determination, see under "Molybdenum," page 96.

28. Hg SOLUTION CONTAINING VANADIUM AND CHROMIUM.

The filtrate obtained from the precipitation of the As and Mo is boiled to expel excess H₂S, and is then poured into a hot 10 per cent solution of NaOH. The Cr is obtained in the precipitate as Cr(OH)₃, while the V passes through into the filtrate. The filtrate is acidified with diluted H₂SO₄, and reduced by HCl or SO₂, and titrated with standard KMnO₄ after the removal of excess reducing agent. (See p. 273.)

27. ESTIMATION OF CHROMIUM.

The Cr in the precipitate is estimated by dissolving in dilute HNO₃ and precipitating as PbCrO₄. The bulk of the HNO₃ is first neutralized with NH₄OH, and the solution made slightly acid with acetic acid. The precipitate of PbCrO₄ is filtered off and dried to constant weight at 105°C, and weighed as PbCrO₄.

BIBLIOGRAPHY ON THE QUANTITATIVE SEPARATION AND ESTIMATION OF ALLOY METALS.

PART II.—CERIUM AND THORIUM.

By J. P. Bonardi.

INTRODUCTION.

CERIUM.

Cerium is usually regarded as belonging to the general group of rare earths, as it invariably occurs in nature associated with the other members of the group, and is very similar to the other rare-earth elements in many of its chemical properties. Before the discovery of monazite, cerite, $H_2(\text{CaFe})_3\text{Ce}_3\text{Si}_5\text{O}_{15}$, which is found principally in Sweden, was the chief source of cerium. Orthite (allanite, $H(\text{CaFe})_2(\text{AlCe})_3\text{Si}_5\text{O}_{15}$) was also an important cerium mineral; it is found mainly in Sweden, Canada, and the United States.

Cerium is now obtained mostly from monazite and from monazite sands. The mineral monazite has the general formula $\text{CeYtPO}_4$, $\text{ThO}_2\text{SiO}_5$. It occurs in Norway, in the Ural Mountains, in North and South Carolina, and in Canada. The disintegration product from the mineral called monazite sand is fine gravel or sand, and occurs in river banks and on the seashore, principally in Brazil, North and South Carolina, Australia, the Ural Mountains, and in the State of Travancore, southern India. Monazite is found also in Norway, Ceylon, South Africa, and Malaya, but none of these countries is now an important producer.

The sand as found naturally consists of particles of monazite, rutile, thorite, cassiterite, topaz, magnetite, quartz, and other heavy minerals. The monazite content varies from a trace up to 4 per cent, so that some method of concentration must be employed, such as washing by placer methods, wet table concentration, or magnetic separation. (See Kithil (52), and Johnstone (48).) In scattered regions of Brazil and India are sands that require little concentration.

The most important use for cerium is in the manufacture of gas mantles for incandescent lighting. The mantle, after it is properly made, is dipped into a solution consisting of 99 per cent Th and 1 per cent Ce, then it is ignited and given special treatment to stabilize the remaining skeleton. For detailed description, see Böhm (10), Johnstone (48), and Levy (58).
Cerium is also utilized in combination with other cerium earths—La, Nd, Pr, Sm—in pyrophoric alloys, and for "tracer" shells and bullets. Alloys of mixed cerium-earth metals are used as reducing agents to produce metal from metallic oxides. A mixture of about 35 per cent Fe and 65 per cent Ce is used for automatic lighters. Various combinations of various metals with Ce have been patented for use in pyrophoric alloys. It is claimed that the addition of 0.2 per cent of Ce metals to Al definitely improved its physical properties. To accomplish this effect, rare-earth fluorides are added to the cryolite melt from which Al is obtained. Cerium earths have been used in the carbon core in the manufacture of flaming arcs. Ce or mixed Ce earths have also been used in the textile industry, in the glass and porcelain industry, in nonferrous and ferrous alloys, photographic processes, medicine, catalysts, and as oxidizing agents. For the use of cerium as a desulphurizing agent in steel, see Gillett (34a).

**THORIUM.**

Thorium, like cerium, is included in the classification of the rare earths, as it is closely associated with the rare-earth minerals; it is precipitated with Ce and the rare earths by oxalic acid in a mineral acid solution, thus being separated from the common base metals.

The chief source of Th, as mentioned above, is monazite sand. Thorite (essentially ThSiO₄) and thorianite (essentially ThO₂·U₃O₈) were once considered as the only valuable sources of Th, but they are not now found in large enough quantities to be important as compared with the large deposits of monazite sand. Many other minerals can be regarded as thorium minerals, but they are not of great consequence.

Thorium as oxide (thoria) forms the chief chemical constituent of the mantles employed for the incandescent gas burner. Thorium nitrate is the chief form in which the Th is finally obtained from the ore to be used for this purpose. Other uses for Th are for catalyst, for intense illumination similar to the Drummond "limelight" for flash powders, and for filament in alloy form in some types of electric lamps.

**METHOD OF DECOMPOSITION AND SOLUTION OF THE RARE EARTHS FROM MINERALS AND OTHER PRODUCTS.**

**DECOMPOSITION.**

The mineral or ore sample must be finely powdered, at least to minus 100-mesh, and then treated with either hot concentrated HCl or H₂SO₄; HNO₃ is very little used alone. Acid treatment generally gives a solution; but some minerals require a fusion, sodium bisulphate being commonly used. Occasionally, digestion is first
made with HF, followed by $\text{H}_2\text{SO}_4$ treatment. Decomposition may sometimes be accomplished by aqua regia, but better results may be expected by $\text{H}_2\text{SO}_4$. Spencer (91, p. 23) makes the following remarks regarding solution of the rare-earth minerals:

The minerals cerite, orthite, gadolinite, thorite, and yttrialith yield readily to treatment with hydrochloric acid. Xenotime, yttrotitanite, thorianite, and monazite require sulphuric acid for their decomposition; while fergusonite, euxenite, polycrase, samarskite, and yttroantalite can only be got into solution by fusion with sodium bisulphate or treatment with hydrofluoric acid. It is always wiser when a mineral has to be fused to use sodium bisulphate in preference to potassium bisulphate, because many of the rare-earth sulphates form sparingly soluble double sulphates with potassium sulphate, whereas those that form with sodium sulphate are much more soluble. When a mineral is digested with hydrofluoric acid the rare earths are left as insoluble fluorides, which must be decomposed by boiling with sulphuric acid in order to obtain a solution. Before a method of separation can be chosen it is necessary to make a preliminary examination of the solution to ascertain which group of elements is present in the larger quantity. A spectroscopic examination usually is sufficient for this purpose, and additional evidence as to the composition of the mixture can be gained from the nature of the mineral from which the earths have been derived.

It will be noted in the above outline that with the exception of those containing large proportions of Cb, Ta, and Ti, the rare-earth minerals are easily decomposed by acids. Fusion with $\text{Na}_2\text{O} \cdot \text{O}_3$ nickel or iron crucible is a quick and energetic method for decomposing nearly all classes of material. A description of the working up of rare-earth minerals is included in a paper by James (45).

Cerite can be conveniently brought into solution for analysis by fusing 0.5 gram of the finely powdered mineral with potassium bisulphate, and the melt dissolved in about 350 c. c. of cold water acidulated with not more than 5 c. c. of concentrated $\text{H}_2\text{SO}_4$; care is taken during fusion that no undecomposed cerite remains on the side of the crucible. The solution is left in contact with the residue over night to insure the solution of all basic salts that may have formed.

Monazites (usually 0.5-gram samples in preparation for analysis) are best decomposed by heating on a hotplate in small porcelain dishes with concentrated $\text{H}_2\text{SO}_4$ for about four hours, until no yellow undecomposed grains remain, the mixture being stirred occasionally. The residue is then poured into at least 300 c. c. of ice-cold water and then allowed to stand over night to complete the solution of all basic salts that might have formed.

**SOLUTION AND PRECIPITATION OF CERIUM, THORIUM, AND THE RARE EARTHS.**

After the powdered mineral has been digested with $\text{HCl}$, $\text{HF}$, aqua regia, $\text{H}_2\text{SO}_4$, or a combination of acids—always finishing with $\text{H}_2\text{SO}_4$ in solution—the solution containing the excess acid is evap-
orated to copious fumes of SO₃. Carrying a solution down to near dryness with H₂SO₄ several times insures the conversion of phosphate minerals into sulphates. The residue is next extracted, as previously stated, with ice-cold water and acidulated with a little concentrated H₂SO₄, to render soluble the rare-earth sulphates, leaving behind the insoluble SiO₂. The solution should remain in contact with the residue over night, or until all basic salts that may have formed are dissolved. If the mineral carries much Ti, Cb, etc., the residue obtained in the above acid treatment should be extracted with HNO₃, then the solution is evaporated to dryness after filtration and the residue is extracted with dilute HCl. If a bisulphate fusion has been made, the melt is extracted with ice-cold water, rendering soluble the rare-earth double sulphates. This solution is carried to dryness, and extracted with dilute HCl. The solution now containing the rare earths as well as the common base metals is saturated with H₂S to remove the second-group elements, and after the excess H₂S has been boiled off is treated with NH₄OH and NH₄Cl, thus precipitating the rare earths and some members of the third group (division A) away from the remaining members of the third group and from elements of the fourth and fifth groups. The precipitate, after being washed, is dissolved in dilute HCl, the dilution being so adjusted that approximately 1 gram of the rare-earth oxides is contained per 60 c. c., and the acidity is not over 0.5 N (about 18 grams HCl per liter). The solution is then heated to 60°, and the rare earths—including Th and Ce—are precipitated by the addition of enough excess oxalic acid to leave 3 grams of oxalic acid per 100 c. c. of final solution. It is best to allow the solution to stand over night if possible—at 60°—then the precipitate is filtered off and thoroughly washed with hot, slightly acidified water. If foreign metals, such as Zr or Ti, are present in much quantity, and especially if the presence of phosphates is suspected, the oxalate precipitate should be ignited to the oxides, dissolved in HCl, and a second precipitation made with oxalic acid. This second treatment will insure the removal of Zr, Ti, and phosphoric acid. Further details for decomposition and solution of rare earths are given in the description of quantitative methods (pp. 50 to 64).

For the decomposition of alloys or of steel and such products, the ordinary acid procedure for such products is carried out, finishing up by an H₂SO₄ decomposition, carrying to near dryness, and extracting in the usual manner with ice-cold water. For a fusion method, Na₂O₂ or a carbonate niter mixture is also recommended, besides the use of bisulphate for opening up the sample. The material must always be very finely powdered.
CHEMICAL PROPERTIES OF CERIUM AND THORIUM.

PROPERTIES AND COMPOUNDS OF CERIUM.

The properties and compounds of cerium are here described because a proper understanding of the quantitative analysis of any element depends largely on an understanding of certain chemical facts. The following information was taken in part from Schoeller and Powell (87), Spencer (91), Roscoe and Schorlemmer (80), and Treadwell and Hall (94).

Metallic cerium can be obtained as powder by the reduction of anhydrous cerous chloride by means of Na, K, Mg, or Al. By electrolysis of the fused chloride, Ce is obtained in coherent form. See Spencer (91), and Roscoe and Schorlemmer (80). It has also been prepared by heating the dioxide with magnesium powder. Cerium is a powerful reducing agent, owing to its great affinity for oxygen; its color and luster are similar to iron, it is soft and ductile, has a hardness approximate to that of lead, and is dissolved readily by dilute mineral acids. Cerium alloys with a number of nonmetals and with various metals to form intermetallic compounds. For numerous industrial purposes cerium alloys have been put into use principally in manufacturing pyrophoric alloys.

Cerium dioxide, CeO₂, is the only oxide of cerium that is obtained when any cerium compound of a volatile oxyacid salt is ignited in air—that is to say, ignition of the sulphate, nitrate, or oxalate—also when the hydroxide or carbonate is ignited. The pure oxide is white, but it is colored light brown to reddish brown when contaminated with any of the rare earths of the cerium group. It is difficultly soluble in HNO₃ or HCl, but is rendered readily soluble in the presence of reducing agents. It is also difficultly soluble in strong H₂SO₄.

Cerous hydroxide, Ce(OH)₃, is produced by the addition of an alkali to solutions of cerous salts. NH₃·H₂O and (NH₄)₂S produce the hydroxide, insoluble in excess of the reagent. In the presence of tartaric or citric acid no precipitation takes place. The white Ce(OH)₃, on standing in the presence of air, becomes yellow on account of being oxidized to the ceric hydroxide, Ce(OH)₄. Oxidation takes place immediately on the addition of chlorine, bromine, iodine, or hypochlorites. Cerous salts can be oxidized in acid solution by ammonium persulphate, or by heating with PbO₂ and HNO₃. Ceric salts in acid solutions are reduced by H₂O₂, hence H₂O₂ will not oxidize cerous to ceric.

Cerous oxalate, Ce₂(C₂O₄)₃·10H₂O, is precipitated by the addition of oxalic acid to a dilute mineral acid solution of the cerous or ceric salt. If pure, the color is white; but if it is contaminated with other rare
earth, a pinkish or cinnamon-colored oxalate is obtained; insoluble in an excess of the reagent, water, dilute acids, and ammonium oxalate (differing in this respect from thorium).

Cerous carbonate, Ce₂(CO₃)₂5H₂O, is precipitated by a solution of Na₂CO₃, K₂CO₃, (NH₄)₂CO₃, and BaCO₃; insoluble in an excess of the reagent. If a concentrated solution is used as a precipitant, a precipitate of the double hydrated carbonate is produced.

Double sulphate of cerium and potassium or sodium, Ce₂(SO₄)₃3.3K₂SO₄, or Ce₂(SO₄)₃·Na₂SO₄, is produced as a white crystalline precipitate on the addition to a neutral solution containing Ce of an excess of K₂SO₄ or Na₂SO₄; difficultly soluble in cold water, and insoluble in a saturated solution of the precipitant, as are also the remaining Ce earths. Thorium sulphate is somewhat soluble in a saturated solution of sodium sulphate, and insoluble in a saturated solution of potassium sulphate.

Cerous sulphate, Ce₂(SO₄)₃, is obtained by heating any one of the cerous hydrated sulphates. There are several hydrated sulphates that can be obtained under the proper regulated conditions. The anhydrous salt is very soluble in ice-cold water. Spencer (91) describes the mode of preparing these sulphates and their solubilities. In comparison with the solubilities of Th, these different sulphates vary enough to make possible separation of these two elements.

In the presence of H₂O₂ in the cold, NH₂OH throws down from solutions of cerous salts a reddish brown precipitate of a peroxide-hydrate. From Th solutions a white gelatinous precipitate is obtained under similar conditions. The reaction for Ce is very delicate, and constitutes one of the best methods for detection. (See p. 26.)

**PROPERTIES AND COMPOUNDS OF THORIUM.**

Thorium, like cerium, belongs to the third analytical group, forming a hydroxide insoluble in the alkali hydroxides. It forms also a double sulphate with potassium or sodium sulphate, insoluble in excess, and hence is found associated with the cerium earths. The chloride, sulphate, and nitrate are soluble in water from which oxalic acid precipitates the oxalate insoluble in dilute mineral acid. Of the common salts, Th differs mainly from Ce in that the carbonate or oxalate is soluble in excess of ammonium carbonate or ammonium oxalate solutions. Thorium forms only one series of salts in which the metal is tetravalent. Thorium differs principally from cerium or the rare earths in having radioactive properties. In the course of decay, it gives rise to mesothorium and other products that are strongly radioactive. Mesothorium is chemically identical with radium, therefore it is classed as isotopic with it. The detection, then, of thorium minerals is performed precisely as radium ores. (See p. 29.) The test, however, does not distinguish between
uranium-bearing minerals—Ra is produced by disintegration of U—and Th minerals; hence, further tests must be made for confirmation.

Thorium has been obtained as the metal by various processes, but not in a chemically pure condition. Some of the processes that have been used are the following: The action of sodium or potassium on the double alkali fluoride or chloride of thorium; the action of sodium or thorium chloride; and the electrolysis of the fused chloride. (See Spencer (91).) Aqua regia dissolves it readily, whereas the single mineral acids are variable in their action. The metal exhibits radio-active properties. Its alloys with a number of metals and inter-metallic compounds have been used for industrial purposes.

Thorium dioxide, ThO₂, is obtained when any Th compound of a volatile oxyacid salt is ignited in air. When mixed with about 1 per cent of ceria (CeO₂) and strongly heated it emits a very brilliant light; this property is utilized in incandescent gas mantles. The pure dioxide is white. Ignited ThO₂ has found application as a catalyst in the preparation of some organic compounds; it is insoluble in acids except boiling strong H₂SO₄. When fused with bisulphate and leached with cold water it is rendered soluble.

Thorium hydroxide, Th(OH)₄, is obtained by adding NH₄OH or caustic alkalies to a solution containing Th salt; it is insoluble in excess of alkalies. The addition of BaCO₃ to a cold solution precipitates the hydroxide. In a boiling solution, thiosulphate precipitates a mixture of the hydroxide and free sulphur, differing from cerium. The hydroxide is readily soluble in dilute mineral acids and in solutions of alkali carbonates.

Thorium peroxide (hydrated Th₂O₃) is a white gelatinous precipitate and is obtained by adding NH₄OH and H₂O₂ to a solution of Th salts. H₂O₂ added to a solution of thorium acetate precipitates a peroxidized salt. From a neutral solution of thorium nitrate, H₂O₂ precipitates a thorium peroxyxinitrate. If Ce is present, a small quantity accompanies the precipitate; a second treatment generally removes the cerium.

Thorium oxalate, Th(C₂O₄)₂·6H₂O, is precipitated similarly to cerium oxalate by the addition of oxalic acid to a dilute mineral acid solution of thorium salt; it is soluble in alkaline oxalate solutions; and is reprecipitated on addition of mineral acid. On ignition it is converted to the dioxide.

Thorium fluoride (ThF₄) is precipitated by the addition of HF or a fluoride to a solution of a thorium salt and is insoluble in HF. Thorium forms a number of double fluorides with alkali fluorides, insoluble in water or dilute acid solution.

Thorium sulphate, Th(SO₄)₂, is obtained by attacking ThO₃ with H₂SO₄, and the excess acid is removed by evaporation. This sulphate is very soluble in ice-cold water, but is reprecipitated as a crystalline
hydrate on boiling, depending on the concentration. If it is allowed to stand without boiling, a series of hydrated sulphates will crystallize out, the composition depending on the conditions of concentration and temperature. This property of forming a number of hydrated sulphates which differ in solubility from the sulphates of the cerium earths serves as a basis for one of the commercial methods of separation of Th from other rare earths, called fractional crystallization of the sulphates. For detailed data on the solubilities of the various rare-earth sulphates, see Johnstone (48), Spencer (91), and Levy (58). Like Ce, Th forms insoluble double salts with a saturated solution of $K_2SO_4$. The ammonium and sodium salts are soluble in water and in alkali sulphate solution, hence the potassium salt is used for this separation.

Thorium carbonate is formed by the addition of alkali carbonates to solutions of thorium salts. The precipitate is basic, no neutral carbonate being known. Basic thorium carbonate is soluble in excess of alkali carbonates to form double alkali carbonates, and at one time formed a basis for an important method of separation of Th from rare earths; the common practice now is to effect a concentration of Th by means of MgO, as the basicity of Th is weaker than that of the other earth. This treatment, when performed on a sulphate solution from the digestion of monazite sands, precipitates a mixture of phosphates. If performed after the phosphoric acid has been previously removed by oxalic acid on a solution of the earths, it gives the hydroxide of thorium in a concentrated form.

Thorium acetate, $\text{Th}([\text{CH}_3\text{COO}])_4$, is formed by adding ammonium acetate to a solution of the sulphate. By boiling a solution of a thorium salt with sodium acetate, thorium basic acetate, $\text{Th}([\text{CH}_3\text{COO}])_2\text{H}_2\text{O}$, is precipitated out.

Phosphates of thorium: Thorium forms many phosphate compounds which are insoluble in water, and some of which are precipitated out in dilute acid solution. Some of the common phosphates are normal thorium phosphate, $\text{Th}_3([\text{PO}_4])_4\cdot 4\text{H}_2\text{O}$; acid thorium phosphate, $\text{ThH}_2([\text{PO}_4])_2\cdot 2\text{H}_2\text{O}$; and thorium pyrophosphate, $\text{ThP}_2\text{O}_7\cdot 2\text{H}_2\text{O}$. They are all formed by the addition of the appropriate phosphate salt to a solution of thorium chloride. The insolubility of the pyrophosphate in dilute acids forms a basis for the quantitative estimation of thorium. Under similar conditions Ce is not precipitated if previously reduced. (See also pp. 28 to 49.)

**QUALITATIVE DETECTION OF CERIUM AND THORIUM.**

**QUALITATIVE DETECTION OF CERIUM.**

**BY MEANS OF HYDROGEN PEROXIDE.**

The rare earths must be previously separated as oxalates from the common base metals, ignited, dissolved in HCl or $\text{HNO}_3$, taken to
dryness, and the residue dissolved in water. If necessary, the process is repeated in order to obtain a neutral solution.

A characteristic reaction for the cerium compounds is the precipitation of orange to reddish brown precipitate by the addition of ammonia to a rare-earth solution in the presence of hydrogen peroxide. (See Treadwell and Hall (94).) Other oxidizing agents, such as sodium hypochlorite and sodium peroxide, may be used. The composition of the precipitate has been given various formulas, such as CeO₂, Ce₂O₃, Ce₂O₃·H₂O₂, CeO₃·H₂O, and Ce(OH)₃O₂H. This precipitate when dissolved in hydrochloric acid evolves chlorine, or in the presence of KI iodine is liberated. When large quantities of foreign earths are present, ammonia should be added drop by drop to a solution containing hydrogen peroxide, until a small permanent precipitate remains; this precipitate will be rich in the weakly basic ceric hydroxide. (See Marc (59).) The color is rather like that of Fe(OH)₃. When solution containing a small quantity of cerium is added to a warm concentrated potassium carbonate solution, followed by a few drops of H₂O₂, a very characteristic yellow color is produced. (See Meyer (66).)

In making the ammonia and hydrogen peroxide test it is not absolutely necessary that NH₄OH be added to a solution previously peroxidized; the order may be reversed if desired by making slightly alkaline, followed by H₂O₂. The characteristic reddish-brown precipitate will be likewise formed from the already precipitated cerium hydroxide.

BY MEANS OF AMMONIACAL SILVER NITRATE.

Ammoniacal silver nitrate when added to a neutral solution of a cerous salt and warmed gives in dilute solutions (1 to 2 mg. per liter) a brown color, and in concentrated solutions a black precipitate. (See Biltz and Zimmermann (8).)

BY MEANS OF TARTRIC ACID AND HYDROGEN PEROXIDE.

Tartaric acid, when added to a cerium solution, then made ammoniacal, and boiled with a few drops of H₂O₂, develops an intense yellowish-brown color. (See Wirth (99).)

BY MEANS OF LEAD PEROXIDE AND NITRIC ACID.

By boiling a solution of cerium with lead peroxide and HNO₃, a deep-yellow color is imparted to the solution by the formation of ceric nitrate. (See Scott (88).)

BY MEANS OF BROMINE ON THE PRECIPITATED RARE-EARTH HYDROXIDES.

To a solution of rare earths add potassium or sodium hydroxide until precipitation of the hydroxide is complete and about 2 to 5
grams of alkali remain in excess. Make the volume up to at least 200 c. c. Bromine water is then added to distinct excess, and the mixture is placed upon a steam bath until most of the bromine has been expelled. This treatment effects a solution of the rare-earth hydroxides except the cerium, which remains undissolved as hydrated ceric oxide with a deep-yellow color. (See Browning and Roberts (22).) When hydrated ceric oxide is dissolved in HCl and treated with KI, it liberates free iodine. None of the tests above given is as delicate as the ammonia and hydrogen peroxide test.

**QUALITATIVE DETECTION OF THORIUM.**

In a solution containing the rare earths that have been separated from the common base metals by means of oxalic acid, thorium can be detected by the following methods:

**BY MEANS OF HYDROGEN PEROXIDE.**

When H₂O₂ is added to a warm neutral solution of the rare earths, it causes only the precipitation of a thorium peroxidized salt. Some Ce will be carried down but a second precipitation will usually keep this in solution. (See Benz (7); Borelli (12); Wyrouboff and Verneuil (104), (105).)

**BY MEANS OF SEBACIC ACID.**

When sebacic acid is added to a neutral solution of the rare earths and boiled, it precipitates thorium sebacate. (See Smith and James (90).)

**BY MEANS OF SODIUM THIOSULPHATE.**

When a solution of sodium thiosulphate is added to a neutral solution of the mixed earths and the solution is boiled, a yellowish precipitate of thorium hydroxide and free sulphur is thrown down, the other earths remaining for the most part in solution. If the precipitate is converted to the oxalate and extracted with ammonium oxalate solution, thorium will be found in solution, leaving behind the insoluble oxalates of the accompanying earths. The addition of a mineral acid to this solution will precipitate crystalline thorium oxalate. (See Benz (7); Drossbach (31); Fresenius and Hintz (32); and Hintz and Weber (41).)

**BY MEANS OF POTASSIUM IODATE.**

The addition of a solution of potassium iodate in concentrated nitric acid solution precipitates thorium iodate. Cerium, if reduced to the cerous condition, remains in solution along with the other earths. (Meyer and Speter (72).) The procedure given by Meyer (68) for this test is as follows: Two solutions are required: A, Fifteen
grams of potassium iodate, 50 c. c. of concentrated HNO₃, and 100 c. c. of water; and B, 4 grams of potassium iodate, 100 c. c. of HNO₃ (sp. gr. 1.2), and 400 c. c. of water. Two cubic centimeters of the solution of the oxides from ignition of the oxalate (free from HCl) is mixed with 5 c. c. of solution A. The precipitate formed contains thorium iodate, together with iodates of the other rare earths. The latter are dissolved by boiling with 10 c. c. of solution B, leaving the thorium insoluble. This method detects 0.0002 gram of thoria in 2 c. c. of solution.

BY MEANS OF PYROPHOSPHATE.

When added to a solution of sulphates or chlorides, with the acidity adjusted to approximately 0.3 N, sodium pyrophosphate precipitates thorium pyrophosphate. The pyrophosphates of the tervalent rare earths are soluble in dilute acids. Cerium, if reduced by SO₂, remains in solution. (See Carnéy and Campbell (23).)

RADIOACTIVITY (ELECTROSCOPIC) AND SPECTRUM (SPECTROSCOPIC) EXAMINATION.

Thorium minerals can be detected by means of the alpha-ray method—using the electroscope as given for uranium-bearing ores—as well as by chemical tests. The alpha-ray test, however, does not distinguish between thorium and uranium, but it serves as a quick method for detecting the absence or presence of these two elements, after which further confirmatory tests can be made by other means. The absence of uranium will then indicate the activity due to thorium, and vice versa.

Thorium is usually associated with other rare-earth minerals, the presence of which can be detected by the aid of a spectroscope. When such minerals are examined spectroscopically (a pocket or hand spectroscope being adequate), the reflection spectra will show the characteristic absorption spectra of the elements contained in the mineral. Kithil (52) states as follows concerning this method of examination:

Determination is best accomplished by spreading some of the concentrated sand on a piece of paper or cloth and holding the spectroscope over the sand at a convenient angle, the natural light falling directly on the sand. A fairly broad dark line will appear between the red and the yellow of the spectrum, and another but narrower line will be seen in the green. These dark absorption bands seem to be due principally to the presence of the rare-earth oxides of neodymium, praseodymium, and erbium contained in the mineral. Such spectrum tests for monazite can be safely relied upon when observed by the trained eye. The entire spectrum used is divided into a scale of 63 mm., the first and broader dark lines becoming visible between the thirteenth and fifteenth mm. lines. The narrow dark lines appear between 21 and 22 mm. of the scale. The spectrum method of testing in the field is most helpful in far-away places where a laboratory is not available.
QUANTITATIVE SEPARATION OF CERIUM AND THORIUM.

SEPARATION OF CERIUM AND THORIUM FROM THE COMMON METAL BASES, AND FROM TITANIUM AND ZIRCONIUM.

Cerium and thorium are members of the third analytical group, along with Al, Fe, Zr, Ti, etc., being separated from the members of this group and other common metal bases by means of oxalic acid added to a slightly acid solution. They are not separated from the other rare earths, as these are also precipitated by oxalic acid. The conditions most favorable for this separation are described by Schoeller and Powell (87); Hintz and Weber (41); Drossbach (31); Benz (7); Hauser and Wirth (40); and Glaser (35).

Schoeller and Powell (87) describe the best conditions as follows:

The chloride solution, containing not more than 1 gram of the oxides per 60 c. c., is adjusted to an acidity equivalent to 0.3N and treated with a saturated solution of oxalic acid sufficient to leave 3 grams of oxalic acid per 100 c. c. of final solution. The flocculent precipitate of the rare-earth oxalates rapidly becomes crystalline. The solution is allowed to stand at 60° for 12 hours, or overnight, after which the precipitate is filtered off and thoroughly washed with hot, slightly acidified water. If much foreign metals are present, it is advisable to digest the precipitate with caustic soda, filter, wash with boiling water till free from oxalates, dissolve the hydroxide in nitric acid, and reprecipitate as before.

The foregoing procedure will effect a complete separation of Ce, Th, and the rare earths from Ti and Zr—two troublesome elements associated with cerium minerals, which interfere in subsequent determinations unless removed. The second-group elements are removed in the usual manner by means of H₂S in an acid solution. Members of the fourth group—the alkaline earths, Mg, Zn, Mn, Ni, and Co—remain in solution when the rare earths are precipitated along with the iron group with ammonia in the presence of ammonium chloride, as in the ordinary qualitative separations.

SEPARATION OF THORIUM FROM CERIUM AND THE RARE EARTHS.

The descriptions of the following separations are here so presented that they serve for the sections on both cerium and thorium. The separation of thorium from cerium can be effected by any of the following methods:

1.—By precipitation of the thorium from the neutral solution of the nitrates with hydrogen peroxide.

2.—By precipitation of the thorium from neutral solution of the chlorides with sodium thiosulphate.

3.—By precipitation of the thorium from strong nitric acid solution with potassium iodate.

4.—By precipitation of the thorium from H₂SO₄ or HCl solution with sodium pyrophosphate. In the filtrate from the thorium pre-
cipitate the other rare earths may then be precipitated with an excess of caustic soda, the hydroxides being filtered off and well washed with boiling water until free from the precipitate. Double precipitation of the thorium pyrophosphate is performed to get rid of the traces of other earths carried down.

5.—By precipitation of the thorium from neutral solution by means of sebacic acid.

BY MEANS OF HYDROGEN PEROXIDE.

The precipitation of thorium from the neutral solution of the nitrates with $\text{H}_2\text{O}_2$ is described by Benz (7); Borelli (12); Wyrouboff and Verneuil (102), (103), (104), and (105); Schoeller and Powell (87); Treadwell and Hall (93); and Spencer (91), pages 51 and 189. The separation of thorium takes place in the presence of cerium and yttrium earths, but if large quantities of these two earths are present, the thorium precipitate always contains small quantities of them. Hence, most of these earths should be previously removed by one of the methods later described, or two or three repetitions made with this method. The procedure for carrying out the separation by the $\text{H}_2\text{O}_2$ method is as follows:

The neutral solution of the nitrates is diluted to 100 c. c., 10 grams of ammonium nitrate is added, the solution is heated to 60 or 80°, and the thorium is precipitated by adding 20 c. c. of 3 per cent hydrogen peroxide. The gelatinous precipitate, $\text{Th}_2\text{O}_7\cdot\text{N}_2\text{O}_5$, is filtered off, washed with 2 per cent ammonium nitrate, redissolved in dilute $\text{HNO}_3$, the solution evaporated to dryness, the residue moistened with water, dried again, dissolved in 100 c. c. of 10 per cent ammonium nitrate, and the thorium reprecipitated by the addition of $\text{H}_2\text{O}_2$. The precipitate is washed with 2 per cent $\text{NH}_4\text{NO}_3$, dried, and ignited to $\text{ThO}_2$. Ammonium nitrate assists the precipitate to settle and to assume a form that is easily washed and filtered. If a neutral chloride solution is used, a repetition of the precipitation is necessary to remove all the cerium. A neutral solution of the nitrates is best effected by evaporating to dryness on the water bath the ignited oxalates that have been dissolved in $\text{HNO}_3$, the residue moistened with water, and again dried. This residue is then taken up in enough water to dissolve the salts. A small quantity of cerium usually accompanies the thorium precipitate, but as a rule it is removed completely by the second treatment.

BY MEANS OF SODIUM THIOSULPHATE.

The separation of thorium by the use of sodium thiosulphate is discussed by Benz (7); Drossbach (31); Fresenius and Hintz (32); Hintz and Weber (41); and Metzger (63). When a solution of sodium
thiosulphate is added to a neutral solution of the mixed earths and the solution is boiled, a yellowish precipitate of thorium hydroxide and free sulphur is thrown down—by hydrolysis of potential thiosulphate and the decomposition of unstable thiosulphuric acid—the other earths remaining mostly in solution. Thorium thiosulphate is not formed, as stated by some writers. Aluminum, zirconium, and titanium, if present, are also precipitated. The precipitation of thorium hydroxide by thiosulphate is not entirely free from the other earths, but if the precipitate is converted into oxalate and the oxalate is extracted with ammonium oxalate solution—in which lanthanum and thorium oxalates are soluble—and then is largely diluted with water to precipitate the lanthanum, a pure thorium oxalate can be obtained from the solution by adding hydrochloric acid. Scandium is also precipitated from all the rare earths by means of sodium thiosulphate, but difficulty arises in its separation from thorium, as described below. The procedure for the separation of thorium from cerium by the sodium thiosulphate method, which is also applicable for a quantitative determination of thorium, is described by Schoeller and Powell (87) as follows:

The hydrochloric solution of the ignited oxalates is evaporated to dryness on the water bath, the residue moistened with 5 c. c. of water and again dried. It is then taken up with 200 c. c. of water, 9 grams of sodium thiosulphate crystals dissolved in 30 c. c. of water are added, and the whole allowed to stand overnight. The solution is boiled 10 minutes, and the precipitate of thorium hydroxide and sulphur filtered off and well washed with water. The filtrate is vigorously boiled for one hour, and any precipitate that forms filtered on a fresh small filter and set aside for further treatment. The main precipitate is washed back with a minimum of water into the same beaker, boiled with 10 c. c. of hydrochloric acid, the liquid filtered into a small evaporating basin, and the residual sulphur well washed. The filtrate is evaporated to dryness, the residue moistened with water, dried again, dissolved in 150 c. c. of water and treated with 3 grams of sodium thiosulphate in strong solution. After standing overnight the solution is boiled 10 minutes, filtered, and the wash precipitate extracted with hydrochloric acid. This solution is evaporated, etc., and again put through the entire process, finally giving a solution of thorium chloride which is precipitated with oxalic acid as follows: Solution containing 10 c. c. concentrated hydrochloric acid is diluted to 150 c. c., heated to 40 to 60°, and precipitated by the addition of 30 c. c. of a cold saturated solution of oxalic acid. The warm solution is allowed to stand half an hour, then stirred vigorously, and set aside three to four hours, or better, overnight at a temperature of 60° C. The white crystalline precipitate is filtered off, washed with warm water, acidified with hydrochloric acid, and ignited wet to ThO₂.

The filtrates from the second and third thiosulphate precipitations are treated with ammonia; if the precipitate thus produced in the third filtrate is appreciable—showing that the thorium is contaminated with rare earths—a fourth precipitation must be made. The precipitate produced by the one hour's boiling of the filtrate from the first thiosulphate precipitation, the ammonia precipitates, and the sulphur residues are ignited together with the filter; the ignited product contains traces of thorium, which are recovered as follows: Fusion with bisulphate, leaching with hot water, precipitation with ammonia, solution of the precipitate in hydrochloric acid, evaporation,
precipitation with thiosulphate, extraction of the precipitate with hydrochloric acid, and precipitation with oxalic acid. The small quantity of thoria thus found is added to that previously obtained.

Scandium, aluminum, zirconium, and titanium will be also precipitated along with thorium by the thiosulphate. The oxalate precipitation leaves aluminum, zirconium, and titanium in solution. Scandium, if present, can be removed from the hydrochloric acid solution of the thiosulphate precipitate by evaporating to dryness, dissolving in a little water, and pouring with constant stirring into 25 c. c. of 20 per cent solution of ammonium tartrate. A clear solution is obtained, which is treated with excess of ammonia and boiled until the precipitate of ammonium scandium tartrate has settled. Thorium remains in solution and can be recovered by evaporating to dryness, igniting to oxide, dissolving in acid, and precipitating with oxalic acid. The precipitated scandium, after being filtered off and washed, is boiled with ammonium tartrate solution, filtered, washed, ignited to scandia, and weighed. (See Spencer (91).

This separation by means of sodium thiosulphate is entirely too long a process for quantitative determination, but it is more applicable to the preparation of pure thorium compounds in which no definite time for completion is fixed.

BY MEANS OF POTASSIUM IODATE FROM STRONG NITRIC ACID SOLUTION.

The addition of a solution of potassium iodate in concentrated HNO₃ solution precipitates thorium iodate. The cerium must be reduced to the cerous condition. Zirconium and titanium, if present, will be precipitated also, but can be removed from the thorium by dissolving out with warm oxalic acid. (See Meyer and Speter (72).) The following procedure is that given by Schoeller and Powell (87):

The solution of the rare earths made up to 100 c. c., treated with 50 c. c. of concentrated nitric acid and cooled. A solution of 15 grams of potassium iodate in 30 c. c. water and 50 c. c. of nitric acid is added, the mixture cooled again, and allowed to stand for half an hour with frequent stirring. The white, flocculent precipitate of thorium iodate is left to settle, filtered off, and washed with 200 c. c. of a solution containing 8 grams of potassium iodate and 200 c. c. nitric acid (1.2 sp. gr.) per liter. The thorium is reprecipitated by adding to the cooled solution 4 grams of potassium iodate dissolved in a little concentrated nitric acid and water, the precipitate filtered, and washed as before. Titanium and zirconium are also precipitated under similar conditions. To remove these, the precipitate is dissolved in hydrochloric acid and a little sulphur dioxide to reduce ceric to cerous condition, the thorium, zirconium, and titanium precipitated with ammonia, washed free of iodides, redissolved in hydrochloric acid, and the thorium alone precipitated by the addition of a saturated solution of oxalic acid in large excess, as described under 2, of previous section; the oxalate can then be ignited and the thoria weighed.
Brinton and James (17) have developed a method for determining cerium (thorium being absent) by precipitation of cerium as ceric iodate by the use of potassium bromate and potassium iodate in a HNO$_3$ solution. The presence of other rare earths does not interfere.

**BY MEANS OF PYROPHOSPHATE.**

(See Carney and Campbell (23); Spencer (91); and Schoeller and Powell (87).) The pyrophosphates of the trivalent rare earths are soluble in dilute acids, those of the quadrivalent earths—Th, Ce (ic), Zr—are insoluble. Cerium is reduced by SO$_2$ and remains in solution. A method based on these facts has been devised for the estimation of thorium, which will be described below. The procedure for the separation by means of pyrophosphates is as follows: To the solution of sulphates or chlorides, the acidity is adjusted with enough hydrochloric or sulphuric acid to make the solution have a total acidity of 0.3N, heated to boiling, and sodium pyrosulphate is slowly added until no more precipitate forms. The solution is then boiled for five minutes, allowed to settle for 5 to 10 minutes, filtered, and washed with 0.3N HCl. The precipitate contains thorium pyrophosphate, ThP$_2$O$_7$, the pyrophosphates of zirconium and titanium, and any quadrivalent cerium that may be present. The acidity should be kept at the figure mentioned; if it is less, some thorium may not be precipitated; if more, some thorium pyrophosphate may be dissolved. The acidity may vary, however, within fairly wide limits. Cerium pyrophosphate dissolves completely in HCl, hence will not contaminate the thorium, which forms an insoluble pyrophosphate in an acid solution.

The washed precipitate is heated with a little H$_2$SO$_4$ and a little sodium or ammonium perchlorate to oxidize organic matter. Water is added slowly, and the solution of sulphate is poured into a solution of sodium hydroxide. The precipitated thorium hydroxide is boiled with dilute hydrochloric acid, sulphur dioxide is passed in to reduce traces of cerium to the cerous condition, the solution is adjusted to 0.3 N, and the thorium again precipitated with pyrophosphate. The precipitate is treated as before with H$_2$SO$_4$, and the solution of the hydroxide in HCl precipitated with oxalic acid, keeping the conditions of the solution the same as outlined on page 30. This precipitation also separates thorium from zirconium and titanium. The oxalate is filtered, washed, and ignited to thorium dioxide, which is weighed.

**BY MEANS OF SEBACIC ACID.**

Smith and James (90) have shown that thorium can be completely separated from the cerium and yttrium earths by adding a boiling solution of sebacic acid to a neutral solution of the rare earths. Tho-
Cerium and Thorium.

Cerium sebacate is precipitated as a flocculent precipitate, which is easy to filter and weigh. This method is the most quantitative, rapid, and reliable means of separating thorium from cerium and the other rare-earth elements.

Several other methods for cerium and thorium have been published but they are not as quantitative and simple as the foregoing methods, since they are intended as a rule for preparing thorium compounds, or are used commercially. For detailed descriptions of numerous methods and references, see Spencer (91) and Browning (18).

Separation of Cerium from Thorium and Other Rare Earths.

Most methods developed for separating cerium from the other rare earths must be repeated several times to insure complete separation. Cerium is usually found with both group members of the rare earths, namely, the cerium group—Ce, La, Nd, Pr, and Sm—and the yttrium group—Sc, Yt, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu. The members of one of these groups may be present in much larger quantities than those of the other group, so that the mineral is characterized as a cerium-earth mineral, or an yttrium-earth mineral. The elements of the yttrium group of rare earths are all tervalent, and give oxides having the general formula $\text{RO}_3$. Europium and samarium, however, give also bivalent salts. As previously mentioned, cerium forms the oxide $\text{CeO}_2$, which is obtained by igniting the oxyacid salts of cerium. $\text{Ce}_2\text{O}_3$ is obtained by reducing the dioxide. Lanthanum, neodymium, praseodymium, and samarium form oxides of the $\text{R}_2\text{O}_3$. Thorium differs from the rare-earth elements in being quadrivalent.

The methods of separating the rare earths have been the subject of much research.

The plans of several writers are discussed by Spencer (91), and Böhm (9). A single operation, either by precipitation or crystallization, is usually insufficient to effect separation of the rare earths; occasionally many hundred repetitions of the process must be made. The separations have been dependent in most cases on two properties: Their basicity; and the solubility of their salts in water or solvents. The first is carried out by fractional precipitation or by fractional decomposition of their salts, the second by fractional crystallization.

Only some of the more positive separations of thorium and the cerium earths from other earths will be described here; namely, those that can be carried out easily by precipitation.

Separation of Cerium by Means of Alkali Sulphates.

The elements of the yttrium-earth groups are much more soluble in a concentrated solution of alkali sulphates than the cerium earths or thorium; that is to say, a fair separation can be made. Urbain (93); Meyer and Marckwald (70); and James (42 and 43). The separation
is effected by slowly adding powdered potassium sulphate to a solution of the rare earths while they are being heated. The addition is continued until a test portion of the solution shows only the faintest trace of didymium—Nd, Pr—by the absorption spectrum. If the solution is too concentrated, the yttrium earths will be precipitated to a greater or less extent; if too much sulphate is added, until the didymium absorption spectrum has disappeared entirely, some of the yttrium earths will be found with the cerium earths that have crystallized out. Sodium sulphate may be used in place of potassium sulphate, but the potassium salt is to be preferred in the presence of thorium, as the double sodium salt is somewhat soluble in alkali sulphate solution.

QUALITATIVE TESTING OF THE COMPLETENESS OF THE SEPARATION BY MEANS OF THE ABSORPTION SPECTRA.

Of the cerium earths the elements neodymium, praseodymium, and samarium give characteristic absorption spectra; in the yttrium-earth group, erbium, thulium, holmium, dysprosium, and europium give absorption spectra; lanthanum of the cerium earths and the other members of the yttrium earths give no absorption bands. The presence of neodymium, praseodymium, and erbium, and of those members that give absorption lines can be readily identified, but the identification of the other members requires wide experience, and occasionally the use of a calibrated instrument. The position of these absorption bands and wave lengths is given by Spencer (91) on page 62 of his book.

Pure cerium compounds show no absorption spectra when examined in thick concentrated layers. This behavior can be regarded as a final test of purity when the compound is prepared from a mixture of rare earths. A qualitative examination is usually effected by interposing the solution, contained in a small test tube, directly between the slit of a spectroscope and an incandescent lamp or the sunlight. It is recommended that if possible a 10 per cent solution be used; if dilute, a thicker layer of the solution must be used. The absorption spectra, however, serve only to detect the presence or absence of a few elements in mixtures. Mention should be made here of the reflection spectra obtained directly from minerals and salts of the rare earths, as these reflect light which examined spectroscopically exhibits the characteristic absorption spectra of the elements contained in the mixture. The examination is made by spreading some of the concentrated mineral or salt on paper or cloth, and holding the spectroscope at a convenient angle over the material while strong light falls directly on it. The light coming from the positive carbon of an electric arc may be concentrated on the material by means
of a quartz lens, and then received into the slit of the spectroscope. Dark lines between the red and yellow of the spectrum and in the green indicate the presence of neodymium, praseodymium, and erbium.

**SEPARATION OF CERIUM AND THORIUM FROM THE RARE EARTHS BY MEANS OF POTASSIUM IODATE.**

The quantitative separation of thorium and cerium from the rare earths by the use of potassium iodate in a $1\text{HNO}_3$ solution has been described (pp. 33 to 34).

**SEPARATION OF CERIUM FROM THE RARE EARTHS BY MEANS OF POTASSIUM PERMANGANATE.**

Separation of cerium by means of potassium permanganate is described in detail by Roberts (79); Lenher and Melocke (57); James (42); Meyer (66); and Meyer and Schweitzer (71). It depends on the oxidation of cerium in alkaline or neutral solution with subsequent precipitation, as the ceric oxide or hydroxide, according to the following equations:

In neutral solution:

(a) $6\text{Ce(NO}_3\text{)}_3 + 2\text{KMnO}_4 + 8\text{H}_2\text{O} = 6\text{CeO}_2 + 2\text{MnO}_2 + 2\text{KNO}_3 + 16\text{HNO}_3$.

(b) $6\text{Ce(NO}_3\text{)}_3 + 2\text{KMnO}_4 + 4\text{H}_2\text{O} = 4\text{Ce(NO}_3\text{)}_4 + 2\text{Ce(OH)}_4 + 2\text{KNO}_3 + 2\text{MnO}_2$.

A neutralizing agent must be present to take up the $\text{HNO}_3$ set free by hydrolysis of the nitrate and to complete the precipitation of the cerium.

\[ \text{Ce(NO}_3\text{)}_4 + 4\text{H}_2\text{O} = \text{Ce(OH)}_4 + 4\text{HNO}_3. \]

Mercuric oxide, milk of magnesia, zinc oxide, bicarbonates, alkaline-earth carbonates, borax, and alkali hydroxides have been used for this purpose, but the use of sodium carbonate, zinc oxide, and magnesium oxide have proved to be the best reagents to employ. The reaction is as follows:

In the presence of an alkali:

\[ 3\text{Ce(NO}_3\text{)}_3 + 4\text{KMnO}_4 + 4\text{Na}_2\text{CO}_3 + 8\text{H}_2\text{O} = 3\text{Ce(OH)}_4 + 4\text{Mn(OH)}_4 + 8\text{NaNO}_3 + \text{KNO}_3 + 4\text{CO}_2. \]

The procedure should be carried out in two stages as follows:

Heat to boiling the solution of the rare earths containing cerium as cerous nitrate, and add a solution of potassium permanganate until the red color begins to be permanent. A solution of $\text{KMnO}_4$ and $\text{Na}_2\text{CO}_3$ in the ratio of 1 gram-molecule to 4 gram-molecules, $\text{KMnO}_4 : 4\text{Na}_2\text{CO}_3$, is slowly added until the solution becomes permanently red. The mixture is then boiled, for several minutes, when hydrated ceric oxide and manganese dioxide settle out. If the pink color fades by boiling, it is restored by adding more permanganate,
until the pink color is permanent. The precipitate is filtered, washed with boiling water, and dissolved in HCl; the solution is then diluted to proper strength, as described above, and the cerium precipitated with an excess of oxalic acid. This method finds application for a quantitative determination. Thorium is also precipitated and must be removed by one of the methods previously given.

SEPARATION OF CERIUM BY THE BROMATE METHOD.

The details of performing this separation in the absence of thorium are described by James and Pratt (46). A solution faintly acid with HNO₃ is heated to boiling and treated with potassium bromate in the presence of small lumps of marble until a test of the filtered solution shows by the peroxide test only a trace of cerium, as described on page 26. If this method is used on a large scale, it is advisable to interrupt the oxidation when all the cerium, except about 1 per cent, has been precipitated. If the operation is carefully carried out, the cerium is obtained free from the other earths. The precipitate, consisting of basic ceric nitrate and bromate, is allowed to settle (the lumps of marble having been previously removed), filtered, and washed with 5 per cent ammonium nitrate solution. The precipitate may be further purified by redissolving in nitric acid, with the aid of H₂O₂, if necessary, taken to dryness, taken through the process again, and reprecipitated.

SEPARATION OF CERIUM BY TREATING THE SUSPENDED PRECIPITATED HYDROXIDES WITH BROMINE OR CHLORINE GAS.

(See Hauser and Wirth (40); Browning and Roberts (22); Johnstone (49); and Browning (20).)

Passing a stream of chlorine or bromine gas into a solution of the suspended mixed hydroxides (in the presence of a small excess of NaOH) of the rare earths effects a conversion of the hydroxides of all the earths except cerium—thorium being absent—into soluble chlorides. The cerium remains undissolved as hydrated ceric oxide. If the process is repeated several times, pure cerium oxide is obtained. Bromine has been substituted for chlorine with many advantages. The chief advantage in the use of bromine is that the ceric hydroxide precipitate does not dissolve in the hydrobromic acid formed in the operation, whereas HCl readily dissolves it. (See Browning and Roberts (22).) The procedure of carrying out this separation is as follows: Dissolve the rare-earth oxides in HCl. The addition of a little H₂O₂ hastens solution by reducing the cerium; the excess must be removed by boiling. The solution is next treated with NaOH to complete precipitation of the hydroxide, filtered, and washed. The precipitated hydroxides are washed back into the original beaker,
made up to 200 c. c. volume, adding a small amount (2 grams) of NaOH. Liquid bromine or bromine water is added in distinct excess, and the mixture placed upon a steam bath until the greater part of the free bromine is expelled. The process is repeated three times, when all the other cerium earths and the yttrium earths will be found in solution without any appreciable solvent action upon the ceric hydroxide. Chlorine gas may be used in place of bromine by saturating with gas until the alkaline solution no longer reacts alkaline. The solution is boiled a few minutes and allowed to stand overnight, after which the ceric hydroxide is filtered off, washed with boiling water, dissolved in HCl, and the above process repeated. Three to five grams of solid iodine may be used with good results in place of bromine or chlorine. The mixture is placed on the steam bath and heated until the greater part of the excess iodine has passed off.

Besides the methods already described, cerium has been separated from the rare earths and from thorium by the following methods, which have been employed with varying degrees of success, though they are not as positive and rapid as those included above.

TREATMENT WITH AN ICE-COLD SOLUTION OF SODIUM PEROXIDE.

By treating a solution of the rare earths with an ice-cold solution of Na₂O₂ the cerium is precipitated as hydrated ceric oxide. The precipitate is washed with cold water, dried, redissolved, and the process repeated. (See Mengel (61) and Spencer (91).)

TREATMENT WITH LEAD DIOXIDE OR BISMUTH TETROXIDE.

A solution of the mixed sulphates is treated with concentrated HNO₃ and lead dioxide or bismuth tetroxide, and boiled until a test portion gives no precipitate with lead acetate. Small quantities of the reagents are added from time to time, or until all the H₂SO₄ has been removed from solution, then boiled with addition of more HNO₃. Lead sulphate is filtered off and the filtrate concentrated to a syrupy consistency on the water bath. The sirup is then poured into 10 times its volume of boiling water, when the cerium is precipitated as basic nitrate. (See Gibbs (33) and Spencer (91).)

TREATMENT WITH PERSULPHATE.

The treatment with persulphate consists in the oxidation of cerous compounds to ceric compounds which are precipitated as basic salts by the addition of potassium or ammonium persulphate to a neutral boiling solution of the rare earths. The solution must be kept neutral, hence the process is carried out in the presence of barium or calcium carbonate; sodium acetate has been used in place of the carbonates. Thorium does not interfere if the solution is diluted. (See Von Knorre (54), and Wyrouboff and Verneuil (102), (103).)
TREATMENT WITH CUPROUS OXIDE.

A solution of the sulphates or chlorides is acidified with a few drops of HCl and then boiled a few minutes with copper turnings. A slight excess of finely divided cuprous oxide is next added, and the solution is boiled for about an hour, when all the thorium is precipitated as hydroxide along with a little cerium. After two or three repetitions the pure thorium compound is obtained. (See Spencer (91).)

SEPARATION OF THORIUM FROM THE RARE EARTHS AND FROM CERIUM BY MEANS OF HYPOPHOSPHATES.

When hypophosphoric acid or acid sodium hypophosphate Na₃H₂P₂O₈·6H₂O, is added to a solution of the rare earths in HCl, thorium is precipitated as hypophosphate. (See Wirth (99), (100), Rosenheim (81), Koss (56), Levy (58), and Spencer (91).) In H₂SO₄ solution double insoluble sodium salts of the cerium earths may separate out with the thorium hypophosphate. A solution of acid sodium hypophosphate is added, drop by drop, to a boiling acid solution of the earths as long as precipitation occurs. This precipitates thorium hypophosphate, ThP₂O₈·11H₂O, along with zirconium or titanium if present in the solution. The precipitated hypophosphates are next treated with a mixture of concentrated H₂SO₄ and HNO₃ and carried to dryness. The residue is taken up with water and the thorium precipitated away from zirconium and titanium by oxalic acid in the usual manner. The thorium may then be filtered off, washed, dried, ignited, and weighed as oxide. This method has been in use for analytical work. (See Rosenheim (81) and Koss (56).)

SEPARATION OF CERIUM AND THORIUM FROM TITANIUM AND ZIRCONIUM BY MEANS OF FLUORIDES AND DOUBLE FLUORIDES.

Thorium tetrafluoride, ThF₄·8H₂O, is precipitated by the addition of hydrofluoric acid to a solution of a thorium salt, or by the action of the acid on the hydroxide. Hydrofluosilicic acid also throws down the fluoride, even in the cold, from solutions of thorium salts. The fluoride is insoluble in water and mineral acids, as well as in excess of precipitant. This behavior allows a complete and easy separation of thorium from titanium and zirconium. Cerium is precipitated as cerous fluoride, CeF₃·H₂O, by the action of an aqueous solution of hydrofluoric acid to a solution of a cerous salt. Rare-earth fluorides are precipitated by HF, but are more easily soluble in concentrated mineral acids than either thorium or cerium fluoride. Incomplete separation of the rare earths from thorium has been made by this method. (See Rosenheim, Meyer, and Koppel (82); Delafontaine (27); and Rosenheim, Samter, and Davidsohn (85).)

Zirconium fluoride, ZrF₄·3H₂O, is soluble in water containing free HF, being different in this respect from thorium. The addition of
potassium fluoride precipitates potassium fluozirconate, $K_2\text{ZrF}_6$, of which one part is soluble in approximately 70 parts of cold and 4 parts of boiling water. Titanium also forms a potassium fluotitanate precipitate, $K_2\text{TiF}_6\cdot \text{H}_2\text{O}$, by the addition of potassium fluoride to a solution of double titanium fluoride. One part is soluble in approximately 96 parts of water at ordinary temperature. On the basis of the above facts, the separation of thorium, cerium, and the rare earths is accomplished as follows:

The mixed fluoride precipitate, if obtained by means of HF or a solution of KF, is filtered off through a rubber funnel into a platinum dish, dried, and fused with acid potassium fluoride, and the cooled melt is extracted with water containing a little hydrofluoric acid. The zirconium and titanium pass into solution as double fluorides, leaving the thorium, cerium, and rare earths completely free from these elements.

**Separation of Cerium and Yttrium Earths from Thorium by Means of Sodium Sulphite.**

When a saturated solution of sodium sulphite is added to a neutral solution of the mixed earths, the cerium and yttrium earths are precipitated, the thorium remaining in solution. Sodium bisulphite, however, precipitates thorium from a cold solution, but not the cerium earths. For detailed description of these methods, see Chavastelon (25), Grossmann (38), and Batěk (4).

**Separation of Thorium from the Cerium and Yttrium Earths by Means of the Solubility of the Double Oxalate of Thorium.**

Thorium oxalate forms a soluble double salt with ammonium oxalate, whereas the cerium-earth oxalates are almost insoluble in a solution of this salt. Thorium oxalate, $\text{Th(C}_2\text{O}_4)_2\cdot 6\text{H}_2\text{O}$, is a white crystalline precipitate formed when acid solutions of thorium salts are treated with oxalic acid. It is insoluble in water, oxalic acid, or dilute acid; is soluble in alkaline oxalate solutions, and is reprecipitated on the addition of mineral acids.

The relative solubility of the various oxalates (calculated as oxides) which, according to Brauner (14), are dissolved by excess of ammonium oxalate, is as follows:

<table>
<thead>
<tr>
<th>$\text{ThO}_2$</th>
<th>2,663</th>
<th>$\text{Nd}_2\text{O}_3$</th>
<th>1.5</th>
<th>$\text{Pr}_2\text{O}_3$</th>
<th>1.2</th>
<th>$\text{La}_2\text{O}_3$</th>
<th>1.0</th>
<th>$\text{Ce}_2\text{O}_3$</th>
<th>1.8</th>
</tr>
</thead>
</table>

The procedure for carrying out this separation is first to precipitate the total rare earths, including cerium and thorium, with oxalic acid, filter, wash with hot water and digest at 100° with a concentrated solution of ammonium oxalate, then dilute and allow to stand overnight. On the following morning the clear liquid is decanted
or filtered, evaporated to a small bulk, and treated with a mineral acid when thorium oxalate precipitates as a crystalline powder. (See Glaser (35), (36), Brauner (14), Benz (7), Rimbach and Schubert (78), and James (44).)

SEPARATION OF THORIUM FROM THE CERIUM EARTHS BY THE CARBONATE METHOD.

(See Meyer (66), Drossbach (31), Hintz and Weber (41), Glaser (35).)

Thorium carbonate forms soluble double salts with certain of the alkali carbonates, and the amount of cerium earths that pass into solution under these conditions is very small. The solubility of thorium basic carbonate in alkaline carbonate once formed the basis of a commercial method for separating thorium from the other rare earths. The soluble double carbonates are formed by adding a solution of an alkali carbonate to a solution of a rare-earth mixture until the part of the precipitate that forms has redissolved. The soluble double salts of thorium are represented by the following formulas:

\[(\text{NH}_4)_2\text{CO}_3\cdot\text{Th}({\text{CO}}_2)_2\cdot6\text{H}_2\text{O};\ 3\text{K}_2\text{CO}_3\cdot\text{Th}({\text{CO}}_2)_2\cdot11\text{H}_2\text{O}; \text{ and } 3\text{Na}_2\text{CO}_3\cdot\text{Th}({\text{CO}}_2)_2\cdot12\text{H}_2\text{O}.\]

Of the double carbonates, the cerium group are the least soluble, then follow the yttrium group with increasing solubility, and next thorium, the most soluble. A rigid and complete separation of thorium by this method can not be made. Soluble thorium-carbonate solution, when heated, precipitates part of the thorium as carbonate, but clears again on cooling.

In addition to the methods of separation that have been given the following references to other methods that have been used are of general interest:

1.—Thorium precipitated by means of potassium azoimide, Dennis (28); 2.—thorium precipitated by means of lead carbonate, Giles (34); 3.—thorium separated by the action of fumaric acid in 40 per cent alcohol solution, Metzger (63); 4.—precipitation of thorium by means of metanitrobenzoic acid, Neish (74) and Kolb and Ahrle (55); and 5.—precipitation of thorium and the cerium earths by the addition of barium carbonate to a cold solution whereby the yttrium earths remain for the most part in solution; Spencer (91), Scott (88), and Treadwell and Hall (94).

QUANTITATIVE DETERMINATION OF CERIUM.

GRAVIMETRIC DETERMINATION.

Gravimetric determinations for cerium are little performed, as a complete and quantitative separation from all members of the rare earths involves long and tedious manipulations. Two methods are used for estimating cerium gravimetrically:
weighing; and 2.—precipitation with potassium iodate, conversion to oxalate, ignition, and weighing.

**PRECIPITATION WITH OXALIC ACID, IGNITION TO THE DIOXIDE, AND WEIGHING.**

When cerium is separated or contained in a solution freed from other earths it can be precipitated conveniently from a hot, slightly acid solution by adding an excess of a saturated solution of oxalic acid. It is best to let the solution stand overnight, filter the precipitate the next morning, wash with a warm acidulated solution, dry, ignite, and weigh as CeO₂. Nonvolatile alkaline salts will give high results if the cerium oxalate has not been thoroughly washed. This method obviates the need for complete removal of all the common base metals by previous precipitations and such processes.

**PRECIPITATION WITH POTASSIUM IODATE, CONVERSION TO OXALATE, IGNITION, AND WEIGHING.**

One of the best methods for precipitating cerium quantitatively from an acid solution of a mixture of rare earths—thorium being absent—is by means of potassium iodate when insoluble ceric iodate is formed. (See for full details Brinton and James (17).) A similar method evolved for precipitating thorium, the cerium remaining in solution if kept in a reduced condition, is described by Meyer and Speter (72). Brinton and James make use of the fact that cerium kept in the ceric condition by use of potassium bromate can be precipitated quantitatively as ceric iodate in a strongly nitric acid solution—similar to thorium iodate—by using 10 times the theoretical quantity of potassium iodate. Cerium must be kept continuously oxidized by the presence of potassium bromate. The method has been shown to work very well in the presence of other earths, but as thorium is also precipitated, it must be previously removed, or removed later from the precipitate, before the cerium can be estimated gravimetrically. The ceric iodate precipitate is boiled with an oxalic acid solution, the cerous oxalate formed filtered, washed, and ignited to the oxide, and weighed.

The method was not worked out for material containing thorium and as its removal required time and extra work, its applicability for rapid ore analysis is probably limited.

**VOLUMETRIC DETERMINATION.**

The rapid estimation of cerium in mixtures of rare earths is best performed by a volumetric method, which does not require the separation of other earths.

Practically all methods that have appeared in technical literature for determining cerium are volumetric, owing to the fact that cerium
is tetravalent and is capable of being reduced to the trivalent condition. Thorium, though also tetravalent, forms only one series of salts, whereas the remaining rare earths are tervalent. Europium and samarium, however, give also bivalent salts, but they do not interfere. Some of the volumetric methods that have been proposed for determining cerium are the iodometric method; the ferricyanide and permanganate method; the hydrogen peroxide and permanganate method; the alkaline permanganate method; and the sodium bismuthate and permanganate method.

**IODOMETRIC METHOD.**

Ceric oxide, CeO₂, or cerium compounds, when heated with hydrochloric acid in presence of KI in a decomposition flask, distills iodine because of the reduction of the cerium dioxide. The liberated iodine can then be collected and titrated by means of sodium thiosulphate in the usual way. Iodine is liberated in accordance with the equation

\[ 2\text{CeO}_2 + 8\text{HCl} + 2\text{KI} = 2\text{CeCl}_3 + 4\text{H}_2\text{O} + \text{I}_2 + 2\text{KCl}. \]

This method gives inaccurate results in the analysis of mixtures of other earths, especially praseodymium and neodymium, as in the presence of cerium dioxide these earths are capable of liberating iodine in the same way. (See Treadwell and Hall (93), Browning (19), Brauner (15), Marc (59), and Power and Shedden (75).

**FERRICYANIDE AND PERMANGANATE METHOD.**

The ferricyanide method is based upon the oxidation of cerium from the cerous to the ceric form by K₄Fe(CN)₆ and determination of the K₄Fe(CN)₆ so formed. The method is applicable in the presence of other rare earths, including thorium and zirconium. (See Browning and Palmer (21).) The method is essentially as follows: An aqueous solution of Ce₂(SO₄)₃ is oxidized by the addition of 20 c. c. of an aqueous solution of K₄Fe(CN)₆ (2 gr. per 100 c. c.) and KOH solution added to complete the precipitation.

\[ 2\text{K}_3\text{Fe(CN)}_6 + \text{Ce}_2\text{O}_3 + 2\text{KOH} = 2\text{K}_4\text{Fe(CN)}_6 + \text{H}_2\text{O} + 2\text{CeO}_2, \]

or

\[ \text{Ce}_2\text{(SO}_4)_3 + 2\text{K}_3\text{Fe(CN)}_6 + 8\text{KOH} = 2\text{Ce(OH)}_3 + 2\text{K}_4\text{Fe(CN)}_6 + 3\text{K}_2\text{SO}_4. \]

The precipitated hydroxide formed as indicated by the foregoing reaction is then filtered off, washed well with hot water, the filtrate and washings acidified with H₂SO₄, and the ferrocyanide present titrated with a standard solution of KMnO₄.

\[ 5\text{K}_4\text{Fe(CN)}_6 + \text{KMnO}_4 + 4\text{H}_2\text{SO}_4 = 5\text{K}_3\text{Fe(CN)}_6 + 3\text{K}_2\text{SO}_4 + \text{MnSO}_4 + 4\text{H}_2\text{O}. \]

From the two reactions above, the amount of cerium present can be calculated. It is claimed by the original workers that the analyses of solutions of known concentrations show close concordance between theoretical values and those obtained by this method.
CERIUM AND THORIUM.

HYDROGEN PEROXIDE AND PERMANGANATE METHOD.

The hydrogen peroxide and permanganate method is based on the fact that ceric salt is reduced in a dilute $\text{H}_2\text{SO}_4$ solution by $\text{H}_2\text{O}_2$ according to the equation

$$2\text{Ce}(\text{SO}_4)_2 + \text{H}_2\text{O}_2 = \text{Ce}_2(\text{SO}_4)_3 + \text{H}_2\text{SO}_4 + \text{O}_2.$$  

The excess of the peroxide is then determined by titration with permanganate according to the equation

$$2\text{KMnO}_4 + 5\text{H}_2\text{O}_2 + 3\text{H}_2\text{SO}_4 = \text{K}_2\text{SO}_4 + 2\text{MnSO}_4 + 8\text{H}_2\text{O} + 5\text{O}_2.$$  

The sulphate solution of the mixed rare earths in which cerium is to be estimated is acidified with $\text{H}_2\text{SO}_4$ and oxidized by means of ammonium persulphate; the excess is boiled until the excess persulphate has been decomposed. The cerium in solution is then reduced with $\text{H}_2\text{O}_2$ and excess titrated back with $\text{KMnO}_4$ as represented by the above reactions. The $\text{KMnO}_4$ does not affect the cerous salt formed, as the reaction is too slow in acid solution at the ordinary temperature. This method is described in detail by Von Knorre (53), (54); and by Power and Shedden (75). The procedure for carrying out this determination is essentially as follows:

The cold neutral solution of cerous sulphate solution is acidified with dilute $\text{H}_2\text{SO}_4$ so that 1 c. c. of acid is contained in 100 c. c. volume; 2 grams of ammonium persulphate contained in a solution are added and the solution is boiled for two minutes. If a precipitate separates out, it will be found to disappear as the oxidation proceeds. It is then cooled to about 50° by immersion of the flask in cold water, 1 gram more of persulphate solution added, and the solution again boiled for five minutes, cooled to 50°, treated with yet another gram of persulphate and a little more $\text{H}_2\text{SO}_4$ (4 c. c. in 20 c. c. volume), and boiled until no further bubbles of gas are evolved. This procedure takes about 15 minutes, at the end of which all the persulphate has been decomposed. The flask is cooled in running water and a standard solution of $\text{H}_2\text{O}_2$—ferrous sulphate may be used—added until the yellow color is just discharged. This step is followed by a small excess which later is titrated back with N/20 $\text{KMnO}_4$ solution. The $\text{KMnO}_4$ can be standardized against oxalic acid, and the $\text{H}_2\text{O}_2$ solution then standardized against the $\text{KMnO}_4$.

From the foregoing equations it is seen that $1\text{H}_2\text{O}_2 = 2\text{CeO}_2$, and that $2\text{KMnO}_4 = 5\text{H}_2\text{O}_2$. Therefore, $2\text{KMnO}_4 = 10\text{Ce}$, equivalent also to 10Fe (since $2\text{KMnO}_4 = 10\text{Fe}$), hence,

$$1 \text{ c. c.} \frac{N}{20} \text{KMnO}_4 = 0.0070125 \text{ gram Ce} = \frac{140.25 \text{ (at. wt. Ce)}}{1000 \times 20}$$

Phosphates and titanium, if present, interfere with this method. One of the greatest difficulties, according to some writers, is the adjustment of the concentration of the sulphuric acid required. If
this be too low, basic ceric sulphate is likely to separate out on boiling, and subsequently the estimation is spoiled; if the concentration be too high, the oxidation of the ceric salt may be hindered and, as claimed by some, even inhibited, owing to the formation of H₂O₂ from the persulphate. Waegner and Muller (96) claim to have overcome the main difficulties by effecting the oxidation to the ceric condition by means of bismuth tetroxide in a nitric acid solution. Besides the above two means of effecting the oxidation of the cerium, Job (47) effects the oxidation by means of PbO₂ in a HNO₃ solution. For the purpose of reduction, a ferrous salt (ferrous sulphate) may be used in place of H₂O₂ with equally good results, as shown also by Von Knorre (53), (54).

The addition of ammonium persulphate to an acid solution containing cerium, as given in the above outline, imparts a characteristic yellow color, due to the ceric salt formed, which can be used as a means of detection for cerium. It is very likely that a colorimetric method might be developed by the use of this color reaction. Unlike H₂O₂, the persulphates do not give orange-yellow colorations with titanium salts, and hence the presence of the latter element would not interfere with such a scheme.

ALKALINE PERMANGANATE METHOD.

The alkaline permanganate method depends on the oxidation of cerium in alkaline or neutral solution with subsequent precipitation as the ceric oxide or hydroxide. The reactions involved, and references to the different workers who have contributed to this method, have already been given. See “Separation of cerium from the rare earths by means of potassium permanganate” (p. 37). It has been shown by Lenher and Meloche (57) that under proper conditions the method is capable of giving accurate results. The method is also suitable for the determination of trivalent cerium in the presence of tetravalent cerium. (See Brauner (16).) High results have been reported by reason of the oxidizing action of the cerium dioxide on the other rare earths present. Another source of error lies in the fact that freshly precipitated cerous hydroxide heated in solution, or allowed to stand for some time, absorbs atmospheric oxygen to such an extent that the subsequent titration with KMnO₄ necessarily yields low results. The effect can be overcome by adding most of the permanganate solution before the neutralizing agent is added. Another source of error that has been pointed out is that due to occlusion; the particles of the gelatinous precipitated cerous hydroxide may become superficially coated with the ceric hydroxide and hydrated manganese dioxide formed by the reaction of the permanganate in the alkaline solution. This coating can be remedied in large part by greater dilution and by adding the most of the per-
manganate before the neutralizing agent is introduced. Zinc oxide has proved a very satisfactory neutralizing reagent, as it does not immediately precipitate the cerous hydroxide. In all cases it is recommended that the titration be finished hot, and that the permanency of the end point be insured by finally boiling the solution for a few moments. To overcome most of the above sources of errors the procedure is carried out as follows: To a measured volume of a solution containing cerium after dilution to approximately 110 c. c., is added an excess of zinc oxide paste. Most of the permanganate is next added in the cold, after which the solution is brought to boiling and the titration finished hot. The permanency of the end point is tested by boiling for a few seconds, the pink color still remaining.

**SODIUM BISMUTHATE—PERMANGANATE METHOD.**

The sodium bismuthate-permanganate method, besides the $\text{H}_2\text{O}_2$ method, constitutes one of the most reliable methods for estimating cerium in any class of material. It is based on the principle that when a dilute $\text{H}_2\text{SO}_4$ solution containing cerium as sulphate in a mixture of rare earths is mixed with sodium bismuthate and ammonium sulphate and boiled, the cerium is oxidized to the ceric condition. The excess bismuthate is then filtered off. A measured excess of standard ferrous ammonium sulphate is added to the filtered solution—excess being shown by change from yellow to colorless—and the excess of ferrous iron is then titrated back with standard permanganate. Rare earths, zirconium, thorium, and titanium, do not interfere. $\text{H}_2\text{O}_2$ has been used in place of ferrous sulphate with satisfactory results. If the earths are in solution as the chloride or nitrate, it is necessary to add concentrated $\text{H}_2\text{SO}_4$ and evaporate to fumes of sulphur trioxide. When cooled, ammonium sulphate crystals are added, the earths dissolved by cold water, and the solution treated as above. The method is rapid, and can be carried out in less than a half-hour after the earths have been obtained in solution in the sulphate form. The presence of ammonium sulphate prevents the precipitation of the basic bismuth salt which is likely to carry with it a small amount of ceric sulphate. As is the case with ammonium persulphate, bismuthate affords a very sensitive test for minute quantities of cerium; as little as 0.2 mg. of CeO$_2$ in 100 c. c. gives a distinct yellow coloration.

The sodium bismuthate method is described in detail by Metzger (62) and by Metzger and Heidelberger (64). A method devised by Waegner and Muller (96) involves oxidation in a strong HNO$_3$ solution by means of bismuth tetroxide, the cerium being then reduced in HNO$_3$ solution by a known excess of H$_2$O$_2$ and the excess of the latter titrated with KMnO$_4$. This method, however, finds little favor,
owing to the ease of carrying out the oxidation by means of bismuthate in a H₂SO₄ solution. Cerium ores are usually decomposed by H₂SO₄, and hence the conversion to the nitrate is avoided.

Besides the fact that the bismuthate method is quick and accurate, it is also to be recommended for its ease of manipulation. It has been found necessary, however, to separate the rare earths as oxalates away from the common base metals, as iron and especially manganese have been found to interfere, giving high results.

**PROCEDURE FOR ANALYSIS.**

After the mineral, if of cerite or monazite, has been decomposed by one of the methods already given under "Decomposition" (p. 26), and brought into solution as the sulphate, the rare-earth oxalates should next be precipitated. This precipitation is done by regulating the acidity, if possible, to approximately 0.5N, then heating the solution, and adding a large excess (100 c. c. or more) of a saturated solution of oxalic acid. It is best to allow this to stand over night; then filter, and wash with hot water containing 1 per cent solution of oxalic acid.

The precipitate and paper are then ignited with a blast lamp in a platinum crucible to the oxide in the ordinary way; the oxides are next warmed with 10 c. c. of concentrated H₂SO₄ until decomposition is complete, allowed to cool, and then carefully poured into 100 c. c. of ice-cold water. This procedure should result in complete solution; if not, add 10 c. c. more of concentrated H₂SO₄ and heat on a hot plate until a clear yellow solution is obtained. This solution is then brought back to approximately 100 c. c. volume, 2 grams of ammonium sulphate and 1 gram of sodium bismuthate added, heated to boiling, cooled, filtered through a Gooch crucible, and washed with 100 to 150 c. c. of 2 per cent H₂SO₄. To this solution is then added an excess of standard N/40 ferrous sulphate solution—color change yellow to colorless—and the excess is titrated back with a standard permanganate N/40 solution. From the burette reading calculate the percentage of cerium.

\[
10\text{Fe}=10\text{CeO}_2, \text{ or } 1\text{Fe}=1\text{Ce},
\]

so that

\[
1 \text{c.c. } N/40 \left(\text{NH}_4\right)_2\text{Fe(SO}_4)_2 \cdot 6\text{H}_2\text{O}=0.004306 \text{ gr. CeO}_2 \times \frac{172.25}{1000} \times \frac{1}{40}.
\]

Besides decomposing the oxalate precipitate as above directed, it can be done by washing the oxalate off the filter paper with hot water and converting the hydroxides by boiling with NaOH. The precipitate formed is filtered off, washed well with hot water, and dissolved through the filter by means of dilute H₂SO₄. The filtrate is made up to 100 c. c. and enough H₂SO₄ added to bring the amount up to 20 grams of concentrated H₂SO₄ and treated with ammonium sulphate and sodium bismuthate, and finished as directed.
CERIUM AND THORIUM.

If the precipitated oxalate is small, it can be decomposed by heating with 20 c. c. of concentrated H₂SO₄, and finished in the usual manner.

SELECTED METHODS.

LINDSAY LIGHT CO.'S METHOD FOR DETERMINATION OF CERIUM.

The following method for determining cerium was received from Mr. V. T. Jackson, chemist for the Lindsay Light Co., Chicago, Ill., to whom full credit is hereby gratefully acknowledged. Thanks are also due to Dr. H. N. McCoy, who made possible this cooperation. The method has been tested thoroughly in the company's laboratories, and has proved satisfactory.

The following is a modification of the method of Metzger:³

REAGENTS NEEDED.

Dilute ammonium hydroxide (1:4).
Solution of oxalic acid (60 grams of crystals dissolved in sufficient water to make a liter of solution).
Sulphuric acid (C. P.)
Sulphuric acid (2 per cent solution).
Fuming nitric acid.
N/40 solution of potassium permanganate. The factor is preferably determined by titrating against a weighed amount of sodium oxalate.
N/40 solution of ferrous ammonium sulphate. This is prepared by weighing out approximately 10 grams of Mohr's salt and dissolving it in 300 c. c. of water containing 50 c. c. of c. p. sulphuric acid. The solution is cooled before adding the salt. The volume is made up to one liter, and then titrated against the permanganate solution to determine its factor.
Ammonium sulphate.
Sodium bismuthate.

PROCEDURE WHEN IRON AND TITANIUM ARE PRESENT.

Measure into an 800 c. c. beaker a known volume of solution sufficient to give a weight of cerium dioxide equivalent to about 0.2 gram. Add ammonium hydroxide until the solution is only faintly but distinctly acid; no precipitate should be present. Make the volume 400 c. c., cover the beaker with a watch glass, and heat the solution to boiling. Add a small excess of the oxalic acid solution (25 to 30 c. c.) and boil for 10 minutes. Rinse down the sides of the beaker and watch glass with distilled water.

Let stand for one hour and then filter through a 124-cm. quantitative filter paper. Wash out the beaker three times with the aid of a "policeman" and water sprayed from a wash bottle with a fine jet. Drain thoroughly and transfer the filter paper and the precipitate to a 300 c. c. Kjeldahl flask. Add 20 c. c. of c. p. sulphuric acid, and with a rotating motion shake the flask until half of the filter paper has been charred. Place a small funnel in the mouth of the flask and carefully add 2 to 3 c. c. of fuming nitric acid (hood).

In case too much nitric acid has been added, and the mixture foams excessively, dip the flask in cold water or spray water into the mouth of the flask. After effer-

vecesence stops, heat the flask with a small Bunsen flame to fumes of sulphur trioxide. Unless the contents of the flask are white or only a pale yellow, cool somewhat and add 1 or 2 c. c. of fuming nitric acid and again heat to fumes of sulphur trioxide. Cool, add 10 to 15 c. c. of distilled water. If brown fumes of the oxides of nitrogen are given off, again heat to fumes of sulphur trioxide, in order to drive off the last traces of nitric acid. Next dilute to a volume of 100 c. c.

WHEN IRON AND TITANIUM ARE ABSENT.

Transfer a sample of such a size as indicated above to a 300 c. c. Erlenmeyer flask. If other acid radicals besides sulphate are absent, this procedure is unnecessary. Add 15 c. c. of sulphuric acid and proceed as directed under the treatment of the sulphate. Add 20 c. c. of c. p. sulphuric acid, place a small funnel in the mouth of the flask, set it on a sand bath, and heat it to copious fumes of sulphur trioxide. Dilute to a volume of 100 c. c.

TREATMENT OF THE SULPHATE.

Add 2 grams of ammonium sulphate and 1 gram of sodium bismuthate. Rinse down the sides of the flask, and make the volume not over 125 c. c. Heat to boiling, and boil one or two minutes—until solution becomes straw colored—and filter the hot solution through a Gooch crucible containing a thick asbestos pad, into a 200 c. c. filter flask. Wash the residue into the Gooch crucible, using several small portions of 2 per cent sulphuric acid, until the volume of the solution amounts to not over 250 c. c.

Run in an excess of standard ferrous ammonium sulphate until the cerium solution becomes colorless. Titrate back excess with standard potassium permanganate solution: \(2\text{Ce}(\text{SO}_4)_2 + 2(\text{NH}_4)_2\text{Fe} (\text{SO}_4)_2 \rightarrow \text{Ce}_2(\text{SO}_4)_3 + \text{Fe}_2(\text{SO}_4)_3 \cdot 2(\text{NH}_4)\text{SO}_4\) c. c. \(\frac{N}{40}\) \((\text{NH}_4)_2\text{Fe} (\text{SO}_4)_2 = 0.004306\) grams CeO₂.

COLORIMETRIC DETERMINATION OF CERIUM.

A colorimetric method for determining Ce in the presence of Th and other rare earths is described by Benz (6) and Scott (88). The method is essentially as follows: The material is either fused with bisulphate or heated with \(\text{H}_2\text{SO}_4\), and taken into solution by means of ice-cold water in the ordinary way. After adjusting the acidity to near 0.5 N the combined rare earths are next precipitated with oxalic acid, ignited, dissolved in \(\text{HNO}_3\), and the liquid evaporated to dryness. The residue is then taken up with water, heated with a measured excess of citric acid and \(\text{H}_2\text{O}_2\), neutralized with \(\text{NH}_4\text{OH}\), and transferred to a measured flask or cylinder. Citric acid prevents the precipitation of the hydroxides, and the characteristic yellow to orange color produced by cerium can then be compared with a standard solution which contains an approximately equal amount of pure thorium nitrate and the same measured quantities of citric acid, \(\text{H}_2\text{O}_2\), and \(\text{NH}_4\text{OH}\) as were added to the sample to be determined for Ce. From the results obtained by comparing the tints the Ce present can be calculated by withdrawing a suitable quantity of the solution from the cylinder in which the color is stronger.
A colorimetric determination is, however, little performed, its principal use being to ascertain the presence or absence of cerium in pure thorium compounds.

**QUANTITATIVE ANALYSIS FOR THORIUM.**

A large number of methods have been published for the determination of Th. Practically all of them are based on precipitating out the Th in some form, either from a neutral or acid solution, and finishing by a gravimetric method. The precipitate is either ignited directly to the dioxide, or is dissolved and precipitated out as the oxalate, with a subsequent conversion to the dioxide by ignition.

**VOLUMETRIC METHOD FOR DETERMINING THORIUM.**

Practically the only volumetric method advocated is one described by Metzger and Zons (65), that makes use of molybdate titration; the procedure is as follows:

Thorium is quantitatively precipitated at room temperature as Th(\(\text{MoO}_4\))\(_2\) from a 7 per cent acetic acid solution containing 1 gram of sodium acetate by means of a solution of ammonium molybdate, \((\text{NH}_4\)\(_2\)\(\text{MoO}_4\)), added from a burette. The other rare earths found in monazite sand are not precipitated under these conditions. Diphenyl carbazide, CO(HN.NH.C\(_6\)H\(_5\))\(_2\), is used as an external indicator. A drop of the carbazide solution shows a deep rose coloration when excess of ammonium molybdate is present. Although this color is said to be definite, it is claimed by some workers to be very evanescent, and will persist for only 15 seconds. See Cazeneuve (24) and Skinner and Ruhemann (89) for the mode of preparing this indicator and for tests made with various metal salts. Owing to the slimy nature of the precipitate, filtration and washing are impossible, so that the determination can not be performed gravimetrically.

Some experience is required to identify the end point produced by the diphenyl carbazide; it is also claimed that the solution of the indicator must be at least two weeks old. The ammonium molybdate solution (20 grams per liter) is standardized against a standard thorium nitrate solution. The indicator—0.5 gram of diphenyl carbazide—is dissolved in 200 c. c. of 95 per cent alcohol and allowed to stand for two weeks before using. For the preparation of diphenyl carbazide—if this can not be obtained from a supply house—the reader is referred to the original discussion (65). The details for carrying out a determination for thorium on monazite sand by this method are as follows:

To 1 gram of powdered monazite sand in a porcelain crucible is added 10 to 15 c. c. of concentrated \(\text{H}_2\text{SO}_4\). After several hours' heating, the crucible is cooled and the contents transferred, a little
at a time and with constant stirring, to about 700 c. c. water which has been cooled to near 0°. After standing several hours (overnight, if convenient) to insure complete solution of the sulphates, the solution is filtered, and the residue thoroughly washed with cold water. The filtrate is nearly neutralized with dilute ammonia, 50 c. c. of a cold saturated solution of oxalic acid is added, and allowed to stand overnight. The oxalates are filtered and washed with a dilute oxalic acid solution. When thoroughly washed, the precipitate and paper are transferred to a beaker; add 20 to 25 c. c. of strong potassium hydroxide solution, and heat to boiling. Dilute, filter, and wash with hot water. Dissolve the precipitate of rare-earth hydroxides off the filter by means of hot, dilute HNO₃. Evaporate to dryness on a water bath. Add a little water and again evaporate to dryness to remove free acid. To the dry residue add 20 c. c. glacial acetic acid, dilute with 300 c. c. water, add 1 gram sodium acetate, and stir until dissolved. Titrate at room temperature with standard ammonium molybdate solution.

**GRAVIMETRIC METHODS FOR DETERMINING THORIUM.**

Thorium is nearly always determined by a gravimetric method. The determination is generally made on monazite and other minerals that contain the other rare earths. The material is treated with concentrated H₂SO₄ in the ordinary way, dissolved in ice-cold water, and the solution filtered from the SiO₂ and undecomposed foreign minerals, such as ilmenite, zircon, and magnetite. Thorium is then precipitated with the other earths, as the oxalates, in order to separate them from the phosphoric acid. If a neutral solution—generally the nitrate—is to be obtained, the oxalates are either ignited to the oxide and treated with HNO₃ or decomposed with fuming HNO₃, then taken to dryness, usually twice to expel all the free acid, and finally taken up in water. A detailed method of treatment will be obvious in the description of the methods to follow. As the above procedure of obtaining a neutral solution requires considerable time, methods have been devised by which thorium is precipitated in the form of a salt, other than the oxalate, from an acid solution as obtained directly from a decomposition treatment. These methods have been designated as "rapid methods." The gravimetric methods are divided into two groups: Those that require a neutral solution, or acid to organic acid, for precipitation; and those that are performed in a mineral acid solution.

**DETERMINATION OF THORIUM BY PRECIPITATION OF A THORIUM SALT FROM A NEUTRAL SOLUTION.**

Determination of thorium by precipitation of a thorium salt from a neutral solution is made by means of (1) sodium thiosulphate; (2)
hydrogen peroxide; (3) potassium azoimide (KN₃); (4) sebacic acid; (5) lead carbonate; (6) metanitrobenzoic acid; (7) fumaric acid in a 40 per cent alcohol solution; and (8) ammonium oxalate.

SODIUM THIOSULPHATE METHOD.

This method, which has been previously outlined in detail, with references (see p. 31 to p. 33), is giving satisfactory results in the Welsbach laboratories. Although it requires somewhat longer time to manipulate than some methods performed in an acid solution, which avoid the precipitation as oxalates to free the rare earths from the base metals and phosphoric acid, its reliability more than offsets the extra time. The conversion of the oxalate into the form of a neutral solution each time a precipitation is to be made requires much time. For further detailed procedure other than that already given, the reader is referred to the published articles by Johnstone (49), Meyer (63), and Kithil (52).

ANALYSIS OF MONAZITE SAND. METHOD USED BY WELSBACH CO.

The following method for determining thorium was received from Dr. H. S. Miner of the Welsbach Co., Gloucester, N. J., to whom full acknowledgment is hereby gratefully made. Concerning the method Dr. Miner remarks:

The method was written out in considerable detail, and we believe that anyone skilled in the analysis of the rare-earth elements will have no difficulty in conducting the operations to their entire satisfaction. It may seem to you that we have gone too much into detail, and yet accurate results are only obtained by the careful observance of the precautions which we have outlined, which really amounts to a detailed description of the process. We are perfectly willing that you publish this method if you desire, and you can authoritatively state that it is really an official method.

Fifty grams of the sand are weighed out and placed in a porcelain casserole of about 500 c. c. capacity. Seventy-five c. c. of H₂SO₄ (66°) are added and heated for about four hours with frequent stirring, maintaining a gentle evolution of fumes during the course of the operation. When the mass has become pasty, it is allowed to cool, and the sulphates are extracted by the addition of about 400 c. c. of cold water, or enough to cool the solution sufficiently so that the sulphates become soluble; this solution is decanted into a liter graduated flask, and the remaining sulphates are extracted by small portions of cold water and decanted into the flask, except that the last extractions, in which the rare-earth phosphates are precipitated, are reserved in a separate beaker. To the remaining sand, which has been dried, 10 c. c. of H₂SO₄ (66°) are added and heated for one hour and a half, maintaining a copious evolution of white fumes. It is then allowed to cool and is extracted as before, using for the first extraction the liquid containing the precipitated rare-earth phosphates, which has been reserved from the previous extraction. The sand is thoroughly washed and the washings decanted into the liter flask. The sand which remains unattacked is thrown on a filter, washed, ignited, and weighed as the heavy unattacked residue.

The sulphate solution in the flask is allowed to cool, diluted to 1 liter, shaken thoroughly, and filtered.
After all the solution has been filtered, the flask is washed out with water containing sulphuric acid and the filter washed with the same liquid. The filter is then burned and the residue ignited and weighed as the light unattacked residue.

When sufficient solution has filtered, 200 c. c. (representing 10 grams of sand) are withdrawn, diluted to 1 liter with water, and precipitated by pouring into 150 c. c. of a cold saturated solution of oxalic acid, adding it in small portions at first, and stirring vigorously until the precipitate is converted to the crystalline form. By far the best results are obtained by using a mechanical stirrer for the oxalic acid solution, and feeding the rare-earth solution into it drop by drop from a separatory funnel. In this way no attention is required for an operation which is very tedious if performed properly by hand. It should be emphasized here that this oxalic acid precipitation is most important as it separates the rare earths, not only from the other bases, but also from phosphoric acid. Unless the latter be thoroughly eliminated, the rest of the analysis will be unsatisfactory. The precipitate is allowed to stand overnight and filtered on the following morning, washing thoroughly by decantation and on the filter until free from acid. The precipitate is then placed in an air bath and dried.

The filtrate and first washings are neutralized with ammonia, and HCl is added so as to have an acidity of from 10 c. c. to 15 c. c. of HCl; this precipitates the remaining rare earths as oxalophosphates. This precipitate is allowed to settle overnight, then filtered and washed with a weak solution of oxalic acid: It is then ignited in a porcelain dish and the residue is moistened with a little water, and dissolved by warming with concentrated HCl. The solution so obtained is filtered and precipitated by the addition of a large excess of oxalic acid. The oxalate precipitate, which is curdy at first, is converted to the crystalline form by warming for a few minutes, and after standing two or three hours, is filtered and washed.

This oxalate precipitate is then transferred to a weighed porcelain crucible (No. 2) and ignited; the main portion of the oxalates, which have been dried in the air bath, are then separated from the filter, the paper burned in the crucible first, then the oxalates are added and the whole ignited to a constant weight and weighed as the "total rare-earth oxides." These oxides have a tendency to absorb H₂O and CO₂ from the air; therefore the porcelain crucible should be used with cover. The oxides are then transferred to a 600 c. c. beaker, moistened with a little water, and dissolved with 100 c. c. of 1:1 HCl by warming for some time over a low flame.

The solution so obtained is transferred to a 1.5-liter beaker, diluted to about 700 c. c., and ammonia is added until the precipitate formed just ceases to dissolve and the solution is either neutral or very slightly acid. Concentrated ammonia may be used at first and a dilute solution toward the end of the neutralization. Concentrated HCl is then added, a drop at a time, until the precipitate just dissolves, then 6 to 8 drops more, making solution slightly acid. The solution is heated to boiling, 100 c. c. of a boiling 30 per cent solution of Na₂S₂O₃ are added, and the boiling is continued for 45 minutes. The precipitate is then filtered on a Büchner funnel and washed with hot water. For this purpose a small Büchner funnel about 2½ inches in diameter serves admirably. The filter paper may be folded so as to cover the entire inside surface of the funnel. In this way, with the aid of vacuum filtration and washing may be finished in a few minutes, whereas by the ordinary filtration means it would take one-half hour or more.

To the filtrate 10 c. c. more of Na₂S₂O₃ are added, and it is boiled for one-half hour; the slight precipitate obtained is collected on a filter, set aside, and designated as "residue No. 1." The filtrate is then rejected.

The first thiosulphate precipitate (paper and all) is placed in the original 1.5-liter beaker in which the precipitation was made and boiled with 75 c. c. of HCl (1:1), using a low flame. In about five minutes the thorium precipitate is dissolved and the filter paper pretty well disintegrated. Without filtering off the residue of filter paper, sulphur, etc., the solution is diluted to 700 c. c. and neutralized with ammonia as de-
scribed above, leaving an excess of 6 to 8 drops of HCl. It is then heated to boiling, and 60 c. c. of boiling 30 per cent solution of sodium thiosulphate added. The boiling is continued 30 minutes, the precipitate is filtered on a small Büchner as described above, and washed with hot water. The filtrate is reserved.

The filter paper from the Büchner containing the thorium precipitate is replaced in the 1.5-liter beaker, dissolved in 75 c. c. of HCl (1:1), the solution diluted, without filtering, to 700 c. c. and almost neutralized, following procedure described above. Solution is heated to boiling, 60 c. c. of 30 per cent sodium thiosulphate added, and the boiling continued one-half hour. The precipitate is filtered as before on small Büchner and washed, the filtrate being discarded.

The paper containing the thorium precipitate is transferred to a 250 c. c. beaker and covered with 40 c. c. HCl (1:1). Solution is boiled with low flame until paper is thoroughly disintegrated. Then it is filtered and washed until free from acid. The filter paper is set aside and designated as "residue No. 2." The solution is diluted to 400 c. c., heated to boiling, and the thorium precipitated as oxalate by adding 50 c. c. of a boiling solution of oxalic acid which is saturated in the cold. The precipitate is allowed to stand over night, filtered on the following day, and ignited in a porcelain crucible and weighed as ThO₂.

Residues Nos. 1 and 2 are combined, ignited in a porcelain crucible, and fused with Na₂H₃O₃. The fusion is extracted with water containing HCl and precipitated with ammonia, and added to the filtrate from the second thiosulphate precipitation, to which ammonia has been added. The precipitate is washed by decantation and dissolved in HCl.

The HCl solution is diluted to 300 c. c., almost neutralized with ammonia, so that the solution shows only a slight acidity, heated to boiling, precipitated by the addition of 20 c. c. of boiling Na₂S₂O₃ (30 per cent solution), and boiled 20 minutes.

The precipitate is filtered on small Büchner, washed, and dissolved in 50 c. c. HCl (1:1). Without filtering, the solution is diluted to 300 c. c., almost neutralized with ammonia, and the thiosulphate precipitation repeated. The last precipitate is dissolved by boiling in a mixture of 5 c. c. concentrated HCl and 20 c. c. H₂O until paper is disintegrated, then the residue of and sulphur is filtered and washed. The filtrate is diluted to 200 c. c., precipitated with 25 c. c. of a cold saturated solution of oxalic acid and heated several hours over a low flame. After standing overnight, the precipitate is filtered off, ignited to the oxide, and the weight of the oxide found is added to that of the ThO₂ found in the main course of operations.

Under certain conditions a small amount of iron may come down with the thorium in the thiosulphate precipitation—sufficient to make the final thorium oxide slightly discolored. This can be avoided by passing H₂S into the solution before the thiosulphate precipitation, thus reducing the ferric iron to ferrous. If this is done before the first thiosulphate precipitation, it will, of course, not need to be repeated before the others.

**HYDROGEN PEROXIDE METHOD.**

The H₂O₂ method has also been outlined under "Separation of thorium from cerium and the rare earths" (p. 31). The precipitation, as in the thiosulphate method, is performed in a neutral solution. A neutral nitrate solution is employed in contrast to a neutral chloride solution for the thiosulphate. This method is also open to the same objections as given under the former method, being rather long and requiring a great many precipitations before the thorium is finally obtained in a pure state.
POTASSIUM AZOIMIDE (KN₃) METHOD.

The KN₃ method, described by Dennis (29), and by Dennis and Kort-right (30), is of particular interest because of the peculiar behavior of the potassium azoimide (hydronitride) and the formation of the weak hydronitric acid. From a neutral solution thorium is precipitated as hydroxide by potassium azide (called also azoimide or hydronitride), the reaction being expressed by the equation:

\[
\text{Th(NO}_3\text{)}_4 + 4\text{KN}_3 + 4\text{H}_2\text{O} = 4\text{KNO}_3 + \text{Th(OH)}_4 + 4\text{HN}_3.
\]

Cerium and the other earths are not precipitated with the thorium, which is alone precipitated because of its weak basicity. The reagent is somewhat difficult to make and besides is very expensive, so that the method has found little use in mineral analysis.

SEBACIC ACID METHOD.

The method is based on the fact that sebacic acid precipitates thorium quantitatively in a neutral solution. It is claimed that solutions of cerium, lanthanum, yttrium, etc., give no precipitate with sebacic acid even upon boiling. (See Smith and James (90).) Thorium sebacate is a voluminous granular precipitate which settles readily and is easily filtered. Sebacic acid is formed by heating castor-oil soap with sodium hydroxide. One part is soluble in 1,000 grams of water at 17°, 40 grams in 1,000 grams of water at 65°, and it becomes fairly soluble at 100°.

A neutral nitrate solution containing thorium is heated to boiling, and a slight excess of a hot solution of sebacic acid is added slowly with continuous stirring. The thorium sebacate precipitate is then filtered, washed with boiling water, dried, ignited, and weighed as thorium dioxide.

In a later article, Whittemore and James (97) show that from a neutral chloride solution of yttrium chloride, ammonium sebacate precipitates yttrium sebacate quantitatively. In another article by the same authors (98), they show that ammonium sebacate precipitates quantitatively from a neutral solution lanthanum, praseodymium, neodymium, samarium, yttrium, and cerium. The above facts then indicate that from a neutral solution sebacic acid precipitates only thorium, whereas ammonium sebacate will precipitate the cerium earths and part of the yttrium earths. The verification of these facts was not attempted by the writer for lack of the necessary reagents.

LEAD CARBONATE METHOD.

The precipitation of thorium from a neutral nitrate solution of the rare earths by means of an excess of pure moist lead carbonate is
described by Giles (34). It is based on the fact that thorium or cerium (ceric) due to their weak basicity are precipitated as hydroxides, the remaining rare earths remaining in solution. Cerium is prevented from precipitating when reduced from the ceric to the cerous state by sulphur dioxide. The precipitate is freed from lead by dissolving in HCl and is treated with H₂S which throws out the lead as sulphide. The thorium is then precipitated from solution as the hydroxide, or the lead carbonate precipitation is repeated. Thorium is finally weighed as the dioxide. This method as far as the writer can learn has never been employed for commercial analysis, although it seems to merit further consideration. The preparation of pure lead carbonate that is required has been claimed by some to be one of its chief difficulties. Zirconium if present in solution (or ferric oxide) is also wholly precipitated by lead carbonate and must be removed before the thorium is finally weighed.

**METANITROBENZOIC ACID METHOD.**

The method is based on the principle that metanitrobenzoic acid precipitates thorium quantitatively as thorium metanitrobenzoate, Th(C₆H₄NO₂CO₂)₄, from a neutral solution of the nitrate. (See Neish (74) and Kolb and Ahrle (55).) When the precipitation is repeated, it affords a complete separation from cerium, lanthanum, didymium, etc. Glucinium, gadolinium, yttrium, titanium, and samarium give no precipitate cold or hot; zirconium is precipitated and increased with heating; erbium precipitates similar to thorium. The method gives no difficulties in precipitation or filtration; the precipitant is not expensive and avoids the use of alcohol as required with certain other organic reagents. Of the three nitrobenzoic acids, the meta acid is used because it is most soluble in water. It is made by the nitration of benzoic acid. This reagent need not be absolutely pure, because the ortho and para acids, as well as benzoic acid, act similarly. Other weak organic acids that precipitate thorium, cerium, and other earths are sebacic acid, mucic acid, anisic acid, aspartic acid, pyrotartaric acid, and oxanilic acid, according to Smith and James (90); and gallic acid, tannic acid, citric acid, salicylic acid, oleic acid, linoleic acid, paratungstic acid, oxyisophthalic acid, benzoic acid, and three nitrobenzoic acids (ortho, meta, para), according to Neish (75). Several of these organic acids will precipitate, either in a neutral or alcoholic solution, thorium quantitatively from cerium and other earths. The precipitate is of a flocculent, slimy, or curdy variety which is difficult to handle. For the detailed use of these acids for separation purposes the reader is referred to the original articles.

To prepare the solution of the precipitant, 4 grams of the metanitrobenzoic acid is dissolved in 1 liter of hot water, allowed to stand
overnight, and filtered. One hundred and fifty c. c. of this solution will give a liberal excess for a thorium solution equivalent to 0.1128 gram ThO₂. The procedure for carrying out this precipitation is as follows:

To a neutral solution of the rare-earth nitrates which has been prepared by the ordinary method—by decomposition of sand by H₂SO₄ solution in ice-cold water, precipitation as oxalates precipitated, ignition or boiling with caustic or fuming HNO₃, evaporation to dryness twice, and final solution as neutral nitrates—150 to 250 c. c. of metanitrobenzoic acid solution is added slowly with constant stirring and heated on the water bath at 60 to 80° until the precipitate has all collected and settled to the bottom. It is then filtered, washed by decantation, using a 5 per cent solution of the precipitant, placed on the filter, and washed with the same solution. The reaction is as follows:

$$\text{Th(NO}_3)_4 + 4\text{C}_2\text{H}_4\text{NO}_2\text{COOH} \rightarrow \text{Th(C}_2\text{H}_4\text{NO}_2\text{CO}_2)_4 + 4\text{HNO}_3.$$  

The precipitate is next dissolved into the precipitation beaker by hot dilute 1:5 HNO₃, the paper is washed well with hot water and diluted to 600 c. c., and methyl orange is added to decided red color, followed by 25 c. c. of metanitrobenzoic acid. The solution is neutralized with dilute 1:10 ammonia until a pink color, due to the weak organic acid, is reached. As the excess of HNO₃ is neutralized, the thorium precipitates again as metanitrobenzoate. If the process of neutralization is carried too far—to the yellow tint—other earths are likely to precipitate. After the pink color is reached, 50 c. c. more of the precipitant is added to insure complete precipitation. The beaker is then heated as before, filtered, and washed. The wet precipitate is next ignited and weighed; a blast lamp is used at the end of the ignition. The precipitate when dry can not be handled without loss, owing to its lightness and electrified properties, hence it is always ignited wet. To avoid neutralization, previous to the second precipitation thorium and the little remaining earths can be precipitated out of solution by a slight excess of potassium hydroxide, the precipitate dissolved in HNO₃, evaporated to dryness, and the process repeated, finally weighing as thorium dioxide. As shown by the original authors this method has given good results for thorium in monazite sands.

**METHOD USING FUMARIC ACID IN A 40 PER CENT ALCOHOL SOLUTION.**

Metzger (63) found that from a 40 per cent alcoholic solution thorium is precipitated quantitatively as thorium fumarate on the addition of fumaric acid—thorium and fumaric acid react, molecule for molecule—whereas no change is produced by that reagent in
solutions of cerium, lanthanum, or didymium. A reprecipitation removes the traces of rare earths carried down with the thorium. Cerium is precipitated in a very small fraction only if the cerium solution is rather strong in the first precipitation.

Fumaric acid forms no precipitate either in the hot or cold in aqueous solutions of cerium, lanthanum, or didymium. Thorium, under similar conditions, forms a precipitate only by application of heat, but is not precipitated completely. The use of 40 per cent alcoholic solution makes the precipitation quantitative. Ammonium fumarate, on the other hand, precipitates thorium, cerium, lanthanum, and didymium from aqueous solutions, insoluble in excess and soluble in mineral acids. With other rare earths it was found that, in a 40 per cent alcohol solution, fumaric acid gives no precipitate with yttrium, samarium, or gadolinium, either hot or cold. Erbium is slightly precipitated in the cold and increases on boiling. Zirconium is precipitated quantitatively on boiling. The procedure for carrying out a determination is as follows:

One gram of the mineral is decomposed by concentrated $\text{H}_2\text{SO}_4$, taken to copious fumes preferably twice in the usual manner, taken up with more $\text{H}_2\text{SO}_4$, and poured into about 700 c. c. of ice-cold water. After the insoluble matter is filtered and washed, the filtrate is nearly neutralized with ammonia to approximately a 0.3 to 0.5 N acidity and treated with an excess of a cold saturated solution of oxalic acid. Filter off the rare-earth oxalates, wash, and then convert the precipitate into soluble neutral nitrates, either by direct solution in fuming $\text{HNO}_3$ carried to dryness, taken up with a little water, and evaporated a second time; or by boiling with an excess of strong caustic potash diluted, filtered, washed, dissolved in dilute $\text{HNO}_3$, and taken to dryness twice—the second time with water alone to drive off the remaining bit of acid. To the solution of neutral nitrates is then added enough alcohol to make the solution of 40 per cent strength. Then add 20 to 25 c. c. of fumaric acid solution—0.1 gram per 10 c. c. of 40 per cent alcohol—heat to boiling, filter hot, and wash with hot 40 per cent alcohol. Return precipitate and paper to original beaker and dissolve in dilute hydrochloric or nitric acid; heat to boiling. To this solution can be added KOH in excess, the precipitate filtered off, dissolved in nitric acid, taken to dryness, etc., and the fumarate reprecipitated as before; or, according to the original method, after solution by HCl the filter paper can be filtered off and washed. The filtrate is evaporated to dryness, the residue stirred with hot water (the carbonaceous matter from the partly decomposed fumaric acid, etc., does not interfere), alcohol added to 40 per cent strength, and the precipitation repeated by the addition of 10 c. c. fumaric acid, heated to boiling, filtered, and washed with 40 per cent
alcohol. Ignite the moist filter containing the precipitate in a platinum crucible, and weigh the thorium dioxide.

This method is said to be considerably shorter than the thiosulphate method, which requires so many repeated precipitations and evaporations. Fumaric acid and other organic precipitants used in precipitating thorium away from other earths, have not been used commercially, as far as known; furthermore, the time spent in obtaining neutral solutions each time a precipitation is made would be unfavorably regarded by commercial establishments on account of the methods devised for work on acid solution (see p. 61).

AMMONIUM OXALATE METHOD.

Determination of thorium by means of ammonium oxalate, which was one of the first methods devised for the purpose (see Glaser (35 and 36)), is based on the solubility of thorium oxalate in excess of ammonium oxalate solution, the cerium earths and part of the yttrium earths being practically insoluble in excess. This method has been severely criticized by several later workers on the ground that yttrium earths are precipitated incompletely by an excess ammonium oxalate and that a rigid and complete separation of the thorium can not be achieved. (See Benz (7), Brauner (14), Hintz and Weber (41), and Drossbach (31).) Moreover, the process is very long and tedious, requiring two or three repetitions, the solution standing overnight for each performance. Benz (7) asserted that one digestion with ammonium oxalate brought into solution only about one-half of the thorium, and repeated digestions of the remaining oxalates with more ammonium oxalate brought much cerium and other earths into solution.

The process is usually carried out by transferring the total rare-earth oxalates to a beaker or evaporating basin, treating with about 100 c. c. of a cold saturated solution of ammonium oxalate, and boiling the solution with the addition of a few cubic centimeters of ammonium acetate. The solution is then diluted (300 c. c.) and allowed to stand overnight and the insoluble rare-earth oxalates filtered off and washed with water containing a little ammonium oxalate. The residual oxalates are re-treated with ammonium oxalate solution as long as the filtrate gives a precipitate with HCl. Thorium is finally precipitated from the solution by the addition of HCl, filtered, ignited, and weighed. It may be further purified—as deemed necessary by some workers—by bringing it into solution by fusion with bisulphate, or by concentrated H₂SO₄, precipitating as hydroxide, dissolving in HCl, evaporating to dryness, taking up with water, then precipitating the thorium from the neutral solution by the thiosulphate method.
The ammonium oxalate method, if used at all, would probably be employed for material high in thorium and low in other rare earths. Zirconium, if present in the rare-earth oxalates, is carried into solution along with the thorium, but is kept from precipitating by the oxalic acid produced by the action of HCl on ammonium oxalate.

**DETERMINATION OF THORIUM BY PRECIPITATION OF A THORIUM SALT FROM MINERAL ACID SOLUTION.**

The advantages of precipitating thorium from a mineral acid solution over the former methods are numerous, comprising principally speed, ease of manipulation, inexpensive reagents, and accurate separation of thorium from cerium and yttrium earths, thus eliminating the many necessary steps required in making a neutral solution and the many reprecipitations, with attendant long standings before filtration. The first precipitation to rid the rare earths from phosphoric acid and common base metals by means of oxalic acid is also unnecessary, hence these processes performed in acid solutions have been termed rapid methods, and include the following three methods now used in commercial laboratories:

1. Precipitation by means of potassium iodate in a nitric acid solution.
2. Precipitation by means of sodium hypophosphate in a hydrochloric acid solution.
3. Precipitation by means of sodium pyrophosphate in a hydrochloric or sulphuric acid solution.

**PRECIPITATION OF THORIUM BY POTASSIUM IODATE IN NITRIC ACID SOLUTION.**

The first method depends upon the fact that, in the presence of a large excess of KI, thorium iodate, Th(IO₃)₄, is rendered insoluble in mineral acids, whereas the iodates of the other rare earths are soluble. (See Meyer and Speter (72).) Cerium, which is precipitated under similar conditions, is kept in solution by reducing from the ceric to the cerous state by sulphurous acid before the iodate treatment. (See Brinton and James (17).) On monazite sand, decomposed with sulphuric acid, this step is not necessary, as the major part of the cerium found in solution will be already in a reduced condition, and what traces remain in the thorium precipitate are removed by the double precipitation. The process follows:

Fifty grams of the sand is heated in the usual manner to 250° for 5 to 6 hours with 100 c. c. concentrated H₂SO₄ in a thick-walled iron or porcelain dish. After decomposition the mass is poured into 500 c. c. ice-cold water and allowed to stand until all soluble salts have dissolved; then it is filtered into a liter flask and made up to the mark. To 100 c. c. aliquot add 50 c. c. concentrated HNO₃, and
when cooled add a cold solution of 15 grams KIO₃ in 50 c. c. concentrated HNO₃ and 30 c. c. H₂O. The white flocculent precipitate of thorium iodate is allowed to stand for one-half hour with frequent stirring, and is then filtered off. The beaker and filter are washed with a solution containing 2 grams KIO₃ in 50 c. c. dilute HNO₃ (1.2 sp. gr.) and 200 c. c. H₂O; any lumps of precipitate should be broken up. After draining, the precipitate is returned to the beaker, stirred up with about 100 c. c. of the wash liquor, and filtered again. It is now rinsed back into the beaker with hot water, dissolved by adding 30 c. c. HNO₃, and boiled. The thorium is recrystallized by adding to the cooled solution 4 grams of KIO₃ dissolved in a little concentrated HNO₃ and water, the precipitate filtered, and treated with the wash liquor as already described. This procedure separates thorium oxide from phosphoric acid and the common metals, as well as from the alkaline earths. Under the above conditions titanium and zirconium are also precipitated as well as cerium (ceric). To remove these impurities the precipitate is dissolved by heating with HCl with the aid of a little sulphurous acid. The thorium, zirconium, and titanium are next precipitated with ammonia, washed free of iodides, redissolved in HCl, diluted to acidity of approximately 0.5 N, and the thorium alone precipitated in the usual way by the addition of a saturated solution of oxalic acid in large excess; the oxalate is ignited and the thoria weighed. Two days only are claimed for carrying out this method so that the rather high cost of potassium iodate is overbalanced by the gain in working time from the earlier methods performed in a neutral solution. Carney and Campbell (23) found that the iodate method checked very closely with their pyrophosphate method, which was adopted later by one of the laboratories of the thorium industry.

**Precipitation by Sodium Hypophosphate in Hydrochloric Acid Solution.**

The method described under "Separation of thorium from cerium" (p. 40) depends on the fact that in an acid solution thorium can be precipitated quantitatively by means of a solution of sodium hypophosphate, Na₃H₂P₂O₆.6H₂O, as ThP₂O₆.11H₂O. The hypophosphate of thorium is insoluble in water or dilute acids or alkalis; it is decomposed by strong alkalis and fuming acids after prolonged boiling.

Several features should be remembered in regard to this method, if it is to be used. Zirconium and titanium are carried down with the thorium precipitate. The reagent sodium hypophosphate, besides being expensive, is hard to make. A difficulty arises also when this reagent is used with a solution of the earths in H₂SO₄, for insoluble sodium cerium earths may separate out with the thorium hypo-
phosphate. It has been suggested that this difficulty can be over-
come by preparing hypophosphoric acid in the solution by the oxidati-
on of yellow phosphorus, or by the anodic oxidation of copper
phosphide, Cu$_2$P$_2$. The method, however, leaves much to be desired.
(See Rosenheim and Pinsker (84) and Rosenheim, Meyer, and
Koppel (83).)

**PRECIPITATION OF THORIUM BY SODIUM PYROPHOSPHATE IN HYDROCHLORIC
OR SULPHURIC ACID SOLUTION.**

General consideration of this method has already been given under
"Separation of thorium from cerium and the other earths" (p. 34).
Although the action of sodium pyrophosphate, Na$_4$P$_2$O$_7$.10H$_2$O, with
thorium salts has been known for years and mentioned in standard
textbooks, its application for a quantitative determination of thorium
was first given by Carney and Campbell (23), who show that the
pyrophosphate method can be completed in a shorter time than
previous methods similarly performed in an acid solution, and at the
same time it is accurate and reliable. The sodium pyrophosphate
reagent is inexpensive and can be readily obtained. A water solution
of this salt is very stable.

In order to precipitate thorium completely as the pyrophosphate,
the solution must be boiled after adding the pyrophosphate. The
acidity should be about 0.3N or equal to approximately 5 c. c. of
HCl (1.19) in 200 c. c. of solution. If the acidity is too low, some
thorium may fail to be precipitated by going into the form of the
double pyrophosphate, Na$_4$Th(PO$_4$)$_2$.2H$_2$O. The addition of a strong
acid to a solution containing soluble double pyrophosphate breaks
it up and causes the precipitation of thorium pyrophosphate. The
pyrophosphates of cerous cerium, praseodymium, neodymium,
lanthanum, yttrium, ytterbium, and erbium are kept in solution
under the condition of acidity used. Zirconium and some titanium
are precipitated from a solution under the same conditions as tho-
rium, but are later kept in solution by oxalic acid, from which
solution thorium is precipitated, ignited, and weighed.

The final precipitate of thorium pyrophosphate may be dissolved
by concentrated sulphuric acid and a small amount of ammonium
perchlorate in a Kjeldahl flask, or by heating with concentrated
H$_2$SO$_4$ and HNO$_3$, as in the detailed method described below.

**DETERMINATION OF THORIUM IN MONAZITE SAND BY LINDSAY LIGHT CO.**

The following complete method as applied to monazite sand is
that in use at the Lindsay Light Co.'s laboratories, and was written
especially for this publication by Mr. V. T. Jackson, chemist for
the company. It has been thoroughly tested in the company's
laboratory with satisfactory results.
After an investigation of the four most common methods for the determination of thorium, it was found that with some modifications the sodium pyrophosphate method of Carney and Campbell (23) is the most satisfactory. The presence of iron, rare earths, titanium, and zirconium does not interfere with its accuracy.

Reagents needed.

Sulphuric acid, C. P.
Sulphuric acid (5 per cent solution).
Solution of sodium pyrophosphate (50 grams of crystals dissolved in sufficient water to make a volume of 1 liter).
Acidulated water (1 drop of hydrochloric acid—density 1.19—in 200 c. c. of distilled water).
Fuming nitric acid.
Twenty-five per cent solution of sodium hydroxide.
Ten per cent solution of sodium thiosulphate.
Hydrochloric acid (density 1.19).
Solution of oxalic acid (60 grams of crystals dissolved in sufficient water to make a volume of 1 liter).

Decomposition of the sand.

The sand for analysis is dried in an air bath at 110° C. for two hours. It is then cooled to room temperature in a desiccator, and 50 grams of the sand is weighed out and transferred to a porcelain dish. The size of the sample of sand should be large enough to bring to the final weighing 0.2 to 0.25 gram ThO₂, with the analysis portion directed below. The capacity of the vessel should be about 500 c. c. and it should be at least 7 cm. deep, since sand baked in a shallow dish does not make a good solution. One hundred c. c. of chemically pure sulphuric acid is poured over the sand, and it is well stirred with a thick rod, which is left in the dish. It is then covered with a watch glass and set on an iron ring, covered with a wire gauze, so as to spread the heat more evenly over the bottom of the dish. The ring should be raised about 15 cm. above the Bunsen burner. The flame should be regulated so that it is as soft as possible and yet does not deposit carbon. It should be 11 or 12 cm. high. This causes a heating of the sand and acid to such a temperature that only very faint fumes of the oxides of sulphur are given off and that there is but little spattering. The material should be stirred every half hour. In from one to two hours the whole mass swells up and turns white. After five hours all of the monazite sand has been attacked; but the material will not go completely into solution. A further heating for 12 hours more is desirable. The mass is then allowed to become perfectly cold.

An 800 c. c. beaker is filled three-fourths full with finely crushed ice. With the help of a porcelain spatula, the decomposed sand and excess acid are transferred, in small portions, to the beaker, stirring well after each addition. Some crushed ice is then put in the porcelain dish to dissolve the small amounts of sulphate remaining there. The whole is allowed to rise to room temperature. Except for the residue of sand, which consists mainly of silica and ilmenite, the contents of the two vessels are completely transferred to a liter volumetric flask. The flask and contents are brought to the temperature indicated on the former and the solution made up to mark. The solution may be a little clouded, owing to silica in suspension, which will likely cause the first sulphate to be clouded also. This silica will be removed as soluble sodium silicate by the first sodium hydroxide treatment.

Analysis of the solution.

Fifty cubic centimeters of the solution are transferred to an 800 c. c. beaker and made up to a volume of 450 c. c. with distilled water. (If several analyses are to be made, scratch a mark under the lip of the beaker to indicate a volume of 450 c. c.) This
will make the acidity of the solution 0.2 to 0.35 normal. The beaker is covered with a watch glass, a stirring rod is put in it, and it is heated to boiling. The liquid should be stirred occasionally to prevent bumping. Add 5 c. c. sulphurous acid to reduce the iron and cerium. If the solution remains yellow, 3 or 4 drops of sodium thiocyanate solution will complete the reduction. Fifteen c. c. of sodium pyrophosphate solution are added from a pipette. The solution is boiled five minutes and is immediately filtered. A very convenient method of filtering is to moisten a 12 cm. quantitative filter paper, press it into a Hirsch funnel, having a filter plate 8 cm. in diameter, in such a way as to hold all of the precipitate in the hollow thus formed. The filtrate is preferably caught in a 750 c. c. flask and then discarded.

The first filtrate may be slightly clouded, due to the oxidation of the iron and cerium by atmospheric oxygen, and its subsequent precipitation by the excess of pyrophosphate. With the aid of a "police" agent and acidulated water, the last traces of thorium pyrophosphate are completely transferred to the filter paper; 120 c. c. of sodium hydroxide solution are poured in the beaker and it is set aside.

After being drained, the filter paper and precipitate are lifted out of the funnel and placed on a piece of clean blotting paper. After being dried thus for 2 or 3 minutes, the filter paper is doubled over the precipitate and rolled into a cylinder. It can now be easily slipped into a 300 c. c. Kjeldahl flask. Fifteen to twenty c. c. of chemically pure sulphuric acid are added, and the flask is gently shaken with a rotating motion until half of the paper has been charred. A small, long-stem funnel is slipped into the mouth of the flask and 2 or 3 c. c. of fuming nitric acid are added to the warm mass (hood). In case of excessive foaming, shake the flask in cold water, or from a wash-bottle add a few c. c.'s of water.

The flask is set in a rack at an angle of about 30°; the tip of the funnel stem is so placed as to rest against the side of the neck of the flask, to prevent spattering. When foaming has stopped, heat to fumes of sulphur trioxide with a small Bunsen flame. If the contents of the flask are not white or only a light yellow, the material is allowed to cool somewhat and 2 c. c. more of the fuming nitric acid is added. The mixture is again heated to fumes of sulphur trioxide.

After the flask has cooled, rinse the funnel into the flask and remove it. Make volume of solution 75 to 100 c. c.

When the material has gone into solution (it may be slightly clouded because of suspended silica) it is poured into sodium hydroxide solution and the flask rinsed three or four times with distilled water. The volume is made up to 450 c. c. and the liquid is boiled for five minutes. The hot solution is filtered from the precipitate immediately, in the manner described for the pyrophosphate. The beaker is rinsed once with hot water. A wash-bottle fitted with a Bunsen valve, to prevent back flow of hot water, is very convenient. After washing the precipitate once, it is allowed to drain and it is then put back in the beaker, along with the filter paper; 12 c. c. of hydrochloric acid (density 1.19) are poured over the paper. It is allowed to stand for five minutes with occasional shaking, when all of the hydroxide should be dissolved; 100 c. c. of hot water are added, and the filter stirred around occasionally. After standing for five minutes the filter paper is drawn up on the sides of the beaker and allowed to drain. It is then well rinsed with hot water. With the fingers it is gathered into a ball and squeezed out. It is again rinsed and squeezed out and then put into the Kjeldahl flask previously used. The small amount of disintegrated filter paper remaining in the solution does no harm.

In order to remove the last traces of rare earths and iron the volume of the solution is made 450 c. c., and the thorium is again successively converted into the pyrophosphate, sulphate, hydroxide, and chloride. Only 10 c. c. of hydrochloric acid are used in making the second chloride solution. The 100 c. c. of chloride solution are filtered through a 9 cm. qualitative filter paper. The filtrate is caught in an 800 c. c. beaker.
The first beaker is washed out several times with hot water until the volume in the second beaker is made 450 c. c.

The solution is heated to boiling and 35 c. c. of oxalic acid solution are added in drops, from a pipette, and then boiled for 15 minutes. By this procedure the thorium is precipitated, while titanium and zirconium are left in the solution. The precipitate is allowed to stand over night and at least five hours on the steam bath. It is then filtered through a 9-cm. quantitative filter paper, using acidulated water and a "policeman" for completely transferring the precipitate to the filter. After a thorough draining, the filter paper and precipitate are transferred to a tarred platinum crucible, which is then placed on a triangle at an angle of 45° over a small Meeker flame. The crucible should be barely touched by the flame. The filter paper is thus dried and charred. The paper and carbon are burned away by heating the side of the crucible with a somewhat larger flame. It is then covered and placed in an upright position and heated in the full Meeker flame for 30 minutes. The residue of ThO₂ should be snow white. The crucible is cooled in a desiccator and then weighed.

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PART III.—MOLYBDENUM.

By J. P. Bonardi.

INTRODUCTION.

Molybdenum is a metal that has come into considerable prominence during the last few years. Up to four or five years ago its main uses were in connection with the manufacture of magnet steel and chemical salts, such as ammonium molybdate and molybdic acid. The World War, however, brought molybdenum into prominence owing to its use in a number of special steels that were the result of considerable experimental work here and abroad. The result was a thorough investigation of the molybdenum deposits in this country, which showed that the United States probably had some of the largest, if not the largest, deposits of these ores in the world.

The two principal ores are molybdenite, or the disulphide (MoS₂), and wulfenite, or lead molybdate (PbMoO₄). There is frequently associated with the disulphide the mineral molybdite, or molybdic ocher (Fe₂O₃·3MoO₃·7½H₂O). This is an oxidation product of the sulphide. The former mineral is usually found in flakes somewhat similar in appearance to graphite, although some molybdenite ores carry the mineral in a more or less granular form. Wulfenite crystallizes in tables which are usually yellow or orange, although they may have a reddish tinge. Molybdite is a canary-yellow mineral which looks somewhat like carnotite. Powellite (CaMoO₄) is not a commercial mineral, and is frequently found associated with tungsten. Other rare molybdenum minerals are described by Horton (50).

Molybdenum is principally used in the manufacture of special steels and alloys. It is also employed in the manufacture of chemical reagents, dyes, glazes, and disinfectants. Molybdenum steel is used for crank-shaft and propeller-shaft forgings, high-pressure boiler plate, rifle and gun barrels, armor plate, magnets, and iron for resistance furnaces, and in connection with chromium, vanadium, and other alloying elements in self-hardening and high-speed machine tools. During the war molybdenum steel was used in Liberty motors and for other purposes.

The analysis of molybdenum products is frequently difficult, owing to the number of other elements that may be associated with this metal. Some of the alloy steels are complicated, and the following elements may be encountered in molybdenum ores and alloys: Cobalt,
chromium, nickel, iron, manganese, tungsten, vanadium, titanium, zirconium, copper, aluminum, zinc, carbon, silicon, phosphorus, arsenic, antimony, and bismuth.

Most of the methods in the following chapter have been thoroughly tested by the United States Bureau of Mines, and its experience with these methods is fully described; however, it has been impossible to investigate the advantages and disadvantages of certain methods as thoroughly as others.

**QUALITATIVE TESTS.**

**METHOD 1.**

One of the most highly recommended tests is to fuse some of the pulverized ore or alloy with sodium or potassium carbonate, to which a small amount of sodium or potassium nitrate has been added. The fusion is treated with water, heated, and filtered, Fe, Cr, Ti, and Zr remaining in the precipitate. The filtrate is acidified with HCl and boiled several minutes to expel all CO₂. Some ammonium or potassium thiocyanate is added, immediately followed by Zn. If Mo is present, a bright cherry-red color will develop, which will only disappear on standing for several minutes, depending upon the amount of Mo present in the solution to be reduced. If H₂O₂ is added to the solution after the cherry-red color has developed, the color disappears, but will return as soon as the peroxide has been reduced. This color reaction is very definite and certain for Mo, but if the mistake is made of adding the Zn first, which reduces the Mo, and then later the thiocyanate, scarcely any color will be obtained. When only small amounts of Mo are present, a concentration of the cherry-red color can be obtained if the solution is shaken with a small volume of ether, when any color in the liquid will be extracted by the ether and intensified as a golden brown in the ether ring that forms at the top of the liquid on standing. This makes color visible that may have been imperceptible before. Should the fusion be imperfect with an extraction of Fe in the leach from the fused carbonates, a cherry-red color will immediately develop on the addition of the potassium or ammonium thiocyanate to the solution. With the addition of Zn, however, the color due to Fe disappears, and unless a large amount of Fe has been brought into solution, which will not be the case if the fusion is properly made, this color will completely disappear prior to the development of any color due to Mo. If this color reaction of Fe and its disappearance on addition of Zn be borne in mind, the above test for Mo is infallible. See Treadwell and Hall (107), Keddesdy (57), Horton (50), page 40, Prescott and Johnson (81), page 97, and Roscoe and Schorlemmer (84). If the above test is to be made on an unknown solution for Mo, it is best that ammonium hydroxide or sodium
carbonate, with a few cubic centimeters of $\text{H}_2\text{O}_2$, be first added, heated, and any precipitate that forms filtered off, and then the filtrate tested as above, by making acid with $\text{HCl}$, followed by thiocyanate and $\text{Zn}$, as directed.

**METHOD 2.**

With molybdic acid solutions acidulated with $\text{HCl}$, potassium ferrocyanide gives a reddish-brown precipitate. A standard test for alkaline solutions of Mo is the addition of tannic acid. If Mo is present, the solution will be red to brown. An alkaline solution acidified with acetic acid gives, with hydrazine sulphate after heating, a blue coloration ($\text{Mo}_2\text{O}_4$); or, by adding an excess of $\text{KI}$ and boiling, I is liberated and the solution turns blue. Pyrogallol, used instead of tannin in a solution acid with acetic, is a sensitive test, an orange coloration being produced. (See Browning (16), Prescott and Johnson (81), and Moir (72).) None of these tests, however, are as sensitive as the ammonium or potassium thiocyanate test given above.

**METHOD 3.**

Mo present in a solution strongly acidified with $\text{HNO}_3$ in the presence of ammonium nitrate is precipitated by a few drops of disodium phosphate solution. The precipitate formed is yellow ammonium phosphomolybdate. The precipitate is soluble in sodium or ammonium hydroxides. Mercurox nitrate precipitates mercurous molybdate from neutral solutions; the precipitate is soluble in $\text{HNO}_3$. Lead acetate precipitates white $\text{PbMoO}_4$ in acetate acetic solutions, soluble in mineral acids. (See Treadwell and Hall (107).)

**METHOD 4.**

A pinch of powdered Mo ore on a porcelain lid, if moistened with a few drops of $\text{HNO}_3$ to make a paste, and heated nearly to dryness, then followed by $\frac{1}{4}$ c. c. concentrated $\text{H}_2\text{SO}_4$, will, after being heated to fumes and allowed to stand, produce a blue color when breathed upon. A drop of alcohol added at this point will hasten this color reaction. The color will disappear on heating, but if allowed to stand for some time will reappear on cooling; water will destroy this color. (See Scott (92) and Wolf (112).)

**METHOD 5.**

The Mo mineral wulfenite, with the blowpipe on charcoal, decrepitates and fuses, giving a yellow coating of $\text{PbO}$ on the charcoal. When heated with soda ash on charcoal, it yields metallic lead. With a salt of P, it gives a yellowish-green glass in the oxidizing flame, which becomes dark green in the reducing flame; with borax in the oxidizing flame, it gives a colorless glass which in the reducing flame becomes opaque black or dirty green.
Molybdenite gives off sulphurous fumes when heated in a closed tube, and a pale yellow sublimate of molybdenum trioxide is formed. The mineral is infusible before the blowpipe and imparts a yellowish-green color to the flame. On charcoal it gives sulphur fumes and a slight sublimate, yellow hot, white cold, and deep blue when touched with the reducing flame. It is soluble in HNO₃, leaving a white or grayish residue. (See Wolf (112) and Horton (50).)

**METHOD OF DECOMPOSITION OF ORES, ALLOYS, STEELS, AND THE GENERAL PRODUCTS OF MOLYBDENUM.**

**CRUSHING SAMPLES FOR ANALYSIS.**

The decomposition of Mo ores, alloy steels, or the commercial products of Mo commonly encountered offers very little difficulty. If the ores or chemical products are ground to minus 100-mesh fineness, this will usually be sufficient. For alloy-steel products it is best to crush to minus 200-mesh fineness before analysis is begun. The reduction of FeMo and Mo steel to such fineness can be performed in a special hardened steel mortar. The necessary pounding can be done, if desired, by a 2-inch Ingersoll Rand piston drill set up vertically in a frame above the mortar and pestle in such a manner that it is used as an air hammer. In preparing ore samples for assay, an amount slightly in excess of the desired weight can be ground to an impalpable powder by a mechanical agate mortar, as shown by Hillebrand (46). When a number of samples are to be prepared this method is indispensable. Oxide ores and ferro-alloys generally require much finer grinding than sulphide ores. It is assumed that the reader is acquainted with the general precautions necessary in the preparation of samples for analysis. Several standard textbooks and bulletins have special chapters describing such procedure. (See Lord and Demorest (61), p. 1, and Hillebrand (46).)

**SOLUTION OF SAMPLE.**

There are two general methods of attacking an ore for analysis, by acid and by fusion.

**DECOMPOSITION BY ACID.**

When treating ores by mineral acids, it is well to remember that, in general, HCl is the best solvent for oxidized material and HNO₃ for sulphide material. Some slags and rebellious silicates may require fusion with alkalis or a combination of HF with one of the common acids, usually H₂SO₄. The choice, then, of the acids selected for decomposition will depend upon the apparent nature of the ore and the subsequent determination to be made. If HCl is used, it is usually followed by HNO₃, and vice versa. Potassium chlorate in
combination with HNO₃ is a powerful solvent for sulphide ores. The use of mixed-acid combinations, for example HNO₃ and H₂SO₄, and HNO₃, HCl, and H₂SO₄, and aqua regia, are very effective for dissolving nearly all classes of materials.

The following facts must be borne in mind in dissolving a Mo ore: That Mo metal is easily soluble in aqua regia, in hot concentrated H₂SO₄, and in HNO₃, and insoluble in HCl, HF, and dilute H₂SO₄; that dilute acids precipitate molybdic acid from alkali molybdate solutions if the solution be sufficiently concentrated, which, however, is soluble in an excess of acid or alkalies; that molybdic anhydride is sparingly soluble in water and possesses basic properties toward stronger acids, dissolving in them to form salts; that MoO₃ is soluble in alkalies to form molybdates, water soluble; that molybdates of the alkaline earth are insoluble in water and soluble in acids; and that MoO₂ heated above 450° sublimes to an appreciable extent, unlike the corresponding W compound. (See Browning (16), Prescott and Johnson (81), and Treadwell and Hall (107).) There are no salts of Mo that are not soluble in mineral acids in some combination; practically the same can be said for Mo minerals, as will be shown.

In treating molybdenite (MoS₂), decomposition by acids is best effected by first treating with concentrated HNO₃ and heating until all brown nitrous fumes have been driven off, which, if the sample has been ground to sufficient fineness, will indicate practically complete oxidation of the sulphide minerals. The decomposition is then finished by adding HCl and taking to near dryness, or by adding H₂SO₄ and carrying to fumes. Either method of solution will completely decompose MoS₂ ores. The solution of wulfenite, the PbMoO₄ mineral, is best effected by a mixed-acid treatment, since HNO₃ or HCl alone will not dissolve wulfenite to any appreciable extent. The two acid mixtures recommended for ores containing this mineral are a combination of HNO₃, HCl, and H₂SO₄, or a combination of HNO₃ and H₂SO₄. It has been found by experience that either of these acid mixtures will completely effect a solution of the Mo. Carrying to fumes with H₂SO₄ must be done to remove the Pb contained in an ore, otherwise the Pb will subsequently interfere, as will be explained later. The residue from such treatments rarely, if ever, will be found to contain any Mo. For digesting Fe-Mo products, such as FeMo or alloy-steel products, the above mixed-acid treatments are very effective for a complete solution. The procedure is usually to start with either concentrated HNO₃ or HCl and to finish with an aqua regia mixture. Solution can also be effectively obtained by a mixture of HNO₃ and H₂SO₄ carried to fumes, or by a mixture of the three acids, carrying to H₂SO₄ fumes. The selection of an acid treatment usually depends upon the subsequent determinations to be made. For further detailed explanation of the acid digestions
adopted by different workers for Mo products, the reader is referred to the following: Blair (9), Johnson (55), Lord and Demorest (61), Treadwell and Hall (106), Collett (21), Horton (50), Crook and Crook (23), Hoepfner and Binder (48), Auchy (2), (3), Cruser and Miller (25), Epperson (32), Travers (103), Wickes (111), and Westling and Anderson (109).

DECOMPOSITION BY FUSION.

The following methods of decomposition have been used by different workers: For fusion with sodium peroxide, or a mixture of sodium hydroxide and sodium peroxide, see Darrock and Meiklejohn (26), Strebingler (95), Crook and Crook (23), and Trautmann (98). For fusion with sodium or potassium carbonates, or mixtures of the carbonates with a small amount of sodium or potassium nitrate to oxidize the sulphides and Fe, see Horton (50), Hillebrand (46), Johnson (55), and Schoeller and Powell (91). For fusion with potassium bisulphate, see Mabee (64) and Kopp (60). For fusion with a mixture of sodium carbonate and peroxide, see Crook and Crook (23) and Mabee (65). For fusion with a mixture of sodium carbonate and S (1:1) in a porcelain crucible, as for Sb ores, whereby the Mo is obtained as a sulpho salt, see Lunge and Keane (63), Schoeller and Powell (91), and Horton (50).

The fusion methods offer rapid and complete decomposition of the ores or of ferro compounds. These methods have one common disadvantage for ores containing SiO₂, since the greater part remains in the leached solution and must be removed if Mo is to be determined by gravimetric methods. A chief advantage of the alkali fusion methods is that Pb, Cu, Bi, Fe, Ti, Zr, P, and parts of other elements are left in the residue from the leach. The solution is then in a better condition for a volumetric method than for a gravimetric method.

A combination treatment, first by an acid digestion, followed by a fusion of the residue, is very often used. The fusion usually employed is potassium pyrosulphate, or some of the alkali fusion methods above mentioned. In treating rebellious silicates, HF is added to the residue in combination with H₂SO₄ before a fusion. As previously stated, the method chosen depends upon the worker’s judgment, and the class of material to be treated.

ALKALINE LEACHING METHODS.

If molybdite—molybdic ochre (Fe₂O₃·3MoO₃·7½H₂O)—(see Schaller (89)) is to be determined separately from MoS₂ ores, as is often required in the flotation products connected with MoS₂ ore, a complete solution from the sulphide can be effectively made by one of
the following reagents: A 10 per cent solution of HCl; a 10 per centsolution of NH₄OH; or a 10 per cent solution of sodium carbonate. Either of these three methods of solution will completely dissolve the oxide of Mo in a boiling solution without affecting the sulphide mineral in the least. This has been thoroughly tried and has always given reliable results. (See Bonardi and Barrett (11).)

Wulfenite, if ground finely enough, is soluble in alkalies, such as sodium carbonates and caustic soda, but great excesses of each are necessary. Sodium sulphide, however, is an efficient solvent for wulfenite in a boiling solution, so much so as almost to offer a quantitative method of analysis. This fact is made use of in one of the commercial methods for extracting Mo from wulfenite ores. (See Bonardi (10b).)

QUANTITATIVE SEPARATION OF MOLYBDENUM FROM THE GROUP ELEMENTS.

Qualitative chemistry should always be thoroughly understood before any quantitative work is performed on an element; moreover, a knowledge should be had of general qualitative analysis, general reactions, and group separations, otherwise one will be practicing "cook-book" chemistry. If, under such circumstances, things appear to be going wrong, one can blame only the operator; and the last thing will be to lay the blame upon any method the unskilled operator might be trying to use, even if this method lacked as much chemical foundation as did the worker. The qualitative chemistry given for Mo in this section has been carefully prepared in order to eliminate the practice of "cook-book" chemistry methods in making a determination for Mo. The separation of Mo from the ordinary group elements will be treated first, followed by a detailed separation from the other members of the rare metal groups, and from those interfering elements most common in any Mo analysis.

GROUP POSITION OF MOLYBDENUM.

Mo belongs to the H₂S group (Group II), and the solubility of its sulphide (MoS₃) in alkaline sulphides places it in group II, division B, with As, Sb, and Sn. Mo, like the corresponding soluble thio compounds of these elements, is decomposed by HCl with the reprecipitation of the trisulphide. The following information on the qualitative chemistry of Mo has been gleaned in part from the references to be cited and in part from personal study by the writer, who, in his work on Mo for a number of years, has had an opportunity to study this phase of the chemistry of Mo and has found the qualitative methods herein presented to be sufficiently accurate in nearly every case to serve as quantitative separations. This will be further borne
out in the section devoted to quantitative determination. The methods presented for the separation of Mo from the interfering elements have been thoroughly tested on ore samples encountered by the writer during his work on Mo. For the detailed general chemistry of Mo, the reader is referred to the following sources: Prescott and Johnson (81), Treadwell and Hall (106), (107), Scott (92), Schoeller and Powell (91), Browning (16), Roscoe and Schorlemmer (84), Mennicke (70), and Rüdisühle (87).

**SEPARATION OF MOLYBDENUM FROM THE MEMBERS OF GROUP I—SILVER, LEAD, AND MERCURY.**

Mo is not precipitated by dilute HCl, either in the cold or hot, and hence is not found in the insoluble chlorides of Ag, Pb, or Hg (mercurous chloride). However, if the solution contains considerable Mo, a soluble molybdate, for example, and this be concentrated to a small bulk, HCl will give a white precipitate of molybdic acid ($H_2MoO_4$), which is, however, soluble if an excess of the acid is used. Tungstic acid, which is precipitated in group I and which is rendered insoluble by taking the solution to near dryness, is left behind when the molybdic acid is dissolved by an excess of acid. This is one of the means for separating Mo from W. It is not, however, a strictly quantitative reaction, since a little W may still remain in solution.

**SEPARATION OF MOLYBDENUM FROM THE MEMBERS OF GROUP II—DIVISION A, LEAD, MERCURY, BISMUTH, COPPER, AND CADMIUM; DIVISION B, ARSENIC, ANTIMONY, TIN, AND TUNGSTEN NOT TAKEN OUT IN GROUP I.**

When a dilute acid solution containing Mo is treated with $H_2S$ with or without pressure, Mo is precipitated as the trisulphide (MoS$_3$) with the members of Group II, divisions A and B. This, then, separates Mo from the members of Group III (Fe, Al, Cr, Mn, Zn, Ni, Co, etc.), from Group IV, the alkaline earths (Ba, Sr, and Ca), and from Group V, the fixed alkalies (Na, K, and Mg).

The separation of Mo from Pb, Cu, Hg, Cd, and Bi is brought about by treating all the sulphides that were precipitated by $H_2S$ with ammonium sulphide ($H_2N_2S$) or sodium sulphide in an alkaline solution, when MoS$_3$ dissolves, whereas Pb, Cu, Hg, Cd, and Bi remain insoluble; copper sulphide is, however, slightly soluble. The Mo will be then found in solution as the sulpho or thio salt ($H_2N_2MoS_3$) with As, Sb, and Sn, which are also soluble in alkali sulphides.

The precipitation of Mo in an acid solution by $H_2S$ separates it quantitatively from the rare metals, V, U, Ti, and Zr, and from Cr and P, which elements must be removed before Mo can be determined quantitatively. Any trace of W which has escaped precipitation and removal in the first group will be found associated with Mo, since its
sulphide behaves like Mo. The prevention of the precipitation of W from Mo can be quantitatively effected by having in the solution 3 to 5 grams of tartaric acid. (See Browning (16), Scott (92), Treadwell (104), Cruser and Miller (25), and Schoeller and Powell (91).) W does not precipitate as the sulphide under such conditions.

The precipitation under pressure of the sulphide of Mo is best performed in a solution containing H₂SO₄ or HCl, but not HNO₃, in an ordinary citrate of magnesia bottle, the rubber top firmly clamped, and the bottle placed in a hot water bath for one to two hours. Under such conditions, the precipitation of Mo is quantitative. A solution containing the soluble thio salts of Mo, As, Sb, and Sn, when acidified with HCl, precipitates the insoluble sulphides of these elements. These can be readily dissolved by HCl plus KClO₃. As, when present as As pentavalent, may be separated by magnesia mixture in an ammoniacal solution (same for phosphoric acid) as ammonium-magnesium arsenate, similar to the phosphate precipitation. (See Schoeller and Powell (91) and Browning (16).) In a strong HCl solution (2 of acid to 1 of the original solution) molybdenum sulphite is not kept quantitatively in solution, as are Sb and Sn. As can be volatilized from a solution containing Mo as trichloride by distillation with strong HCl and KI, or in the presence of ferrous chloride, cuprous chloride, or other reducing agents. (See Schoeller and Powell (91) and Scott (92).)

Sb is separated from Mo in solution by granulated Pb. The solution should be acid with HCl and free from nitrates or sulphates, and contain 20 to 25 c. c. of strong HCl in a bulk of 100 c. c. Two grams of granulated Pb is added to this solution and boiled. Sb precipitates in the metallic state, Mo remaining in solution in a reduced state. (See Schoeller and Powell (91).)

Mo is precipitated free from Sn by H₂S (pressure precipitation) after addition of 15 grams of H₂C₂O₄ per 100 c. c. of liquid; the Sn is not precipitated under these conditions. Molybdenum sulphide is insoluble in a boiling solution of H₂C₂O₄, thereby SnS is soluble. See Schoeller and Powell (91), and Prescott and Johnson (81). Sn, if occurring originally as cassiterite in an ore, will be found remaining with the SiO₂, being insoluble in ordinary acids. When a HCl or H₂SO₄ solution containing Mo, As, Sb, Cu, and Sn in solution is treated with Zn, As and Sb are partly converted to the metal and partly evolved as arsine and stibine, Cu and Sn being precipitated as the metal. Mo remains in solution in a reduced condition. Copper occurring in an ore in large proportions can be separated from Mo in solution by potassium or sodium sulphocyanates after first being reduced with SO₂ gas in a weak sulphuric acid solution. This forms the basis of a quantitative method. See Bonardi and Shapiro (12).
SEPARATION OF MOLYBDENUM FROM THE MEMBERS OF GROUP III—ALUMINUM, CHROMIUM, IRON, ZINC, NICKEL, COBALT, MANGANESE, ZIRCONIUM, TITANIUM, AND THE RARE EARTHS.

One of the best ways to separate Mo quantitatively from members of Group III, A and B (Al, Cr, and Fe, and Mn, Zn, Ni, Co, etc.), and from the members of Group II, A, is by (NH₄)₂S, which is added in excess to an acid solution containing Mo until the solution has turned sufficiently alkaline; or by passing H₂S gas into a solution after it has been made ammoniacal. The precipitate from such a treatment will contain all the Al, Fe, Cr, Mn, Zn, Ni, and Co, as well as Ti, Zr, and U, and all the rare earths, if present. The filtrate will contain Mo, V, W, and members of Group II, B (As, Sn, and Sb), and possibly a trace of Cu, as well as the members of Groups IV and V, the alkaline earths and fixed alkalies. Three to five grams of tartaric acid and 15 grams of oxalic acid per 100 c. c. of liquid are next added to the filtrate, as directed under separation of Mo from W and Sn, previously given. The solution is then made slightly acid with H₂SO₄ and heated in a pressure flask until the precipitate has settled and the supernatant liquid appears colorless or slightly blue. The solution may be colored slightly blue due to V, which also forms a soluble sulphide with alkali sulphides, from which brown V₂S₅ is precipitated on the addition of acid. The precipitation of V₂S₅ is not quantitative, as is Mo, and hence a little V may remain in solution in a reduced condition along with the alkaline earths and alkalies. The filtrate contains W and Sn, while the precipitate contains Mo, V, As, and Sb sulphides, which can then be dissolved in aqua regia or HCl, with a little KClO₃, and the Mo separated as the sulphide with H₂S under pressure, whereby the V remains quantitatively in solution. As and Sb and any trace of Cu occurring in solution are then separated from the Mo precipitate as previously given. In an ordinary analysis, however, where the amounts of these elements are small no attention need be given them provided the Mo is determined by either the gravimetric or the volumetric method described later. NH₄OH in excess in a hot solution in the presence of NH₄Cl precipitates Fe and Al quantitatively from Mo. Cr can be precipitated quantitatively by first reducing it in solution by SO₂, oxalic acid, or alcohol when on the addition of NH₄OH it will precipitate quantitatively with the Fe and Al; the solution must be boiled well. An easier separation can be made with (NH₄)₂S and ammonia.

As and Sb are precipitated out quantitatively with Fe(OH)₃ provided 10 times as much Fe is in solution as As and Sb. For a more detailed explanation, see the description given for the gravimetric method adopted.
SEPARATION OF MOLYBDENUM FROM THE MEMBERS OF GROUP IV AND GROUP V—THE ALKALINE EARTHS AND FIXED ALKALIES, INCLUDING MAGNESIUM.

The quantitative separation of Mo from the alkaline earths and the fixed alkalies, including Mg, is performed by H₂S under pressure in a slightly acid solution, as previously described above. Mo can also be separated from the alkaline earths by fusing the substance with mixed carbonates and niter, extracting the melt with water and filtering. The filtrate contains all the Mo as alkali molybdate, while the alkaline earths remain undissolved as carbonates.

GENERAL CONCLUSION OF THE SEPARATION OF MOLYBDENUM FROM THE GROUP ELEMENTS AND THE RARE METALS.

The separation of Mo from the rare and common metals associated with it in ores, commercial steels, and alloy products will be further taken up in the discussion that follows on all the quantitative methods proposed to date. The detailed separation of Mo from the interfering elements can be better treated in the discussion of the analytical methods proposed for Mo than separately, without any direct connection to any process. The separation of Mo from V, W, U, Cr, Cu, As, Sb, Zr, Ti, Fe, Mn, and P, which are the elements most likely to interfere in a volumetric or gravimetric determination of Mo, has practically been given, in a general way, in the foregoing discussion of the separation of Mo from the different groups and from members of its own group. Although the methods of separation have been described from a qualitative standpoint, they are all applicable for a quantitative separation. For example, the H₂S method of precipitating Mo under pressure in an acid solution will separate it quantitatively from V, W (when tartaric acid is present), U, Cr, Zr, Ti, Fe, Mn, Ni, Co, P, alkaline earths, and alkalies, besides many other elements not precipitated by H₂S in an acid solution. NH₄OH, on the other hand, removes Fe, Al, Cr (when reduced to "chromic"), As, Sb, and Sn when precipitated in the presence of Fe₃(OH)₉. The sulphides that are carried down with Mo sulphides, or those capable of forming thio salts with Mo, are as a rule easily taken care of, or do not interfere in the course of an ordinary analysis. This is also true for elements that are soluble in excess NH₃ and NH₄Cl, and are carried along with the Mo if no previous sulphide precipitation had been made.

REVIEW OF QUANTITATIVE METHODS IN GENERAL USE.

Methods in general use for the determination of Mo in ores or steel products and those that have been presented in technical literature on the subject are as follows:

1. Precipitation as the sulphide from acid or alkaline solution, followed by dilute acid with or without increased pressure.
2. Precipitation as mercurous molybdate.
3. Precipitation as lead molybdate.
4. Titration with lead acetate.
5. Titration with potassium permanganate.
6. Titration with methylene blue.
7. Titration with ferric chloride after reduction with titanium chloride.
8. Iodometric method.
9. Titration with potassium iodate.
11. Determination of molybdenum by volatilization.
   (a) In a current of carbon tetrachloride vapor.
   (b) In a current of dry hydrochloric acid gas.
12. Liberated iodine from a molybdic solution precipitated as silver iodide.

**ABSTRACTS OF ABOVE METHODS, WITH COMMENTS.**

**METHOD 1. PRECIPITATION AS THE SULPHIDE.**

Precipitation as the sulphide in acid solutions with or without increased pressure, or by formation of soluble thiomolybdate followed by precipitation in an acid solution, has been most discussed in chemical literature. Such processes are all based on the fact that MoS₂ is quantitatively precipitated from members of the third, fourth, and fifth group elements. The precipitation is performed in a slightly acid solution, preferably H₂SO₄, not HNO₃, with or without increased pressure, or by first forming the soluble thio salt of Mo, and subsequently the MoS₃ by making the solution acid.

**a. IN COLD DILUTE ACID SOLUTION WITHOUT PRESSURE.**

The precipitation of Mo without pressure is incomplete unless separated several times, as stated by Blair (8), Rose (86), and Döhler (29). Johnson (55) states that the Mo should be precipitated from as nearly neutral a solution as possible, for if an attempt is made to precipitate Mo from a solution containing much free acid, a colored filtrate is obtained (not to be confused with the blue color produced by reduced V) which contains much of the Mo in a reduced form that is difficult to precipitate as the MoS₃. Since practically all the methods described for precipitating Mo in an acid solution recommend increased pressure, and the results obtained by the writer on this method have proven unreliable, this means of precipitation will not be considered further.
6. BY SATURATING A COLD SOLUTION, SLIGHTLY ACID WITH HYDRO-
CHLORIC \(^3\) OR SULPHURIC ACID, WITH HYDROGEN SULPHIDE AND
HEATING IN A PRESSURE FLASK.

The precipitation of Mo from a dilute acid solution under increased
pressure is complete. The solution from which the Mo is to be pre-
cipitated is placed in an ordinary pressure flask. A citrate of mag-
nesia bottle with a rubber-capped stopper or a mineral bottle with
a screw stopper can be used. The flask containing the solution,
after being saturated with \(\text{H}_2\text{S}\), is placed in a hot water bath and
maintained at this temperature for two or three hours.

The precipitation requires either that the precipitated sulphides
be converted to some weighable form, such as MoO\(_3\) or MoS\(_2\), or that
the sulphides be dissolved and determined volumetrically or by one
of the gravimetric methods. Those who have worked with this
method are: Zinberg (115), Herrstein (45), Trautmann (98), (99),
Collett and Eckhardt (21), Hoepfner and Binder (49), Chesneau (19),
Chatard (18), Horton (50), Johnson (55), Lunge and Keane (63),
Wolf, K. (113), Scott (92), Treadwell and Hall (106), Schoeller and
Powell (91), Binder (6), Crook and Crook (23), Westling and Ande-
erson (109), Mennicke (70), Evans (33), and Blair (8).

The precautionary measures necessary for the conversion of MoS\(_3\)
to a weighable form, such as MoO\(_3\) or MoS\(_2\), are best illustrated by
the following citations. Binder (6) states that:

When molybdenum is precipitated as MoS\(_3\) and then ignited to oxide, the oxidation
is not complete unless the substance, after preliminary ignition, is treated with
HNO\(_3\), evaporated, dissolved in ammonia, reprecipitated with HNO\(_3\), evaporated,
and ignited. A correction must be made for any traces of matter which remain
insoluble when the ignited residue is dissolved in NH\(_4\)OH.

Wolf (113) states that:

The conversion of a precipitate of molybdenum sulphide into MoO\(_3\) by ignition is
not quantitative if the temperature rises above 450° as sublimation then occurs to an
appreciable extent. A temperature of 400° suffices and it is most convenient and
certain to ignite the precipitate in an electrically heated furnace at a temperature of
425° C.

MoO\(_3\) can be completely volatilized at temperatures around 700° C.,
although this volatilization begins at around 500° C. To avoid loss
of Mo by volatilization, various schemes and modifications of the
treatment before weighing have been proposed. One by Treadwell
and Hall (106) is as follows:

The moist precipitate and filter is placed in a tared crucible and dried upon the
water bath. The covered crucible is then gently heated until volatile hydrocarbons
have been driven off. The cover is then removed and carbon burned from the sides
of the crucible at as low a temperature as possible, and, by raising the temperature

\(^{*}\) For the separation of Mo from Ba, Sr, and Ca it is recommended that the precipitation be made in a
HCl solution.
gradually, the sulphide is changed to oxide. The operation is finished when no more sulphur dioxide is formed. After cooling, a little mercuric oxide suspended in water is added to the contents of the crucible, the mixture is well mixed, evaporated to dryness on the water bath, the mercuric oxide is removed by gentle ignition, and the residue of molybdenum trioxide is weighed. The mercuric oxide is then added in order to remove particles of unburned carbon.

The procedure outlined above for igniting a Hg salt with MoO$_3$ is similarly performed as in the gravimetric mercerous molybdate method to be described. In the method given by Westling and Anderson (109), the precipitated sulphide is dissolved in aqua regia, evaporated to fumes of SO$_3$, and finished by volumetric titration with standard lead acetate, using tannic acid as an outside indicator. Evans (33) suggests that the sulphides be dissolved by HNO$_3$ and Br, and the Mo determined gravimetrically, weighing as PbMoO$_4$.

The conversion of MoS$_3$ to MoS$_2$ in a stream of H in a Rose crucible requires many ignitions and weighings. The process, as with the conversion to MoO$_3$, requires considerable care and practice. The addition of S to the molybdenum sulphide has been recommended; usually an amount equal to about one-half the weight of the sulphide is added and then ignited over a Bunsen burner at a dull-red heat in a stream of arsenic-free H for about 15 minutes. Horton (50) advocates this method of determining Mo by weighing as the sulphide (MoS$_2$). (See also Collett and Eckhardt (21), Trautmann (99), Chesneau (19), and Zinberg (115).)

c. INTERFERING ELEMENTS CONNECTED WITH THE SULPHIDE PRECIPITATION METHOD IN ACID SOLUTIONS.

As outlined in the quantitative separation section, elements like U, Cr, V, Zr, Ti, W (in the presence of tartaric acid), and P do not interfere when Mo is precipitated as the sulphide in an acid solution. One disadvantage, however, of this method of determination, especially for low-grade ores, lies in the fact that the sulphide of Mo may be contaminated with SiO$_2$ (not dehydrated in acid decomposition or carried down from solution if fusion has been made), Cu, As, Sb, and Sn sulphides, and remaining Group II elements, if these are present in the ore. A trace of Fe is also usually found with the precipitate. The presence of these impurities necessitates laborious and painstaking manipulation before the Mo can be weighed as the pure sulphide or oxide.

d. PRECIPITATION OF MOLYBDENUM BY SATURATING AN ALKALINE SOLUTION WITH HYDROGEN SULPHIDE, ACIDIFYING WITH EITHER HYDROCHLORIC OR SULPHURIC ACID, AND HEATING IN A PRESSURE FLASK.

The method of saturating an alkaline solution with H$_2$S previous to precipitating the MoS$_3$ in an acid solution, followed by pressure,
has many advantages, since this affords a means of eliminating many elements from Mo. When a solution is made alkaline with $\text{H}_2\text{S}$, or $(\text{NH}_4)_2\text{S}$ added until the solution has assumed a cherry-red color, the following elements are precipitated: Fe, Al, Cr, Mn, Zn, Zr, Ti, U, Cu, Cd, and all the rare earths, if present. These can be filtered off and the Mo precipitated from the cherry-red solution by making barely acid and then heating in a pressure flask as in the previous method. W is kept from precipitating by tartaric acid, while some of the V which precipitates incompletely with the Mo can be removed later or determined volumetrically with the Mo and then subtracted. As or Sb do not interfere in the volumetric method, but must be removed with V if the Mo is weighed as the sulphide or oxide. The separation of these elements has been previously described in the qualitative section. This method of precipitating Mo is of advantage when a small amount of Mo is present with a large amount of other metals, as in steel products.

The coagulation of small amounts of Mo is best performed when a solution is heated in a water bath under pressure. The removal of the other elements with ammonia and $(\text{NH}_4)_2\text{S}$ previous to precipitation also favors the coagulation of small amounts of molybdenum sulphide, especially when followed by heating under pressure in a dilute acid solution. When large amounts of Mo are present, the heating under pressure need not be done if after making acid more $\text{H}_2\text{S}$ is added and the solution heated. This is advocated in the following method.

c. PRECIPITATION FROM AN ALKALINE SOLUTION BY COAGULATION OF MOLYBDENUM SULPHIDE IN AN ACID SOLUTION WITHOUT PRESSURE.

An alkaline solution is saturated with $\text{H}_2\text{S}$, acidified with HCl or $\text{H}_2\text{SO}_4$, coagulated, and filtered. The filtrate is evaporated to dryness, heated to expel the greater part of the ammonia salts, the residue extracted with water containing a small amount of ammonia, and $(\text{NH}_4)_2\text{S}$ added and then acidified with HCl; this removes the last trace of Mo, which is added to the bulk precipitate. Such a method of procedure as outlined was adopted by Horton (50), who gave it as the method at that time adopted by the Bureau of Mines; it is also described in detail by Collett and Eckhardt (21). This method has been completely discarded, as being too long and requiring too many refinements, especially for a determination of Mo in low-grade tailing products. Coagulating molybdenum sulphide from an alkaline solution, after being made acid, has also been described in methods given by Hoepfner and Binder (49), Johnson (55), Horton (50), Schoeller and Powell (91), Collett and Eckhardt (21), and Trautmann (98), (99), (100).
f. CONCLUSIONS CONCERNING THE SULPHIDE METHODS.

After considerable work on the sulphide methods, in order to establish all the precautionary measures outlined on all classes of ores and steel products, it was finally decided that the methods outlined for precipitating sulphide and weighing as MoS₂ or MoO₃ offered too many pitfalls for the ordinary analyst. The methods are not reliable for low-grade materials assaying around 0.10 per cent Mo. Traces of Fe, Al, and SiO₂ often contaminate the precipitate, in addition to Cu, As, and Sb, if present in an ore. Although these impurities can be quantitatively removed as previously outlined, the time required is usually prohibitive. Too many factors, unless accurately observed, will give erroneous results, especially in igniting and weighing as the disulphide or trioxide. The methods were principally discarded, since a volumetric and gravimetric method has been later developed which, besides being reliable and accurate, could be performed in a fractional part of the time required for the sulphide methods. These two methods have been recently described by Bonardi and Barrett (11), and will be described later in detail. The sulphide method, however, is applicable to certain classes of material that require several determinations to be made on one weighing, and may also be used when the sample contains no other sulphide or impurities that are liable to be carried down in an acid solution by H₂S, as in various steel products. The precipitation, then, of Mo under pressure in a dilute acid solution could be used to special advantage.

METHOD 2. PRECIPITATION AS MERCURIOUS MOLYBDATE.

The precipitation of Mo in a nearly neutral solution as mercurous molybdate requires the same care in igniting the mercurous molybdate to MoO₃, in which form it is weighed, as in the sulphide method. In addition, SiO₂, Cr, P, V, As, and W interfere. The method is very little used on commercial materials at the present time. It is, however, applicable to pure Mo salts. The method is described by Scott (92), Low (62), Hillebrand (46), and Treadwell and Hall (106).

The precipitation is usually performed after an alkali carbonate fusion has been used for decomposition. The greater part of the alkali is neutralized with HNO₃, then a barely acid solution of mercurous nitrate is added until no more precipitate forms. The solution is heated to boiling and allowed to stand in order to settle the black precipitate, consisting of mercurous carbonate and mercurous molybdate, Cr, V, W, As, P, Al, and some SiO₂, which was carried in solution if a fusion was made. The precipitate is then filtered and washed with a dilute solution of mercurous nitrate. The precipitation of mercurous carbonate from the slightly alkaline solution counteracts any acidity resulting from the decomposition of the
mercurous nitrate. After filtering, washing, and drying, the bulk of the precipitate is removed and transferred to a watch glass. The precipitate remaining on the filter is dissolved in hot dilute HNO$_3$ and received in a large porcelain crucible. This is evaporated to dryness and the main portion of the precipitate added, which is then heated until the Hg has completely volatilized, care being taken not to heat it above 400° C., as Mo is liable to volatilize as trioxide. The resulting MoO$_3$ is weighed, and the results calculated. If interfering elements above enumerated are present, they must be removed, SiO$_2$ and W by dehydration with aqua regia; Cr, V, W, P, and Al by precipitating Mo by H$_2$S in the presence of tartaric acid under pressure in a dilute acid solution; and the As removed by volatilization, or by a magnesia mixture. The Mo must then be reprecipitated and weighed. As outlined above, this method offers no special advantage over the sulphide methods, so that it has been given very little consideration. On certain ores which are free from the above interfering impurities the method could be worked, but even then the subsequent weighing of the trioxide would require special care. The many weighings necessary to constant weight and the danger from the volatilized Hg fumes are additional disadvantages of this method.

**METHOD 3. PRECIPITATION AS LEAD MOLYBDATE.**

The estimation of Mo as PbMoO$_4$ has been found to be undeniably one of the best methods for determining Mo on account of its many advantages and easy manipulations, besides being accurate and quick on practically all classes of material. The interfering elements can be taken care of easily, and the precipitation is simpler than that of mercurous molybdate. The PbMoO$_4$ is stable at high temperature, incineration does not require any special precautions, no separation of the precipitate from the filter is necessary, and, finally, the Mo is weighed in a compound having a high molecular weight. The conversion factor 0.2615 is of especial advantage in calculating the results.

The method has been described by the following authors: Scott (92), Rather (83), Rüdisülle (87), Strebinger (95), Schoeller and Powell (91), Weiser (108), Evans (33), Lord and Demorest (61), Chatard (18), Cruser and Miller (25), Brearley (13), and Ibbotson and Brearley (51). The work of Brearley (13) on the analysis of Mo compounds by the PbMoO$_4$ method deserves special attention, as he has brought forward many good points and precautions for the determination of this element when occurring with others. Since the precipitation of Mo by this method has been in use by the Bureau of Mines at Golden, Colo., as a gravimetric method, a detailed outline will be given later in this chapter (see p. 96), and the interfering elements discussed at length.
METHOD 4. TITRATION WITH LEAD ACETATE.

Titration with lead acetate is the reverse of Alexander's ammonium molybdate method for the determination of Pb, and has the same limitations. The color change of the tannic acid is not sharp enough for use on very low-grade materials. The titration with lead acetate was tried only on low-grade material assaying less than 0.15 per cent Mo. It was unsatisfactory, as the insoluble PbMoO₄ did not precipitate immediately and the end point with freshly made tannic acid was not dependable (0.10 gram tannic acid in 20 c. c. water). The method is as follows:

The molybdate solution, after being acidified with acetic acid—the mineral acid having been previously suppressed by ammonium or sodium acetate—is heated to boiling and titrated with lead acetate solution (20 grams per liter; 1 c. c. equal to approximately 0.005 gram Mo) until a drop of the solution fails to give a yellow tint with dilute tannic solution on a spot plate. Detailed manipulation for this method is given by Schindler (90), Darroch and Meiklejohn (26), Westling and Anderson (109), Epperson (32), and Evans (33). The process is shorter than the gravimetric one, and on pure solutions is equally accurate. However, on working with low-grade ores, it was found unreliable, owing to a large amount of dissolved salts. If an alkali fusion has been made and the melt leached, practically all of the Al₂O₃ and SiO₂ will be found in the filtered liquid, with other bases soluble in excess of alkali. By an acid digestion, this can in part be remedied, but even then on low-grade material the results were found unsatisfactory.

Some of the difficulties cited in standard textbooks and in the literature concerning the titration of a low-grade Pb by standard ammonium molybdate, which is the reverse procedure of titrating a low-grade Mo with a standard lead acetate solution using tannic acid as outside indicator, are as follows (in the writer's opinion the reasons outlined below have all been substantiated by experiments):

1. The very low percentage of Pb (or Mo) is difficult to determine on account of the slowness of the reaction.
2. The large amount of dissolved salts that is necessary in the analysis hinders the separation of Pb as molybdate, and also obscures the end point with tannic acid.
3. An excess of ammonium salts and ammonium acetate must be avoided because if such excess is present the results obtained will be too high.
4. Fe, if present, gives a color with tannic acid.
5. Ca, Ba, and several other bases form more or less insoluble molybdates that interfere with the results.
6. The method is not accurate.
In view of the erratic results obtained with this method, it was not deemed advisable to investigate further, especially since a method was sought that would be reliable for all classes of material, regardless of grade. The determination of Mo on low-grade tailings produced by metallurgical processes, such as flotation, required a degree of accuracy hitherto not attempted. Many a commercial laboratory has reported a “trace” when as much as 0.10 per cent was known to be present. Although it has been claimed by some that 0.0001 gram of Mo will produce distinct cloudiness with lead acetate in a faintly but decidedly acid (acetic) solution kept within definite limits, the writer has found this to be not the case, especially on ore samples. It is, however, produced on pure solutions. On low-grade material, assaying less than 0.10 per cent, it was found that the addition of lead acetate to a volume containing 400 c. c. of solution did not produce any perceptible precipitate, and neither did the tannic acid outside indicator show any change in color. After boiling the solution for at least 15 minutes, a precipitate is formed which, on swirling the solution with a glass rod, will collect on the bottom at the center of the beaker. If, after boiling the solution for an hour and then allowing it to stand overnight, no precipitate is formed, it can be assumed that no Mo was present in the solution, if all mineral acid had been changed by acetate. Unless this is done, erroneous conclusions are made that no Mo is present or only a “trace,” as stated before. This also applies to the gravimetric procedure wherein the PbMoO₄ precipitated is weighed as such.

METHOD 5. TITRATION WITH POTASSIUM PERMANGANATE.

Titration with KMnO₄ involves reducing the Mo solution in a specially constructed Jones reductor and titrating the reduced Mo with KMnO₄. This is a very reliable method and gives accurate results. The variables are easily controlled, and the method can be used for assaying high-grade as well as low-grade material. In brief, the method is as follows:

The ore, alloy, or steel product is decomposed either by acids or by fusion into a soluble molybdate, and the insoluble compounds of the other constituents of the material taken. The molybdate is filtered, H₂SO₄ added, and the acid solution passed through a Jones reductor where the MoO₄ is reduced to Mo₂O₇. The Mo₂O₇ is titrated with standard KMnO₄ and the percentage of Mo calculated. The following workers have given a description of the permanganate titration method, with discussions on some of the necessary precautions and limitations to be observed: Wickes (111), Miller and Frank (71), Lunge and Keane (63), Mabee (64), (65), Noyes and Frohman (76), Rudisilde (87), Mennicke (70), Edgar (30), Kopp (60), Gooch (38), Scott (92), Crook and Crook (23),
Cruser and Miller (25), Auchy (2), (3), Randall (82), and Crook (22).

The volumetric method, reduction by Zn in a Jones reductor, has given such excellent results, when the conditions have been properly standardized and observed, that this method has been in use by the Bureau of Mines laboratory at Golden, Colo. The method has been carefully standardized, and all necessary factors and precautionary measures accurately determined on a series of several hundred determinations. The measures to be taken with interfering elements have also been determined and standardized. This method, which will be described later in detail (see p. 109), has been found to be reliable, quick, and accurate.

Mo, besides being reduced by Zn in a Jones reductor, has been reduced satisfactorily, according to some writers, by other means without the Jones reductor. The use of granulated Zn without the Jones reductor is mentioned in Low's (62) appendix, which states:

The method gives good results when all conditions are kept as nearly alike as possible, the main uncertainty being the point to which the molybdenum oxide is reduced.

This method was accordingly given a thorough try-out in comparison with the reduction in a Jones reductor, since if the reduction could be performed as claimed without a Jones reductor, considerable time could be saved in running a battery of determinations. After experiments along this line, it can be safely stated that the reduction of Mo by granulated Zn in a beaker, even covered by a watch glass and heated for two hours, is too uncertain and unreliable. It was found that if the solution was neutral or only weakly acid, the blue oxide of Mo was formed; with stronger concentrations of acids, a brown solution was obtained corresponding to the oxide Mo$_2$O$_5$. In only rare instances was there obtained a clear green solution, as is always the result with a Jones reductor. A green solution indicates complete reduction, corresponding to Mo$_2$O$_5$. When a perfectly reduced solution of Mo (green solution) is oxidized by permanganate, the first few cubic centimeters added always produce a brown solution indicating an oxide (Mo$_2$O$_5$), which gradually turns colorless as more permanganate is added, until the end point is reached, which is the pink of the permanganate.

The use of powdered or sheet Al has been advocated by some writers as effecting a reduction of a Mo solution, followed by titration with permanganate. One is given by Wickes (111) for determining Mo in the presence of Cu. The method consists in reducing the Mo with powdered Al and titrating with a standard permanganate. The reduced solution is filtered through absorbent cotton into a beaker containing a strip of Al foil (to prevent reoxidation
of Mo), and 50 c. c. drawn off and titrated with 0.1 N KMnO₄. Johnson (55), describing a volumetric determination of Mo in steel by effecting a reduction of the Mo by Al foil, states that the reduction is usually complete in half an hour.

The reduction by Al in any form, as with granulated Zn without the reductor, was found to be unquestionably unreliable and uncertain for the same reasons as given for granulated Zn. Powdered Mg has also been advocated, but has been found to be subject to the same objections.

**METHOD 6. TITRATION WITH METHYLENE BLUE.**

Knecht and Atack (58) describe a reduction method which depends upon the reduction of Mo to MoCl₃ by Zn and HCl in an atmosphere of CO₂, and the reduced solution titrated with methylene blue. The method is outlined as follows: To the Mo solution in a flask add 50 to 75 c. c. strong HCl and a few pieces of granulated Zn, maintaining a stream of CO₂. After the Zn is dissolved, lower a zinc rod to insure complete reduction, then raise the rod and wash with freshly boiled water and titrate the warm solution with standard methylene blue. During the reduction the solution becomes successively blue, green, orange, straw yellow, and finally pink. During the oxidation with methylene blue, the pink changes to straw yellow, then (in the absence of Fe) to pale green, which appears when the titration is half completed; finally one drop excess gives the characteristic shade of methylene blue. The reaction occurs in two distinct stages, represented by the equations:

\[
2\text{MoCl}_3 + 2\text{HCl} + \text{O} = 2\text{MoCl}_4 + \text{H}_2\text{O}, \text{ and} \\
2\text{MoCl}_4 + 2\text{HCl} + \text{O} = 2\text{MoCl}_3 + \text{H}_2\text{O}.
\]

FeCl₂ does not reduce methylene blue; hence, the method can be used in the presence of ferrous iron. The method was not tried out, as it requires too much attention and did not seem to offer rapid solution.

**METHOD 7. TITRATION WITH FERRIC CHLORIDE AFTER REDUCTION WITH TITANIUM CHLORIDE.**

This method is described by Travers (103). The method in outline is as follows: The steel is dissolved in HCl with the aid of H₂SO₄, Fe oxidized with KMnO₄ without excess and precipitated with caustic, filtered, and an aliquot part taken and acidified with HCl. The solution is cooled and the Mo reduced with an excess of TiCl₃ solution, 1 c. c. of which is equivalent to 0.001 gram Fe, and titrated back with FeCl₃ solution (1 gram per liter) with KCNS as indicator. The reduction proceeds according to the equation 2MoO₃ → Mo₂O₅ + O, for Mo concentrations less than 0.05 gram per liter, and with
an acidity of 1 c. c. HCl per 100 c. c. of solution. With greater concentrations, MoO$_3$ is oxidized by the FeCl$_3$. The method appears to be too delicate an operation and unless kept within restricted limits is unreliable. Its applicability was not tried out as there seemed to be also some doubt as to whether the reduction is as stated and quantitative.

**METHOD 8. IODOMETRIC METHOD.**

A solution containing molybdenum trioxide (MoO$_3$) is boiled in the presence of KI and HCl, the volume having defined limits. Free I is liberated and can be expelled while the molybdenum trioxide is reduced to a lower oxide. The reaction is as follows:

\[
2\text{MoO}_3 + 4\text{KI} + 4\text{HCl} = 2\text{MoO}_2\text{I} + \text{I}_2 + 4\text{KCl} + 2\text{H}_2\text{O}, \text{or}
\]

\[
2\text{MoO}_3 + 2\text{HI} = \text{Mo}_2\text{O}_3 + \text{I}_2 + \text{H}_2\text{O}.
\]

The reoxidation of the reduced Mo can be effected by a standard I solution, performed in a solution previously neutralized by NaHCO$_3$ and in the presence of tartaric acid to prevent precipitation during the neutralization. The reaction between I and the reduced Mo is slow and the mixture must be set aside in the dark for an hour or two. The excess of I which has been added is then titrated back with a standard sodium arsenite solution. The reoxidation with permanganate is rather tedious, requiring an excess of standard KMnO$_4$ in the presence of a titrating mixture of manganous sulphate. To this solution is then added a standard sodium arsenite equivalent to the excess permanganate, then 3 grams of tartaric acid; this is finally neutralized with bicarbonate and titrated back with a standard I solution, using starch as an indicator.

Another procedure is to carry out the determination in a small distillation flask in a current of CO$_2$, the liberated I being collected and titrated as usual.

For detailed explanation of the iodometric method, the reader is referred to the following authors, in whose works will be found all the information bearing upon the subject: Gooch (39), Gooch and Norton (41), Gooch and Pullman (42), Gooch and Fairbanks (40), Scott (92), and Treadwell and Hall (106). Treadwell and Hall state that the method finds no practical application, since it is difficult to obtain a quantitative reduction in accordance with the above equation. It is readily seen, however, that this method, if used at all, would require a solution being practically free from those elements that are reduced under similar conditions. The method offers very little encouragement in view of the delicate reactions and manipulations involved, and hence is not considered. Furthermore, the results by the above workers were obtained chiefly on pure Mo reagents.
METHOD 9. TITRATION WITH POTASSIUM IODATE.

This method described by Andrews (1) to work on other metals was perfected by Jamieson (53) for determining Mo. It is essentially as follows:

A solution containing Mo is made acid by HCl, heated, and passed through a Jones reductor into a receiving flask containing 5 c. c. of iodine monochloride, 25 c. c. of concentrated HCl, 5 c. c. of water and 7 c. c. of chloroform, made up to 500 c. c. volume. The reduced Mo solution is then titrated with a standard solution of KIO₃. The reaction is as follows:

\[\text{KIO}_3 + \text{Mo}_2\text{O}_3 + 2\text{HCl} = \text{Mo}_2\text{O}_5 + 1\text{Cl} + \text{KCl} + \text{H}_2\text{O}\]

The reaction is complete when the chloroform indicator is decolorized. If the titrated solution be allowed to stand, the pentoxide slowly oxidizes to the trioxide. The action is accelerated by exposing the solution to direct sunlight. It is claimed that two days are required for complete oxidation, which is as follows:

\[3\text{KIO}_3 + 2\text{Mo}_2\text{O}_3 + 6\text{HCl} = 4\text{MoO}_3 + 3\text{Cl} + 3\text{KCl} + 3\text{H}_2\text{O}\]

It is not practicable, however, to wait for this reaction to take place, as it was found that a sharp end point could be obtained when the pentoxide was completely formed.

Since this method, in common with others that have been proposed for determining Mo, was performed by working on pure chemical solutions of Mo, its application to an ore sample would require much painstaking experimentation to standardize accurately the many factors involved, besides taking care of the interfering elements that are found to be present in a determination.

METHOD 10. COLORIMETRIC METHOD.

A method has been described by Spurge (94) for colorimetric estimation of Mo in low-grade ores and tailings. The method is essentially as follows: An ammonium molybdate solution obtained from filtering off the NH₄OH precipitates is acidified with acetic acid. The Mo is determined by the color imparted by adding 2 c. c. fresh tannic acid solution (0.5 gram per 100 c. c.) against a standard solution similarly treated. Colors are compared in Nessler tubes. The method is recommended by Spurge for material carrying 2 per cent or less of Mo.

This method was not tested, as too many objections have been offered and it is subject to criticism for some of the reasons outlined in the lead acetate titration method, using tannic acid as an outside indicator.
METHOD 11. DETERMINATION OF MOLYBDENUM BY VOLATILIZATION.

a. IN A CURRENT OF CARBON TETRACHLORIDE VAPOR.

A method for volatilizing Mo as the chloride and the oxychloride by carbon tetrachloride vapor and CO₂ is described by Jannasch and Laubi (54). The volatilized products are absorbed in a mixture of 85 c. c. water and 15 c. c. HNO₃, and evaporated to dryness in a porcelain crucible until the molybdic oxide is obtained. This method is practically designed for Mo salts, pure minerals, and for ferromolybdates free from elements that would be also volatilized under similar conditions. W and V, if present, for example, would be also volatilized and would have to be separated from the molybdic oxide.

b. IN A CURRENT OF DRY HYDROCHLORIC ACID GAS.

Smith and Oberholtzer (93) describe a method whereby Mo can be separated from W in a current of dry HCl gas, when lead molybdate containing lead tungstate can be purified and the Mo obtained by difference. The reaction is:

\[ \text{PbMoO}_4 + 4\text{HCl} = \text{MoO}_2 \cdot 2\text{HCl} + \text{PbCl}_4 + \text{H}_2\text{O}, \]
while PbWO₄ is not effected.

The applicability of this method was not tried out, since W can be more easily separated from Mo by other means heretofore given.

METHOD 12. LIBERATED IODINE FROM A MOLYBDIC SOLUTION PRECIPITATED AS SILVER IODIDE.

Perkins (78), who describes this method, shows that Mo, V, Se, and Te may be determined gravimetrically by making use of the following reaction in regard to Mo:

\[ 2\text{MoO}_3 + 4\text{KI} + 4\text{HCl} = 2\text{MoO}_2 \cdot 4\text{KCl} + \text{H}_2\text{O} + \text{I}_2. \]

The liberated I is made to combine with specially prepared electrolytic silver, forming AgI, which is weighed. The method was devised for special research work on pure compounds and not for commercial products.

METHOD 13. ACIDIMETRIC METHOD.

The acidimetric method, described by Schoeller and Powell (91), is for determining the purity of MoO₃ when other soluble acid oxides are not present. MoO₃ is dissolved in N/2 NaOH, the excess of which is titrated back by N/2 acid in presence of phenolphthalein.

\[ \text{MoO}_3 + 2\text{NaOH} = 2\text{Na}_2\text{MoO}_4 + \text{H}_2\text{O} \]
1 c. c. N/2 NaOH = 0.096 gram MoO₃.

METHOD 14. ELECTROLYTIC METHOD.

Mo belongs to the class of metals which is obtained as an adherent oxide on the cathode. The adherent deposit, which is in the form of
hydrated sesquioxide, can be washed and dissolved in \( \text{HNO}_3 \), evaporated in a porcelain crucible (platinum has a reducing action) to the trioxide and weighed as such, or dissolved and determined by a gravimetric or volumetric method. The electrolysis can be performed in a dilute \( \text{H}_2\text{SO}_4 \), HCl, or acetic acid solution. (See Wherry and Smith (110), Kollock and Smith (59), Fisher and Weise (33), Wolf, K. (114), and Classen and Hall (20).) In converting the hydrated sesquioxide into the trioxide the ignition should be carried out not higher than between 400 to 425\(^\circ\) C., since, as pointed out before, sublimation of the trioxide occurs at about 450\(^\circ\) C. Myers (75) found that from a dilute \( \text{H}_2\text{SO}_4 \) solution Mo could be deposited as an amalgam on a mercury cathode. It is then possible to weigh the Mo directly, as a product of electrolysis. Myers also gives a separation of Mo from V, whereby Mo is deposited, while the V remains in solution.

Treadwell (105) gives a method whereby Cu can be separated electrolytically from Mo in an ammoniacal solution containing NaHSO\(_4\). Hoepfner and Binder (48) precipitate Cu electrolytically from Mo after acidifying an ammoniacal solution with \( \text{H}_2\text{SO}_4 \) and adding \( \text{HNO}_3 \). McCay and Furmann (68) give several methods and details for electrolytically separating Cu from Mo, Cu from W and Mo, Pb from W and Mo, Hg from Mo, Hg from Sn, W, and Mo, and Ag from Sn, Sb, W, and Mo. The electrolytic methods referred to above were not devised for analyzing commercial products, hence very little attention has been given to such products. An electrolytic method could probably be operated to advantage for a particular class of material, but in commercial work the chances are that by the time all the conditions have been properly met, with all the interfering elements removed, it would have been much quicker to carry out a determination by other means. For the detailed conditions required for the solution, including the voltage and current density for an electrolytic determination of Mo, the reader is referred to the references cited.

**TWO ACCURATE METHODS OF DETERMINING MOLYBDENUM.**

Now that a digest and comments on it have been given for practically all the methods that have been proposed for determining Mo, the remainder of Part III will cover the two methods which have proved quick, accurate, and reliable, namely, the lead molybdate gravimetric method, and the permanganate volumetric method. These two methods were thoroughly tested out in the Bureau of Mines laboratories at Golden and at Seattle on several hundred determinations of commercial ore products and on products made from electric furnace experiments. They have, in the main, been recently described by Bonardi and Barrett (11). One of the best
ways to test the accuracy of a series of chemical analyses upon metallurgical products, produced either in some concentration work or in electrometallurgical experiments, is to total the Mo content of all the products made in any one experiment and to calculate whether the Mo footing recovery corresponds with the original amount of Mo in the feed or head sample. It was very common, by the methods to be outlined, to total within 2 per cent, either high or low, on analyzing metallurgical products collected in many series of experiments.

**GRAVIMETRIC DETERMINATION OF MOLYBDENUM BY PRECIPITATING AND WEIGHING AS LEAD MOLYBDATE.**

As stated in the abstract of method 3 (see p. 87), precipitation as lead molybdate has been found to be undeniably one of the best methods for determining Mo. The references have already been given on page 87 and it only remains to outline the details of manipulations and the precautions to be taken in carrying out a determination.

**GIST OF METHOD.**

The ore, alloy, or steel product is decomposed by one of the acid treatments outlined under "Solution of samples," (see p. 74) or by a fusion method. If a mixed-acid treatment is used, the material is decomposed first with \( \text{HNO}_3 \), followed by HCl or by \( \text{H}_2\text{SO}_4 \), and carried nearly to dryness; with \( \text{H}_2\text{SO}_4 \), it is carried only to copious fumes. Then, after diluting with water, it is treated with \( \text{NH}_3 \) to form ammonium molybdate, and after filtering is next titrated with a dilute solution of lead acetate until no further color is produced by a tannic acid outside indicator. The precipitated \( \text{PbMoO}_4 \) is weighed and the weight of the Mo is calculated. If a fusion method of decomposition is employed, the melt is leached, filtered, washed, reprecipitated, filtered, washed, and the Mo obtained in solution as sodium molybdate.

**PROCEDURE FOR DECOMPOSITION OF SAMPLE BY ACIDS.**

Weigh 0.25 to 5 grams of the finely pulverized material (depending upon the grade of sample, not to contain over 0.15 gram Mo, equivalent to 0.25 gram MoS\(_2\)) into a 250-c. c. Erlenmeyer flask. Add 15 c. c. of \( \text{HNO}_3 \) and heat until the brown fumes are gone. This is the most effective manner of decomposing the sulphides in an ore. Carefully add 5 to 10 c. c. of HCl and heat about 20 minutes, or until the ore is carried down nearly to dryness. If SiO\(_2\) is to be determined, carry to complete dryness. For wulfenite ores, steels, and alloy products, it is best to add \( \text{H}_2\text{SO}_4 \), after the HCl treatment as given above has been taken to the point where water has been added to dissolve the base salts present. The \( \text{H}_2\text{SO}_4 \) solution is then carried to fumes. After the sample has been given one of the above acid treatments,
cool, wash down the sides of the flask with water, and heat about 10 minutes longer to dissolve as much of the base metal salts as possible. If the sample is high in Mo, pale-yellow molybdic acid \((\text{H}_2\text{MoO}_4)\) will separate out, which is only carried in solution again with an excessive amount of HCl or HNO₃, but is readily soluble when H₂SO₄ has been used. However, it is not necessary that the molybdic acid be totally dissolved, since NH₄OH, which is next added in excess, will readily dissolve it.⁴ The solution, which has been made strongly ammoniacal, is heated a few minutes and filtered hot, washing with hot water at least five times. Puncture the filter paper and wash the residue of insoluble material, iron and aluminum hydroxides, into the flask in which decomposition was made, add sufficient HCl to dissolve the precipitated hydroxides, make the solution strongly ammoniacal, heat, and filter into the same beaker used for the first titration. Wash well with hot water. This second treatment is made in order to prevent an appreciable amount of Mo from being held mechanically or in chemical combination with the iron hydroxide. The Mo is now in the form of ammonium molybdate in a solution free from SiO₂, Fe, and Al₂O₃ and Pb, if the sample was taken to fumes with H₂SO₄.

**PROCEDURE FOR DECOMPOSITION OF SAMPLE BY FUSION.**

If a fusion method is employed, a 0.25 to 5 gram sample is taken and fused with 8 to 10 parts of one of the following combinations in a nickel or iron crucible. The proper proportion of flux used depends on the material to be treated.

a. Sodium carbonate and peroxide \((1:1)\).

b. Sodium or potassium carbonate with small amount of nitrate \((10:2)\).

c. Sodium peroxide.

d. Sodium hydroxide and sodium peroxide \((1:1)\).

The fusion is leached with water, boiled, filtered, and washed at least five times. Redissolve the precipitate in HNO₃ and reprecipitate with NaOH, heat, and filter into the same beaker used for the first filtration. Wash well with hot water. The Mo is now in the form of sodium molybdate. If the sample contains much SiO₂ as an ore, it is best to determine the Mo by the volumetric method, to be later described (see p. 109), rather than the gravimetric, since SiO₂ is liable to separate out with the PbMoO₄ when the alkaline solution is neutralized with HCl or HNO₃, boiled, and treated with ammonium acetate and lead acetate. The removal of SiO₂ from an alkaline leach solution can be effected in a great measure by making the caustic solution acid to hydrochloric, then boiling for 15 minutes, making it next strongly ammoniacal, adding ammonium chloride, boiling, filter-

⁴ In analyzing wulfenite ores the insoluble matter is filtered off to remove the lead, as explained later.
ing, and washing. SiO₂ will be precipitated with the Al and traces of Fe and other metals carried in solution by the strong caustic solution. If such a treatment is used, what little SiO₂ remains in solution usually will not contaminate the PbMoO₄ precipitate formed. However, with highly siliceous ores, if a fusion has been made, it is best to finish the determination by the volumetric method, or else to carry the leached liquor after being made acid to dryness; however, the above precipitating procedure for eliminating SiO₂ works very well. The small amount of SiO₂ found occurring in high-grade ores, products, and steels or alloys will not affect the gravimetric procedure. The two solution procedures which are thus far outlined and which will be continued assume that no interfering elements are present. The notes on the process to follow this outline will explain in detail the precautionary measures to be observed for every interfering element that might be encountered with a Mo determination.

FURTHER PREPARATION OF THE SOLUTION.

The Mo, now in the form of a soluble molybdate, should have approximately 350 c. c. volume. Make the solution acid with HCl, using methyl orange as an indicator, adding about 5 c. c. excess of acid. Add 5 to 10 grams of sodium or ammonium acetate and 2 to 5 c. c. of acetic acid. Ammonium acetate is better, since less washing would be required than with the nonvolatile sodium salt. The use of HCl and the acetate as given causes the PbMoO₄ which is to be precipitated to become granular in form, to settle rapidly, and to be easily filtered and washed. The use of HCl in neutralizing is preferred to HNO₃ or acetic acid, as some writers advocate, since the presence of ammonium chloride will hold in solution many of the third and fourth group elements which might otherwise be precipitated with the PbMoO₄; and, further, chloride salts are more highly ionized than the acetates and, hence, are stronger electrolytes, thus tending to prevent the formation of a colloidal precipitate. Weiser (108), who has worked out the physical character of precipitated PbMoO₄, recommends the addition of a small amount of HNO₃ before precipitating the Mo. After the soluble molybdate solution has been treated as above outlined, it is set on the hot plate and heated to boiling, after which it is ready for the precipitation of PbMoO₄.

PRECIPITATION.

Precipitation is now made in the boiling hot solution by titrating the Mo content in the solution with a lead acetate solution (about 18 grams crystallized lead acetate per liter) added slowly from a burette until a test drop taken from the solution gives no color change with a drop of freshly made tannic acid solution (about 0.10 gram dissolved in 20 c. c. of water, the same as for Alexander’s lead titration
method) used as an outside indicator. The disappearance of the brown color indicates that all the Mo has been removed from solution by precipitation. Next add 2 to 5 c. c. excess of the lead acetate solution and 5 to 10 c. c. of acetic acid (the amount depending upon the presence of Cu, Ca, Zn, Ni, Co, Mn, Cd, Al, and other metal salts, since these are kept in solution by acetic acid), and replace the beaker on the hot plate and keep at the boiling point about 15 to 30 minutes, depending upon the Mo present, or until the precipitate PbMoO$_4$ has crystallized and settled. Low-grade Mo will require a longer time for complete coagulation. When settled, filter hot and wash well with hot water, followed by a dilute 2 or 3 per cent solution of ammonium acetate. If ammonium acetate has been used for neutralizing the excess mineral acid, washing with hot water, just short of the point where the precipitate tends to become colloidal, will suffice. If any colloids start to run through the filter, the washing should be stopped, which indicates that sufficient soluble salts have been washed out of the precipitate. As a rule, it is best, if the precipitate is bulky, to wash by decantation two or three times with the dilute solution of NH$_4$NO$_3$, then to transfer to the filter and wash at least five times more. With a bulky precipitate it is best not to wash too much with pure water, since PbMoO$_4$, in common with other precipitates, tends to be converted into a colloidal form in the absence of a common ion of the precipitant and, consequently, to run through a filter paper.

The washed filter is placed in a fire-clay annealing cup and ignited at a dull-red heat in a muffle. The filter need not be previously dried or the paper ignited separately. Prolonged ignition at a much higher temperature than is necessary to destroy the paper does no harm. After cooling, the ignited precipitate can be brushed out of the annealing cup onto a balance pan and weighed directly. No difficulty will be found with the ignited precipitate adhering to the cup if the precipitate has been properly washed and is yellowish-white. The weight of the PbMoO$_4$ times 0.2615 gives the weight of the Mo in the precipitate.

COMMENTS ON PROCESS. PROCEDURE IN PRESENCE OF INTERFERING ELEMENTS.

REMOVAL OF LEAD.

If the sample carries much Pb, for example, a wulfenite ore (PbMoO$_4$), it should be fumed with sulphuric acid as previously stated, cooled, about 50 to 75 c. c. of water added, and heated to dissolve the soluble sulphates. Cool and filter to remove the insoluble material and the lead sulphate. Lead sulphate is somewhat soluble in NH$_4$ salts, hence the insoluble matter is removed before
adding NH₃, for if this is not done Pb is liable to be carried in solution and be precipitated as PbMoO₄ with the Fe precipitate. After the removal of the lead sulphate, proceed with the solution in the usual way.

**EFFECT AND REMOVAL OF PHOSPHORUS, ARSENIC, AND ANTIMONY.**

P, As, and Sb interfere with the gravimetric precipitation by forming insoluble phosphates, arsenates, or antimonates with various base metals insoluble in an acetic acid solution. In an ordinary analysis for Mo, enough ferric salt is usually present to keep these from entering the solution with the Mo, since the addition of NH₃ precipitates them with the Fe group. If the material carries appreciable amounts of P, As, or Sb, this can be effectively removed with the Fe and Al precipitate by ferric chloride. If phosphates of Group IV and fixed alkalies be present, they are precipitated with Group III metals by NH₄OH in the usual course of analysis. Of the phosphates of the metals of Groups III, IV, and V, those of Al and Fe are insoluble in acetic acid while chromium phosphate is only dissolved with difficulty. The phosphates of the remaining metals of these groups are readily soluble in acetic acid. Ferric phosphate is somewhat soluble in a solution of ferric acetate, so that the separation of P is better performed in an ammoniacal solution than in an acetate solution, if Ca, Mg, or Ba is not quantitatively desired in the filtrate.

Ferric hydroxide carries down quantitatively the As and Sb in combination with the Fe. (See Lord and Demorest (61), p. 222; Prescott and Johnson (81), p. 62; and Heath (44), p. 200.) The addition of 2 grams of ferric chloride or sulphate before precipitation with NH₄OH is usually sufficient to take care of all the Sb and As present. P under similar conditions precipitates as ferric phosphate. As a general rule, the Fe should be at least 10 times the weight of the As and Sb judged to be present. If much As, Sb, or P is present it is best to precipitate the Mo as the trisulphide in a dilute acid solution under pressure; the sulphides should be ignited and dissolved in HNO₃, and the As removed by Mg mixture in an ammoniacal solution, or by the method of Schoeller and Powell (91), who recommend removing the As and Sb from ignited MoO₃ as follows:

It is digested with strong hydrochloric acid and a slight excess of saturated potassium iodide solution; the liquid is transferred to a boiling flask, and repeatedly boiled down with strong hydrochloric acid over a free flame whereby arsenic is volatilized. The residue is taken up with 10 c. c. of strong hydrochloric acid, the latter diluted to 50 c. c. with water, and the solution reduced with lead for 20 or 30 minutes. The precipitated antimony is filtered off, washed with hot water, and the molybdenum precipitated by the addition of ammonia and ammonium acetate. If the hydrolytic sulphide precipitate is small, it is dissolved without previous ignition in hydrochloric acid and bromine. The excess of the latter is boiled off, potassium iodide solution added, and finished as above.
MOLYBDENUM.

EFFECT AND REMOVAL OF CHROMIUM.

Cr in an ore or in steel products in appreciable amounts will, if in the condition of a chromate, be precipitated with the Mo. If present in large amount, its removal from Mo is best effected by precipitating out molybdenum sulhide in an acid solution under pressure, Cr remaining in solution. Ammonium sulphide precipitates Cr quantitatively in an ammoniacal solution, while Mo remains in solution. Cr in the form of a soluble chromate can be transformed to the condition of a "chromic" compound by making the solution acid with HCl and reducing the chromate with SO₂, oxalic acid, or alcohol; Mo remains unaltered if acid concentration is about 10 c. c. in 100 c. c. volume. NH₄OH or NaOH will then precipitate out the Cr as hydroxide if boiled for at least 20 minutes. (See De Benneville (28), Lord and Demorest (61), Cruser and Miller (25), and Brearley (13).)

The presence of ammonium chloride in the boiling solution aids this precipitation and decreases the solubility of the precipitate similarly to aluminum hydroxide precipitation. The presence of ferric hydroxide greatly hinders the solution of reduced Cr in fixed alkalies. Cr when in a reduced condition forms no precipitate in the acetic acid acetate solution by lead acetate under the conditions given for Mo.

SEPARATION OF MOLYBDENUM FROM LARGE AMOUNTS OF IRON.

The occurrence of Mo in Fe materials has given rise to varied opinions as to its removal from Fe. Several writers advocate that the solution containing the Mo be heated to boiling and added slowly and carefully with vigorous agitation to an excess amount of hot caustic solution. Under such conditions the iron hydroxide is precipitated free from Mo. A study of these methods will usually reveal the fact that the solution after such a precipitation is made up to some definite volume, and an aliquot part taken for analysis, nothing being said about reprecipitation of the hydroxides. (See Lord and Demorest (61), Scott (22), Auchy (2), (3), and Cruser and Miller (25), who advocate the caustic soda method of separating Mo from Fe.) The precipitation of the Fe and Al by concentrated NH₄OH has been found satisfactory if at least two precipitations are made and an excess of NH₃ is added to each precipitation, boiled, and filtered hot. Boiling off the excess of NH₃ should be avoided, as an insoluble basic ferric molybdate of uncertain composition is liable to form. The simplest form of the reaction may be expressed as follows:

\[ 3(\text{NH}_4)_2\text{MoO}_4 + \text{Fe}_2(\text{SO}_4)_3 = 3(\text{NH}_4)_2\text{SO}_4 + \text{Fe}_2(\text{MoO}_4)_3 \]

When an alkali is added to an acidified mixture of ferric sulphate or chloride and molybdic acid, a point is reached where an insoluble
basic ferric molybdate is formed and no perfect separation of the two metals is possible unless sufficient NH₃ or caustic has been added to decompose this compound. No trouble will be experienced with the Mo remaining in the Fe precipitate if at least two precipitations are made with an excess of alkali in a hot solution and filtered in a hot condition. After the precipitation with alkali, the solution should not be allowed to stand overnight before filtering. When only one precipitation is made, the use of caustic soda is to be preferred.

**EFFECT OF SULPHURIC ACID ON THE PRECIPITATION OF MOLYBDENUM BY LEAD ACETATE.**

Writers describing the lead molybdate gravimetric method often state that the presence of sulphates tends to increase the results by the precipitation of insoluble lead sulphate with the Mo. This is not surprising, since the writer has at times obtained results that ran considerably high, due to the presence either of lead sulphates or of insoluble lead chloride which was carried along with the PbMoO₄. Several trials showed that this trouble was caused by the promiscuous addition of lead acetate in large excess over that required to precipitate the Mo. Methods described by various writers for precipitating PbMoO₄ usually advise adding an excess of lead acetate or precipitant until no more precipitate is formed. By following such a procedure it is absolutely impossible to determine accurately when the exact point is reached by simple observation, for if the precipitate is bulky, the solution will be obscured by the white colloidal nature of the precipitate. After experiments on this point, it was found that the exact point when all the Mo had been precipitated out of solution could be accurately determined by the use of tannic acid outside indicator, as outlined for the lead acetate titration method.

In order to determine the effect of H₂SO₄ on the precipitation of Mo by lead acetate, the Mo was determined in samples taken from a solution of ammonium molybdate when no H₂SO₄ was present and in samples containing amounts of Mo equal to those of the first sample in the presence of as much as 15 c. c. of concentrated H₂SO₄. The concentration of the solutions and the procedure were the same as outlined in the detailed gravimetric method. Fifteen c. c. of H₂SO₄ were used, as that amount represented approximately 2.76 grams of H₂SO₄—more sulphates than would be present in any material taken for analysis, even after it had been fumed with as much as 10 c. c. of concentrated H₂SO₄.

**EXPERIMENTS OF BONARDI AND BARRETT.**

The detailed results of this work have already been given by Bonardi and Barrett (11), which showed that H₂SO₄ does not interfere with the precipitation of Mo by lead acetate if the precautions
are taken as described in the details of the gravimetric method, especially as given under "Precipitation" (see p. 98). Since the solution containing Mo was titrated with a lead acetate solution and only 2 to 5 c. c. excess added, the amount of lead sulphate or chloride which might form would be readily soluble in the boiling hot condition of the solution and in the presence of the excess acetate. The amount of lead sulphate formed by the small excess of the dilute lead acetate added to the solution would in any event be slight under the conditions. If, however, lead sulphate is carried down mechanically with the PbMoO₄, this will, under the vigorous boiling made after precipitation, be rendered soluble during the change in form of the bulky PbMoO₄ to the granular form.

Schoeller and Powell method.

Schoeller and Powell (91) advise carrying out the precipitation in presence of ammonium chloride and a large excess (50 c. c.) of strong ammonium acetate solution as follows:

The PbMoO₄ precipitate is filtered off, dissolved in strong HCl, and 100 c. c. of boiling water added to the clear solution, followed by 5 grams of ammonium chloride and NH₃ until a precipitate forms. The latter is redissolved in a small quantity of HCl, a few drops of lead acetate solution are added, and, finally, 50 c. c. of strong ammonium acetate solution. The solution is heated and the precipitate allowed to settle, then filtered and determined in the ordinary manner. By the use of the following procedure Schoeller and Powell have obtained satisfactory results in the presence of sulphate by means of a single precipitation. They describe the procedure as follows:

The solution of alkaline molybate is acidified with an excess of 4 c. c. of 33 per cent acetic acid; 10 grams of ammonium chloride and 50 c. c. of 25 per cent ammonium acetate solution are added. The liquid now occupying a volume of 200 c. c. is precipitated while actually boiling with a 4 per cent lead acetate solution added drop by drop (from a burette). The further treatment of the precipitate is the same as described above. The precipitation of lead molybdate can be carried out in the presence of soluble salts of mercury, copper, cadmium, zinc, nickel, cobalt, manganese, and thus provides a method of separating molybdenum from these elements.

This is essentially the method recommended by the writer, with the one important exception that in the method as given in this chapter under "Precipitation" (see p. 98), the end point when all Mo has been precipitated is determined with tannic acid outside indicator; whereas in the above method no indicator is used for determining this point. Sulphates may also be separated from Mo in a hot HCl solution by precipitating the sulphate with a 10 per cent barium chloride solution, added drop by drop. The filtrate from this solution is treated with excess sodium carbonate, to eliminate the excess barium carbonate. This procedure is rather lengthy when a number of determinations are to be made, but works very well.
BREARLEY METHOD.

Brearley (13), who studied the effect of $H_2SO_4$ on the Mo precipitation, states that $H_2SO_4$ does not interfere if the procedure is as follows:

Heat to boiling the solution of molybdic and sulphuric acid (part of the $H_2SO_4$ may be present as free acid) and to an amount of lead acetate more than sufficient to precipitate the molybdenum add, say, 30 c. c. of strong ammonium acetate; heat this also, and then pour the second mixture into the first; bring the whole to boiling, filter, etc. The precipitate was tested in each case for sulphuric acid, with negative results.

None of the methods outlined, however, is superior to that given under "Precipitation" (see p. 98). If the directions are carefully followed in regard to titration with dilute lead acetate in a boiling hot solution, as outlined, no high results will be obtained by the amount of $H_2SO_4$ formed by decomposing a sulphide ore, or by fuming a sample with $H_2SO_4$ within ordinary limits. Fuming an ore to $H_2SO_4$ fumes is practically only resorted to when much Pb is present. This must be removed as the sulphate, for if a solution contains Pb when this is neutralized with NH$_3$, PbMoO$_4$ will be precipitated with the Fe group and be lost.

EFFECT AND REMOVAL OF BARIUM, STRONTIUM, AND CALCIUM.

Ba, Sr, and Ca form molybdates in neutral solutions. Ba readily forms a molybdate, even in slightly acidified (acetic) solutions without much boiling. Calcium and strontium molybdates are less and less readily formed as the amount of free acetic acid in the solution is increased. Their behavior in this respect is in the Ba, Sr, Ca order, Ba being decidedly the most refractory. Brearley (13) states that:

When solutions of 200 c. c. contain one to two tenths of a gram of Ba, Ca, and Sr along with about 20 c. c. of acetic acid, the molybdates can be formed, even on long-continued boiling, only with barium.

The writer has confirmed these results. Ba can be completely removed with $H_2SO_4$, as Pb can be removed. The amount of Sr encountered in any material associated with Mo need not be considered. Ca may occur as calcite in some Mo samples, but under the conditions of precipitating Mo, the presence of 20 c. c. of acetic acid will keep this in solution. In a series of experiments by Bonardi and Barrett (11), it was shown that the presence of as much as 3 grams of CaCO$_3$ dissolved in HCl in the presence of Mo, under the conditions outlined for precipitation, only affected the results approximately 3 per cent, the result being lowered due to the formation of the lower molecular weight of calcium molybdate. The presence of as much Ca as is contained in 3 grams of CaCO$_3$ would in all probability not be encountered in an ordinary analysis. If the material should contain much lime, it is best to remove it from the solution by sodium
carbonate. This could be used in place of NH₃ in precipitating out the Fe group. In such event, two precipitations should be made with excess Na₂CO₃, washing the precipitate well each time; then the precipitation of Mo can follow after making acid with HCl.

INFLUENCE OF THE RARE METALS URANIUM, ZIRCONIUM, TITANIUM, TUNGSTEN AND VANADIUM, AND ANY RARE-EARTH METALS LIKELY TO OCCUR WITH MOLYBDENUM.

U, Zr, Ti, and the rare earths are easily separated from Mo by being precipitated by (NH₄)₂S in an ammoniacal solution, while W, V, and Mo remain in solution. NH₄OH in excess will also effect this separation. U remaining in a leached solution when a carbonate fusion has been made will not come down in the acetate precipitation if free acetic acid is present. In general, the separation of Mo from W and V can be easily effected by H₂S under pressure in a dilute HCl acid solution. The presence of 3 to 5 grams of tartaric acid will keep W from precipitating as the sulphide. (See Treadwell and Hall (106), p. 296.) The precipitation of MoS₂ away from V must be performed in a solution that has not been previously treated with ammonium sulphide in an ammoniacal solution, since, if this solution is made acid, V will be partly precipitated as the sulphide with the Mo. The procedure must be followed on an acid solution that has received no previous ammoniacal sulphide treatment. W can also be separated from Mo by taking the solution containing these two elements to near dryness with aqua regia, whereby tungstic acid remains insoluble when taken up with the water, while the Mo dissolves in an excess of HCl or HNO₃.

SEPARATION OF TUNGSTEN FROM MOLYBDENUM.

W interferes with the gravimetric method, as it is also precipitated by lead acetate under the conditions of the precipitation. It may be removed from the ignited and weighed PbMoO₄ by treating with HCl, as given by Ibbotson and Brearley (52), or by Crookes (24), page 196, who states:

The HCl solution of the ignited lead salts, to which a few drops of HNO₃ has been added, is evaporated, preferably over the water bath, until nearly pasty, when the WO₃ will have almost entirely separated. The mass is then diluted with 100 to 200 c. c. dilute HCl (3 water to 1 acid), the solution boiled, and the WO₃ filtered off. The weak acid precipitates any WO₃ still unseparated by the evaporation, and is yet strong enough to hold the molybdenum in solution.

Ruegenberg and Smith (88) effect the separation of W from Mo by a method based on the fact that tungstic acid is insoluble in concentrated or dilute H₂SO₄, hot or cold, whereas MoO₃ is very easily and rapidly dissolved. It was found that H₂SO₄ of specific gravity 1.378
dissolved MoO₃ very readily, and apparently did not affect the WO₃. Acid of this concentration was used with the following results:

0.7355 gram of tungsten trioxide and 0.0185 gram of molybdenum trioxide were digested for a few minutes with 25 c. c. of warm sulphuric acid. The insoluble portion was filtered out, and washed with water containing sulphuric acid. After drying, it was ignited and weighed. It equaled 0.7350 gram. The other trials, conducted in precisely the same manner, were as follows:

<table>
<thead>
<tr>
<th></th>
<th>II grams</th>
<th>III grams</th>
<th>IV grams</th>
<th>V grams</th>
<th>VI grams</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tungsten trioxide taken</td>
<td>1.0938</td>
<td>0.0371</td>
<td>0.3588</td>
<td>0.8868</td>
<td>0.3996</td>
</tr>
<tr>
<td>Molybdenum trioxide taken</td>
<td>2.2712</td>
<td>0.6871</td>
<td>1.1590</td>
<td>1.1966</td>
<td>1.0779</td>
</tr>
<tr>
<td>Tungsten trioxide found</td>
<td>1.0930</td>
<td>0.0870</td>
<td>0.3557</td>
<td>0.8966</td>
<td>0.5996</td>
</tr>
</tbody>
</table>

The filtrate containing the dissolved molybdic acid showed no tungstic acid upon examination.

These results indicate that when the two oxides are present together, this mode of separation is of value and merits consideration. (See the modification by Hommel described in Treadwell and Hall (106), p. 294.)

Smith and Oberholtzer (93) give the details where the ignited PbMoO₄ can be volatilized from lead tungstate by a current of dry HCl gas passed over the molybdates while being heated to about 300° C. The reaction is as follows:

\[ \text{PbMoO}_4 + 4\text{HCl} = \text{MoO}_3 \cdot 2\text{HCl} + \text{PbCl}_2 + \text{H}_2\text{O} \]

PbWO₄ + HCl remaining intact. (See also Pechard in Treadwell and Hall (106), p. 295.)

Marbaker (66) effects the quantitative separation and determination of W from M by the use of Mdivani's reagent (50 grams SnCl₂ · 2H₂O in 200 c. c. concentrated HCl) in a solution containing the tungstate and molybdate of sodium. The procedure is here given as it merits consideration. It is as follows:

To a boiling solution containing the tungstate and molybdate of sodium in appropriate amounts (the separation worked very well with quantities up to and including 0.3000 gram of each constituent) add the tin solution (Mdivani's reagent) in the proportion of 20 c. c. for each 0.15 gram WO₃ present. This amount of the reagent should be carefully regulated, because less will not effect a complete separation and more will be correspondingly harder to handle in the determination of molybdenum. The dilution of the solution for analysis should be kept between 60 c. c. and 300 c. c., depending on the amount of tungsten present. After boiling a few minutes allow the blue precipitate of W₂O₅ to settle and then pour the orange supernatant liquid through a filter. Wash the precipitate thoroughly by decantation with hot 5 per cent hydrochloric acid until the washings give no test for molybdenum by the zinc and thiocyanate method. Bring the precipitate on the filter and allow to drain. If the amount of precipitate is small, the filter may be ignited wet, but if the amount be large it is better to heat it until the greater part of the water has been driven off. Place the filter in a porcelain crucible and ignite gently to WO₃. Cool in desiccator and weigh.

The filtrate and wash water are united and the whole evaporated to a small bulk. If the amount of tungsten and molybdenum taken has been large, cool and dilute to
MOLYBDENUM.

250 c. c. and use aliquot portions of 50 c. c. To this solution add from 5 to 10 grams of 20-mesh zinc. The tin will come out as metal. Pour off the green solution when the precipitation of the tin is complete (this takes about 10 minutes), and wash the cake of tin several times with hot water. Unite the filtrate and wash water and heat to 60°. Pass through the reductor in the order named, 50 c. c. dilute HCl (containing 2.5 per cent by volume of the strong acid), the solution containing the molybdenum, 150 c. c. 2.5 per cent (vol. conc. HCl), and finally 150 c. c. hot distilled water. These pass into the flask of the reductor, which has been previously charged with 20 c. c. 10 per cent. ferric ammonium sulphate and 20 c. c. of the "titrating solution." (Consists of 90 grams manganese sulphate, 650 c. c. distilled water, 175 c. c. syrupy phosphoric acid, and 175 c. c. concentrated sulphuric acid.) The reduced solution is next titrated with approximately 0.1/N potassium permanganate and the amount required calculated to MoO₃. If it is desired to determine the amount of tungsten in a sodium tungstate solution, add to that solution a quantity of sodium chloride solution, and proceed as when molybdenum is present. A fairly accurate separation of tungsten and molybdenum may be effected when they are present as ammonium salts, but the method is not to be highly recommended.

SEPARATION OF VANADIUM FROM MOLYBDENUM.

V is precipitated from solution as lead vanadate in precisely the same manner as lead molybdate. Lead vanadate, however, is not used as a quantitative precipitate and determined as such as PbMoO₄, since the composition of the precipitated lead vanadate has not always the same definite composition. If V is suspected in the sample, the solution of the dissolved PbMoO₄ precipitate can be tested for V by H₂O₂. The solution will become colored reddish brown if V is present, due to the formation of pervanadic acid (HVO₄). This is a very delicate reaction. (See Treadwell and Hall (107), p. 436, and Lord and Demorest (61), p. 156.) The separation of V from Mo has already been given, V remaining in solution when Mo is precipitated as the trisulphide by H₂S in an acid solution. V, if precipitated with the lead molybdate as lead vanadate, can be determined from the precipitate by several procedures and the Mo obtained by difference. This procedure is best adapted where only small amounts of V are present. With large amounts, it is best to remove the Mo by H₂S. The ignited and weighed precipitate of lead molybdate and lead vanadate should be dissolved in HNO₃, taken to fumes with H₂SO₄ to remove Pb, and the V determined by reducing with SO₂, according to Edgar (30). (See also Gooch (38) for theoretical considerations and data on accuracy of method.) There is no reduction of MoO₃ when 0.4 gram is present with 5 c. c. H₂SO₄ in 25 c. c. volume. Reactions in SO₂ reduction:

1. V₂O₅ + SO₂ = V₂O₄ + SO₃ (no action on MoO₃).

The reduced V is then titrated with a standard KMnO₄.

2. 5V₂O₅ + 2KMnO₄ + 3H₂SO₄ = 5V₂O₅ + K₂SO₄ + 2MnSO₄ + 3H₂O.

Mo and V may be then determined together by passing the solution through a Jones reductor and titrating the combined acids reduced.
by the amalgamated Zn with a standard permanganate solution. (See Scott (92).)

**Zinc reduction:**

3. \( \text{V}_2\text{O}_5 + 3\text{Zn} = \text{V}_2\text{O}_3 + 3\text{ZnO} \).
4. \( 2\text{MoO}_3 + 3\text{Zn} = \text{Mo}_2\text{O}_3 + 3\text{ZnO} \).

**KMnO\(_4\) oxidation:**

5. \( 5\text{V}_2\text{O}_5 + 6\text{KMnO}_4 + 9\text{H}_2\text{SO}_4 = 5\text{V}_2\text{O}_3 + 3\text{K}_2\text{SO}_4 + 6\text{MnSO}_4 + 9\text{H}_2\text{O} \).
6. \( 5\text{MoO}_3 + 6\text{KMnO}_4 + 9\text{H}_2\text{SO}_4 = 10\text{MoO}_3 + 3\text{K}_2\text{SO}_4 + 6\text{MnSO}_4 + 9\text{H}_2\text{O} \).

From reactions 2 and 5 it is seen that three times the amount of KMnO\(_4\) is required to oxidize \( \text{V}_2\text{O}_3 \) to \( \text{V}_2\text{O}_5 \) as is required for \( \text{V}_2\text{O}_5 \). Hence, the total cubic centimeters of KMnO\(_4\) required in oxidation of the zinc-reduced oxides, minus three times the cubic centimeters of KMnO\(_4\) required in oxidizing the tetroxide of V formed by the SO\(_2\) reduction, equals the cubic centimeters KMnO\(_4\) required to oxidize MoO\(_3\) to MoO\(_2\). From these data, M and V may readily be calculated. Another method for determining the V is that of Campagne, whereby V is reduced by HCl. (See Moore and Kithil (73).) It has been found that Mo does not interfere with this reaction, and that it is absolutely safe to carry out the procedure as outlined for V.

**CONCLUSIONS ON THE GRAVIMETRIC METHOD.**

Conclusions as to the influence of excess acetic acid, lead acetate, and ammonium acetate in the precipitation of PbMoO\(_4\), substantiated by the work of Brearley (13) and Rather (83), are as follows:

a. **Influence of acetic acid.**—The acidity may be varied within wide limits; too much acetic acid tends to decrease the granular form of the precipitate and make it more liable to run through the filter.

b. **Influence of lead acetate.**—The quantity of lead acetate does not greatly affect the results, if no sulphates are present, and in such circumstances an excess of not over 3 to 5 c. c. of a 2 to 4 per cent solution should be used, as outlined, titrating with tannic acid.

c. Prolonged washing with pure water tends, in the later stages, to give opalescent washings; a dilute solution, 2 to 3 per cent, of ammonium nitrate will remedy this effect.

d. The paper need not be ignited separately and no special precautions are necessary in igniting the PbMoO\(_4\).

e. **Influence of alkaline salts.**—PbMoO\(_4\) does not appear to hold associated alkaline salts very tenaciously, as it was found that prolonged washings gave the same results as only three or four washings.

f. Too much ammonium acetate causes the precipitate to be powdery.

g. The quality of the lead acetate reagent does not affect the determination, as the same results can be obtained with "technical" lead acetate.

h. The ignited PbMoO\(_4\) is not contaminated with SiO\(_2\) or base metal salts.
i. Brearley (13) states from the results of his work that the following metals do not interfere with the precipitation of PbMoO₄ when carried out in a small excess of acetic acid and ammonium acetate: Mn, Cu, Co, Ni, Zn, Mg, Hg (ic), U, Cd, and Al. Scott (92) states that 10 to 15 c.c. strong HCl when added in excess to a molybdate solution, followed first by sufficient ammonium acetate to combine with the free mineral acid, and then by the PbMoO₄ precipitation, will effect a separation of Mo from Ba, Ca, Sr, As, Sb, Cd, P, Al, U, Mn, Co, Ni, Zn, Cr, Mg, Hg, and Cu, as well as Fe.

In an ordinary ore analysis, in which the Fe group elements have been precipitated by NH₃ or sodium carbonate, the presence in the original solution of all the above elements in small amounts would in all probability not interfere with the Mo results; but if present in appreciable amounts, special attention should be given to the removal of Pb, Ba, Ca, Si, As, Sb, P, Cr, Al, Fe, sulphates and V and W, as outlined. The other elements will remain soluble in the acetic acetate solution.

j. No special equipment is necessary, no standard solutions are needed, and no special manipulative skill is required.

k. No special precaution need be taken with Ti, Zr, Cb, Ta, and the other rare metals or rare earths, since these can be practically all precipitated by \((NH₃)_2S\) in an ammoniacal solution, whereas Mo remains in solution.

l. The gravimetric method is applicable to high-grade as well as low-grade material, and only a very short time is required for carrying out a determination.

VOLUMETRIC (POTASSIUM PERMANGANATE) METHOD FOR DETERMINING MOLYBDENUM.

The volumetric method presents no advantage over the foregoing gravimetric method, but is useful and extensively used in practice when many determinations are made in a single day. The gravimetric process is advisable where only an occasional determination is required. The volumetric method is easier for those who have had experience with all the necessary manipulations. It is generally conceded by those acquainted with chemical analysis that one knows a method well only when he knows its limitations.

The opinions of others who have worked upon the volumetric method for determining Mo have already been given under “Abstracts of methods,” No. 5 (see p. 89).

If a standard system is developed for carrying out the gravimetric method as outlined in this chapter, it will be found that, although the volumetric method eliminates the precipitation, igniting, and weighing (which can be performed in batteries of 16),
the individual attention which must be given to each sample in manipulating the Jones reductor properly nearly offsets the time gained by the elimination of the above steps in the gravimetric method. For technical results and plant control the volumetric method would in most cases be chosen, since the results will be accurate enough, even if no special attention were given as to rate of reduction, temperature, wash solutions, and refinement of reduction, as will be outlined later. If carefully performed, the volumetric is in every way as accurate as the gravimetric method, and experienced operators can carry out a great many determinations in one day. The method to be given here for the volumetric determination is essentially that given by the writer in a previous publication. (See Bonardi and Barrett (11).)

GIST OF METHOD.

The ore is decomposed, either by acids or by a fusion method, into a soluble molybdate and insoluble compounds of the other constituents of the ore. The molybdate is filtered, acid added, and the solution passed through a Jones reductor where the MoO₃ is reduced to Mo₂O₃. The Mo₂O₃ is then titrated with KMnO₄ and the percentage of Mo present calculated.

PROCEDURE FOR ACID DECOMPOSITION.

Take ½ to 5 grams of ore or steel product, according to richness not to exceed 0.08 gram Mo—the reason for different sizes is explained under “Titration” (see p. 115)—and decompose with aqua regia in an Erlenmeyer flask. Heat for 15 minutes, cool, add 10 c. c. of 1:1 H₂SO₄, evaporate to fumes, cool again, dilute the solution, and filter if lead or barium sulphates are present; if not, without filtering off the insoluble matter neutralize and add 10 c. c. excess of concentrated NH₄OH, boil, filter, and wash with hot water at least five times. Redissolve the precipitate back into the original Erlenmeyer flask by puncturing the filter paper and washing the content into the flask and dissolving with dilute H₂SO₄. Reprecipitate, boil, filter, and wash well. The filtrate should be clear and colorless. After it is made acid with dilute H₂SO₄, so that there will be present after neutralizing all the NH₃ at least 12.5 c. c. of concentrated H₂SO₄ for 250 c. c. of solution, it is ready to be reduced by passing through the Jones reductor.

INTERFERING ELEMENTS.

This method of solution by digesting with aqua regia, followed by evaporation to fumes of H₂SO₄ and digesting with NH₃, brings all the Mo into solution. The residue from such an acid treatment rarely, if ever, contains Mo. HNO₃ used in place of aqua regia,
followed by H$_2$SO$_4$ to fumes, will also give excellent results. Either of these methods of acid decomposition will dissolve the Mo in molybdenite and wulfenite ores and in FeMo if ground to sufficient fineness. The SiO$_2$, Fe, Al, Pb, and other insoluble sulphates, in addition to the rare elements insoluble in hydroxide, will be found in the precipitate.

**REMOVAL OF COPPER, ARSENIC, TIN, AND ANTIMONY.**

Cu, As, Sn, and Sb, if carried through into the ammoniacal filtrate, can be removed from solution by adding several grams of Zn to the acid solution before passing through the reductor. Cu and Sn are precipitated as the metal, while the As and Sb are partly carried down as the metal with the Cu and partly evolved as arsine and stibine. If much As and Sb are present, the addition of a few cubic centimeters of a 10 per cent solution of copper sulphate before adding Zn will precipitate them along with the Cu; or they may be removed along with P by adding a few cubic centimeters of ferric chloride solution before adding NH$_3$, as given under the separation of these elements in the gravimetric procedure.

**REMOVAL OF CHROMIUM, VANADIUM, AND TUNGSTEN FROM MOLYBDENUM.**

The procedure for the separation of Cr, V, and W from Mo has already been given in the gravimetric section. These elements must be removed before the solution is passed through the reductor or else determined separately and subtracted from the permanganate titration, as previously outlined in the gravimetric method.

Of the three elements, however, Cr tends to give only slightly higher results after passing through the reductor, and if present in only small quantities need not be reckoned with.

**DECOMPOSITION BY FUSION.**

Decomposition by fusion, in preparing a sample for the volumetric method, is carried out in a very similar manner, as described in the fusion methods for the gravimetric procedure.

**PROCEDURE.**

Take a 0.5 to 5 gram sample, depending on the grade, the content of Mo not to exceed 0.15 gram Mo. (The reason for different sizes is explained under "Titration.") Place the weighted sample in a 60 c. c. iron-spun or nickel crucible and thoroughly mix with 8 to 10 parts of one of the fusion mixtures previously given. Na$_2$O$_3$ works very well for high siliceous ores. Cover the crucible with a lid and place in an electric muffle maintained at about 600° C., or heat the crucible in the flame of a Meeker burner until perfect fusion is ob-
tained; fusion takes place in about 10 minutes in the muffle and in about five minutes over the burner. Allow the crucible to cool for a few minutes, then while still warm place in an 800 c. c. beaker containing 400 c. c. water. After solution, which occurs quickly if peroxide has been used, remove the crucible, cover with iron tongs, and wash with water from a wash bottle. Make up the volume in a graduated flask to 500 c. c. and filter the solution through four folded sheets of 8-inch qualitative paper in a 5-inch funnel.

Paper of good grade should be used, for when unbleached paper is used the organic matter dissolved by the hot caustic solution will require for a blank several cubic centimeters of permanganate solution. A grade of paper has been encountered so poor that as much as 10 c. c. of 1/20 N KMnO₄ was required to color the filtrate permanently, after it had been made acid. The blank in the peroxide fusion should never exceed over 0.8 c. c.

Filtration takes place quickly, and when 250 c. c. have filtered through, add enough 1:1 H₂SO₄ solution so that after the caustic has been neutralized the solution will contain approximately 12.5 c. c. of free H₂SO₄, as in neutralized alkaline solution in acid digestion. Heat the solution on the hot plate for several minutes to drive off any peroxide that might be present. The solution is then ready for the Jones reductor and is subject to the removal of the same interfering elements as given in the acid digestion, except Cu. If gelatinous SiO₂ separates out before the solution can be treated in the reductor, this can be removed, as described under the fusion procedure for the gravimetric method.

**COMMENTS ON THE FUSION DECOMPOSITION METHOD.**

The method of solution by Na₂O₂ or by one of the fusion mixtures previously outlined will completely and readily convert all of the Mo into soluble sodium molybdate when the fusion is dissolved in water. The Fe will be completely precipitated with other insoluble hydroxides, including Cu. The major portion of the P, As, and Sb will remain with the ferric hydroxide. For low-grade material the amount of Mo retained by the bulky precipitate is of no consequence in the calculations. However, with high-grade material the precipitate should be redissolved in dilute H₂SO₄ and again precipitated. As only an aliquot part of an ordinary fusion filtrate is taken for analysis, the amount of Mo retained by the bulky Fe precipitate may materially affect the results if no reprecipitations were made.

If the alkali-leached solution is rich in SiO₂, and then made only barely acid, colloidal silicic acid is precipitated when heated and, if passed through the reductor and titrated with permanganate, will give low results and the end point will fade quickly and be uncertain. The concentration of acid, 12.5 c. c. in 250 c. c. volume, prevents this
olloidal precipitation if not boiled for too long a period. If too much illicic acid separates, it is best to take a new sample, or to remove the SnO₂ by methods already given in the gravimetric procedure, rather han to attempt to run the gelatinized solution through the reductor. A great deal of trouble will also be experienced by the gelatinous SnO₂ clogging the reductor.

**JONES REDUCTOR.**

The Jones reductor is illustrated and described by Lord and Demorest (61) and by Scott (92). It consists of a glass tube con-
tracted at the bottom, with a 3-inch funnel inserted at the top; the internal bore and length of the tube are described below in detail, as these dimensions are important. The stem of the funnel enters a small one-hole rubber stopper which fits tightly into the top of the lass tube. The stem, or contracted end, enters a rubber stopper of a -liter side-neck pressure flask which is connected to a suction pump. The Zn for the reductor should be of 20-mesh size and contain less than 0.01 per cent Fe. It is best amalgamated as follows:

With very dilute H₂SO₄—about 3 c. c. to 100 c. c. of water—
oisten a quantity of Zn in a beaker sufficient to fill the reductor; dd a small drop of Hg, and stir it until the Zn shows uniformly he white Hg color. Wash the Zn free from acid and put it into the ube. One-half gram of Hg is sufficient for 150 grams of Zn; avoid sing more than just enough. The reductor is filled by placing some lass beads at the point of contraction of the tube; on top of this placed some glass wool mixed with bits of small broken glass ods to keep the glass wool from forming a compact thick plug which might later hinder the passage of the solution. Above this lass wool may be placed a perforated platinum disk or gauze, which will also assist in the clear passage of the solution and prevent clog-
ing. The tube is then filled to within a few inches of the top with he amalgamated Zn.

The internal bore of the reductor should not be greater than five-
eighths inch, and should be 20 to 30 inches long. Shorter reducers, anging down to 10 inches, and larger bores than five-eighths inch ave been tried but the results were unsatisfactory, for the follow-
ing reasons:

1. The Mo solution was not completely reduced by passing the auid through once; this necessitated passing the solution through a econd time, and required larger blank correction.

2. The amount of solution or wash water necessary to wash a eductor completely, when using one of larger bore than five-eighths inch, makes the bulk of solution too large to titrate. The solution ust not be too dilute to obtain a sharp end point. The titrations btained on blank runs with several reductors of different construction
have ranged from 0.5 to 1.5 c. c. In one run the titration was as high as 2 c. c. of 1/20 N permanganate when the same amount of acid and solution were used as in a Mo determination. This largest blank was later proved to be due to overamalgamation of the Zn, as the reductor had been used for several hundred determinations and much of the zinc had been dissolved.

Operation. A stock solution of acid wash water should be made up, containing about 50 c. c. of concentrated H₂SO₄ per liter. One hundred c. c. of acid wash is first passed through the reductor at a temperature of 60 to 70°, or as hot as can be conveniently handle. This heats the Zn, makes the reduction more effective, and removes air from the apparatus. This is followed by the Mo solution of the same temperature, then 200 c. c. more of hot acid wash, followed by 200 to 250 c. c. of hot water. The reduced solution should be immediately titrated.

The rate should not be greater than 50 c. c. in 30 seconds; this can be accurately controlled by a suction pump connected with pressure tubing to a 2-liter side-neck receiving flask. A faster rate may bring erratic results, especially with high-grade material.

Care should be taken that no air is drawn through the zinc. This happens and the air is immediately followed by dilute acid; the liquid running through is sometimes oxidized, possibly from the formation of H₂O₂; hence, while the solution and wash water are running through the reductor, the surface of the Zn must be kept covered continually with liquid. (See Gooch (38).)

At no time is the funnel on the Jones reductor drained before more liquor is passed through, or when the run is finished.

Complete reduction is denoted by the green color imparted to the solution in which the Mo has been completely reduced from MoO₃ to Mo₂O₅. On low-grade material operating under these conditions no ferric phosphate solution is deemed essential in the receiving flask of the Jones reductor, as is necessary with high-grade ore.

3. Only the smallest amount of wash liquid that is necessary remove the Mo completely should be used. Too much wash increases the blank and makes the titrating solution too large to obtain a sharp end point. After several runs, 200 c. c. of hot acid was followed by 200 to 250 c. c. of hot water was found to wash the Mo completely from a reductor 20 to 30 inches long, and to give a blank determination of 0.35 c. c. to 0.50 c. c. of 1/20 N KMnO₄. This was as good as could be obtained. Fifty c. c. of concentrated H₂SO₄, 1 liter of water proved to be the best concentration of acid was Greater concentration of acid, however, is not detrimental. The above concentration of acid in 250 c. c. of Mo solution should 12.5 c. c.
MOLYBDENUM.

As 1 c. c. of 1/20 N $\text{KMnO}_4$ solution is equivalent to 0.0016 gram Mo, or 0.16 per cent Mo on a 1-gram sample, too much care cannot be taken in the use of the reductor.

**TITRATION.**

The determination of the Mo in solution will be accurate and dependable only when the following detailed directions given for volumetric titration with $\text{KMnO}_4$ are carefully considered and carried out. The sample of the reduced Mo solution that is to be titrated should not be too large nor the permanganate solution too strong, and before the Mo solution is titrated a blank determination should be made exactly like the Mo determination.

A 5-gram sample should be taken of any ore supposed to assay less than 3 per cent Mo, a 1-gram sample of an ore assaying in the vicinity of 15 per cent Mo, and a 4-gram sample for ore assaying above 15 per cent, and a proper aliquot solution used when titrated with a weak permanganate solution. The reason for controlling the size of sample used is apparent. When titrating an aliquot portion, for example, one-half the weight of the sample taken, as in the sodium peroxide fusion method the reading for 1/20 N $\text{KMnO}_4$, should fall on the scale of a 50 c. c. burette.

**NORMALITY OF POTASSIUM PERMANGANATE.**

An approximate 1/20 N $\text{KMnO}_4$ was selected for low-grade material, as 1 c. c. of such a solution will represent 0.0016 gram Mo or 0.16 per cent on a 1-gram basis. A 5-gram sample of ore containing 0.16 per cent Mo would then require only 5 c. c. of the permanganate solution, as the Mo to be determined in low-grade material usually falls below 0.10 per cent; stronger solutions were not advisable because too little of the permanganate would be required to be controlled accurately.

An attempt was made to use a weaker $\text{KMnO}_4$ solution of 1/100 normal, where 1 c. c. would represent 0.00032 gram Mo, or 0.032 per cent on the 1-gram basis, but the end point with such a weak solution was uncertain and could not be controlled within 1 c. c. and often not within several cubic centimeters. Moreover, a blank determination required several cubic centimeters, which is unreliable. On very high-grade material, it may be necessary to use stronger permanganate than 1/20 N so that a larger sample may be taken for analysis.

**EFFECT OF BLANK.**

When the amount of permanganate needed for a blank run is determined, the acid concentration of the solutions, the volume of wash water used, and the manipulations of the reductor should be the same as in the determination when Mo is present. One large
chemical concern that buys and sells Mo ore has not been subtracting a correction factor for ore assaying more than 5 per cent Mo, but does subtract the correction for Mo content below 5 per cent. The following experiments were made to determine the effect of the blank in titrating reduced Mo solutions of different strengths. The blank requirement for the reducer used in these experiments was 0.35 c. c. of 1/20 N KMnO₄.

Two grams of approximately 100 per cent MoO₃ were dissolved in NH₃ and made up to 500 c. c. Aliquot portions were drawn off with five pipettes of different sizes so that the content of Mo would correspond to the amount found in various grades of ores. The Mo was very carefully determined in each pipette by the gravimetric method, weighing as PbMoO₄. The number of cubic centimeters of permanganate consumed is given for each volumetric determination so that the limit of accuracy can also be determined, as explained in detail later.

RESULTS OF FIRST SET OF EXPERIMENTS.

1. 50 c. c. solution = 0.1327 gram Mo by gravimetric (PbMoO₄) method.
   \[ \begin{align*}
   & 50 \text{ c. c. solution} = 82.50 \text{ c. c.} \\
   & 50 \text{ c. c. solution} = 82.80 \text{ c. c.} \quad \text{1/20 N KMnO}_4 \text{ volumetric method.}
   \\
   & 50 \text{ c. c. solution} = 82.80 \text{ c. c.} \\
   & \quad \quad \text{Average c. c. required} = 82.73 = 0.1324 \text{ gram Mo.}
   \\
   & \quad \quad \text{Difference from gravimetric} = 0.0003 \text{ gram Mo (minus).}
   \\
   \end{align*} \]
   No blank subtraction necessary.

2. 25 c. c. solution = 0.0664 gram Mo by gravimetric (PbMoO₄) method.
   \[ \begin{align*}
   & 25 \text{ c. c. solution} = 41.20 \text{ c. c.} \\
   & 25 \text{ c. c. solution} = 41.40 \text{ c. c.} \quad \text{1/20 N KMnO}_4 \text{ volumetric method.}
   \\
   & \quad \quad \text{Average c. c. required, 41.30 = 0.0661 gram Mo.}
   \\
   & \quad \quad \text{Difference from gravimetric} = 0.0003 \text{ gram Mo (minus).}
   \\
   \end{align*} \]
   No blank subtraction necessary.

3. 10 c. c. solution = 0.0264 gram Mo by gravimetric (PbMoO₄) method.
   \[ \begin{align*}
   & 10 \text{ c. c. solution} = 16.90 \text{ c. c.} \\
   & 10 \text{ c. c. solution} = 16.90 \text{ c. c.} \quad \text{1/20 N KMnO}_4 \text{ volumetric method.}
   \\
   & \quad \quad \text{Average c. c. = 0.02705 gram Mo.}
   \\
   & \quad \quad 16.90 - 0.35 \text{ c. c., blank subtraction = 16.55 c. c. = 0.0264 gram Mo.}
   \end{align*} \]
   Blank subtraction required.

4. 5 c. c. solution = 0.0128 gram Mo by gravimetric (PbMoO₄) method.
   \[ \begin{align*}
   & 5 \text{ c. c. solution} = 8.40 \text{ c. c.} \\
   & 5 \text{ c. c. solution} = 8.60 \text{ c. c.} \quad \text{1/20 N KMnO}_4 \text{ volumetric method.}
   \\
   & \quad \quad \text{Average c. c. = 8.50 = 0.01360 gram Mo.}
   \\
   & \quad \quad 8.50 - 0.35 \text{ c. c. blank subtraction = 8.15 c. c. = 0.0130 gram Mo.}
   \\
   & \quad \quad \text{Difference from gravimetric} = 0.0002 \text{ gram Mo (plus).}
   \end{align*} \]
   Blank subtraction required.

5. 1 c. c. solution = 0.002484 gram Mo by gravimetric (PbMoO₄) method.
   \[ \begin{align*}
   & 1 \text{ c. c. solution} = 1.80 \text{ c. c.} \\
   & 1 \text{ c. c. solution} = 1.90 \text{ c. c.} \quad \text{1/20 N KMnO}_4 \text{ volumetric method.}
   \\
   & \quad \quad \text{Average c. c. = 1.85 = 0.002960 gram Mo.}
   \\
   & \quad \quad 1.85 \text{ c. c. - 0.35 c. c. blank subtraction = 1.50 c. c. = 0.00240 gram Mo.}
   \\
   & \quad \quad \text{Difference from gravimetric} = 0.00008 \text{ gram Mo (minus).}
   \end{align*} \]
   Blank subtraction required.
The above results were so significant that the operation was repeated. A different molybdate solution that had been standardized against pure Pb was used, and the Mo solution was titrated against lead acetate. In 1 liter of water, 4.74 grams of \((\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}\) were dissolved and standardized against 0.20 gram of pure lead foil, as given by Low (62), in the determination of Pb, using a standard molybdate solution.

**RESULTS OF STANDARDIZATION.**

Ten c. c. of the molybdate solution = 0.0054 gram Pb = 0.02502 gram Mo. By gravimetric \((\text{PbMoO}_4)\) method, 10 c. c. of solution = 0.02472 gram Mo.

Difference = 0.00030 gram Mo.

Average for 10 c. c. = 0.02487 gram Mo.

**RESULTS OF SECOND SET OF EXPERIMENTS.**

**Volumetric method against \(1/30\) \(N\) \(\text{KMnO}_4\).**

1 c. c. solution requires 1.90 c. c. permanganate - 0.35 c. c. blank = 1.55 c. c. = 0.002400 gram Mo.

5 c. c. solution requires 7.80 c. c. permanganate - 0.35 c. c. blank = 7.45 c. c. = 0.01202 gram Mo.

10 c. c. solution requires 15.90 c. c. permanganate - 0.35 c. c. blank = 15.55 c. c. = 0.02488 gram Mo.

25 c. c. solution requires 38.60 c. c. permanganate no blank subtraction = 38.60 c. c. = 0.06176 gram Mo.

Difference on 1 c. c. .................. 0.000007 gram Mo (minus)

Difference on 5 c. c. .................. 0.0004 gram Mo (minus).

Difference on 10 c. c. .................. 0.0001 gram Mo (plus).

Difference on 25 c. c. .................. 0.0004 gram Mo (minus).

**COMMENTS ON RESULTS.**

These results clearly indicate that no blank should be subtracted on a Mo solution that requires more than 16 c. c. permanganate, which corresponds to 0.0256 gram Mo, on the basis of a 1-gram sample, and is equivalent to 5.12 per cent Mo. For a permanganate consumption below 16 c. c., a blank should be subtracted. The reason for the above conclusion concerning the blank subtracted is not absolutely clear, but when one considers the following facts concerning the use of such a weak solution as \(1/20\) \(N\) permanganate, the effect of the blank is reasonable.

Pure distilled water containing the same acid concentration as is used in a determination will usually require 0.20 c. c. of \(1/20\) \(N\) permanganate to effect a color in 250 c. c. also, when a blank is run through a reductor; if any \(\text{H}_2\text{O}_2\) is formed and an oxidized condition takes place in the liquid, some \(\text{KMnO}_4\) may be consumed.

If such oxidation takes place when a weak solution of Mo is run through the reductor, possibly the weak effect of any oxidizing substance due to a trace of \(\text{H}_2\text{O}_2\) does not act upon the reduced Mo, but when a strong solution is run through the reductor an oxidizing effect
may act upon the reduced Mo and thus compensate for the blank subtraction.

Whether the above is an explanation or not, the fact remains that when titrating a strong Mo solution no blank need be subtracted. Although the correction may be important when a solution representing \( \frac{1}{4} \) gram of a sample is titrated, the blank effect is small if the sample represents 2.5 grams or over. The small blank, 0.35 c. c. or 0.50 c. c., would be divided by 2.5 or more for the calculations on a 1-gram basis to obtain the percentage, and a fraction of a tenth of a cubic centimeter represents a negligible amount of Mo.

**PRECAUTION AGAINST A FADING END POINT.**

In titrating the Mo solution obtained from an ore high in SiO₂ that has been fused, the end point vanished. This was due possibly to the SiO₂ and other salts in solution, which perhaps retarded the reaction, as this effect did not occur when pure MoO₃ or ammonium molybdate or the solution prepared by the acid digestion method was titrated. In order to overcome this difficulty, a titrating mixture was made as follows: 100 grams of pure \((NH₄)₂SO₄\), \(Fe₂(SO₄)₃\cdot24H₂O\) were dissolved in 1 liter of water; this was mixed with 1 liter of a "titrating solution" consisting of 90 grams MnSO₄, 650 c. c. distilled water, 175 c. c. sirupy \(H₃PO₄\) and 175 c. c. concentrated \(H₂SO₄\). The phosphoric acid rendered the solution colorless. When mixed, the two solutions contained 2 liters, 50 c. c. of which would be equivalent to approximately 0.275 gram Fe, or 0.1584 gram Mo, and would be sufficient for an ordinary Mo determination. The two solutions may be kept separate and 25 c. c. of each taken and mixed as required. The use of this mixed solution in the receiver of the reductor tended to give a sharper end point, as is true when titrating a reduced Fe solution in the presence of a "titrating solution," which contains manganous sulphate, \(H₃PO₄\), and \(H₂SO₄\) as given. On the other hand, a larger blank subtraction was necessary in each run. This applied to small or large amounts of Mo in solution when titrated and was in part possibly due to some ferrous iron in the titrating mixture or to other causes as given under "Effect of blank," page 115. This indicated that a blank obtained in using the reductor without a titrating mixture in the receiver is due mostly to other causes than dissolved ferrous iron from the zinc in the reductor. The following will make this statement clearer:

Fifty c. c. of titrating mixture in 250 c. c. of water required 0.50 c. c. of 1/20 N permanganate, whereas 50 c. c. titrating mixture in a Jones receiver followed by blank run required 0.80 c. c. of the permanganate. Twenty-five c. c. of a Mo solution, as was shown under "Effect of blank," required 41.30 c. c. of KMnO₄ solution, whereas
when the titrating mixture was used the permanganate reading was 42 c. c., therefore a blank must be subtracted when a titrating mixture is used in the receiving flask. One c. c. of Mo solution required 1.85 c. c. of KMnO₄ without the mixture and 2.60 c. c. with the mixture; thus, the use of this solution in the receiver was of no special advantage with the strengths of solutions titrated, although many analysts claim that its use is absolutely necessary to prevent the reduced Mo from being oxidized and to give a sharper end point. The reduction or oxidation gave no trouble in titrating low-grade solutions containing not over 10 per cent Mo when the extra length of reductor was used as directed.

The end point, however, can easily be checked by passing the solution through the reductor a second time (not possible if a titrating mixture has been used in the receiver), which should give the same result as passing the solution through once. The bright green color indicates complete reduction; the solution should be titrated immediately. If it is allowed to stand, the ferric phosphate solution as given should be used, as recommended by Randall (82) and also as given in several standard textbooks. (See Gooch (38) and Scott (92).)

PRECAUTIONS FOR HIGH-GRADE ORE.

In working with material of higher grade, above 10 per cent Mo, Randall's precaution is recommended, as this would prevent reoxidation of a strong reduced Mo solution on exposure to the air and would give more consistent results with low-grade material, especially if solutions are allowed to stand long before titration. This precaution is not absolutely necessary but the use of the ferric phosphate solution in the receiver would perhaps be advisable for beginners.

If the volumetric method is used to assay ores containing over 50 per cent MoS₂, a large sample should be digested, an aliquot portion should be taken, and a stronger solution of KMnO₄ than N should be used. However, it must be understood that the error in such event must be multiplied by a factor for the aliquot portion taken to reduce to a 1-gram sample, in order to calculate the percentage. The chances of error in working with aliquot parts are, however, small for high-grade material by the gravimetric method, as a larger sample can be taken for analysis than in the volumetric method. A further advantage of the gravimetric method is the small factor (0.2615) that is used in multiplying the weight of PbMoO₄ to obtain the weight of Mo.

STAGE OF REDUCTION OF THE MOLYBDENUM SOLUTION.

Much has been written concerning the state of reduction of the molybdenum after it has passed through the reductor. (See Miller and Frank (71), Noyes and Frohman (76), Blair (9), Blair and Whitfield (10), Edgar (30), and Gooch (38).) This controversy has been
taken up in detail in Randall's article (82), and the reduction of the molybdenum to MoO$_3$ has been proven conclusively. None of the writers has, however, determined the full effect of the blank on varying concentrations of Mo solutions, and probably if this had been done, a great deal of the controversy might have been eliminated.

**LIMIT OF ACCURACY.**

In the check determination for the volumetric method in the analysis given under "Effect of blank," and in many other analyses that were made, a variation of 0.20 c. c. was quite common for duplicate determinations on the same sample. This difference, when calculated against 1/20 N permanganate, represents 0.032 per cent Mo, or a weight of 0.00032 gram on the basis of a 1-gram sample. This would, no doubt, be about the limit of accuracy in comparing checks for Mo determined as, say, the sulphide, ignited as MoO$_3$ and weighed. But in the latter method of determination, the separation of the sulphide from all other elements, especially Cu, As, Sb, and SiO$_2$ and the necessary accurate ignition to MoO$_3$ is unsatisfactory and uncertain, and must be attended with much precaution, particularly with low-grade material. This is given in detail under the procedure for the gravimetric method.

The difference between the Mo determined gravimetrically as PbMoO$_4$ and the Mo determined volumetrically by lead acetate titration with tannic acid as an outside indicator was 0.0003 gram, which on a 1-gram sample would represent 0.03 per cent; however, if the solution titrated represents a large sample, as 2 to 5 grams, the limit of accuracy is calculated as 0.01 per cent or less. This is also the limit of accuracy in the permanganate titration if the liquid titrated represents a 2.5 to 5 gram sample.

**INFORMATION FOR ANALYSTS.**

An analyst not only has to determine Mo in alloy-steel products, but also has to determine several of the deleterious impurities on which a penalty settlement is made. These elements are usually present in very small amounts and often only as traces. The elements upon which penalties are made as a rule include: C, S, Si, As, and P. The effect of these elements in steel technology has received much attention, and their accurate control in the ferro or steel charge or their removal down to allowable limits requires special care. Consequently, there is need of much analytical work to determine these impurities.

In order to aid an analyst in selecting a method for carrying out these determinations, the following list of workers who have published their methods for determining C, S, Si, As, and in Mo alloys or steel products is given: Müller and Bernardo (74), Noyes and Froh-
man (76), Trautmann (101), (102), Gherardi (37), Binder (7), Blair (8), (9), Zinberg (115), and Johnson (55).

For determining W, Cr, Mn, Ti, V, Ni, Co, U, and B in Mo iron products, see Gherardi (37), Svennson (96). Blair (8), (9), Pozzi-Escot (79), Fettweis (34), Chesneau (19), Zinberg (115), and Johnson (55).

Writers who have published methods for determining Mo in steels and alloys include: Crook (22), Hoepfner and Binder (49), Mabbe (65), Travers (103), Mennicke (70), Johnson (55), Auchy (2), (3), Cruser and Miller (25), Brearley (14), Brearley and Ibbotson (15), and Chesneau (19).

Most of these references have already been cited in the text of Part III, but they are repeated as a further aid to the use of the bibliography (pp. 125–130).

CONCLUSIONS ON THE VOLUMETRIC METHOD.

1. Decomposition with Na₂O₂ is the most rapid and reliable fusion method for obtaining Mo in solution for low-grade ores.

2. The Jones reductor must be prepared and used according to the directions given in order to insure accurate results.

3. The size of sample desirable for analysis and the strength of KMnO₄ in titration depend on the grade of the ore.

4. A correction of the results of titrating should be made to counteract the "blank effect."

5. The limit of accuracy is below 0.01 per cent on the basis of a 1-gram sample, if the proper procedure is observed.

6. Interfering elements found in Mo ores can be removed or determined.

7. The Mo in high-grade ores and in ferromolybdenum can be determined by this method if proper precautions are taken.

APPENDIX.

ANALYTICAL METHOD USED BY THE BUREAU OF STANDARDS.

The United States Bureau of Standards, in reply to a request concerning analytical methods for Mo, made the following reply under date of March 16, 1920, after the work for Part III had been completed. It is given here, because it carries many of the important points previously discussed in Part III. Although the method is rather long and tedious for commercial work where many runs are to be made, it serves as a contrast to the shorter gravimetric method recommended by the writer. The reply from Director W. S. Stratton is as follows:

Inclosed you will find a copy of the method which we developed by the Electro Metallurgical Co. in cooperation with Ledoux & Co. We have tested this method quite thoroughly, and we believe that it is of more nearly universal application than any other method. Our work on the analysis of molybdenum in its ores is not yet complete.
ANALYTICAL METHODS FOR CERTAIN METALS.

DETERMINATION OF MOLYBDENUM IN ALLOYS.

For the determination of molybdenum in ferros and in steels we prefer to precipitate the molybdenum as sulphide from a 2 per cent (by volume) sulphuric acid solution containing 3 grams of tartaric acid per 100 c. c. and to digest the solution for an hour or so on the side of a steam box before filtering.

In dealing with materials high in vanadium or tungsten we believe that it is advantageous to wash the molybdenum sulphide with a 1 per cent sulphuric acid, saturated with hydrogen sulphide and containing 3 grams of tartaric acid to the liter.

DETERMINATION OF MOLYBDENUM IN WULFENITE AND MOLYBDENITE.

1. METHOD OF SOLUTION OF WULFENITE.

One (1.000) gram of the agate-ground ore is dissolved by treatment with 15 c. c. of nitric acid (sp. gr. 1.42) and 7 c. c. of sulphuric acid (sp. gr. 1.840) at a temperature just short of boiling, in a 150 c. c. covered beaker. When practically complete decomposition has been effected, the liquid is evaporated until fumes of sulphur trioxide are freely expelled. After cooling, addition is made of about 40 c. c. of water, the solution is boiled to dissolve the bulk of the molybdenum, cooled to tap-water temperature, and filtered into a 150 c. c. beaker. The residue consists of lead sulphate, silica, and possible small amounts of undecomposed ore, or tungstic and molybdic acids. Both the residue and the filtrate are reserved.

The residue remaining, which consists principally of lead sulphate and silica, is washed thoroughly with a jet of boiling sodium acetate solution (prepared by mixing one volume of a cold saturated solution of the salt with two volumes of water and adding 25 c. c. of 99 per cent acetic acid) to remove all lead sulphate. Ignition of it is then made in a platinum crucible, and the silica is removed by treating it with a drop of sulphuric acid and several cubic centimeters of hydrofluoric acid, and evaporating to the expulsion of fumes of sulphur trioxide. If an appreciable residue remains after this treatment, it is fused with potassium pyrosulphate and tested for molybdenum by means of tartaric acid and ammonium sulphate as further described. The residue seldom contains any molybdenum.

2. METHOD OF SOLUTION OF MOLYBDENITE.

From 0.5 to 5 grams of the finely pulverized sample, the weight used varying with the grade of the ore or concentrate, are treated with from 10 to 35 c. c. of nitric acid (sp. gr. 1.42), and 7 to 10 c. c. of sulphuric acid (sp. gr. 1.84) in a 250 c. c. beaker provided with a clock-glass cover. The solution is digested at a temperature somewhat below the boiling point until most of the molybdite appears to have been decomposed, and then evaporated until strong fumes of sulphur trioxide are evolved. When the beaker and its contents have cooled, addition is made of 50 c. c. of water and the solution is boiled briskly for a few minutes and filtered on an 8-cm. paper into a 150 c. c. beaker. The residue is washed with hot water, then six or eight times with dilute (1:3) ammonia, and finally with hot water, the washings being allowed to run into the main filtrate.

The siliceous residue (which will contain also the greater part of any lead present in the ore) is burned at a very low red heat in a porcelain crucible, cooled, transferred to a platinum crucible, treated with 2 or 3 drops of concentrated sulphuric acid and several cubic centimeters of hydrofluoric acid, and evaporated until sulphuric acid has been completely expelled. Any small residue remaining is fused with sodium carbonate, dissolved in water, and added to the main solution.

3. METHOD OF ANALYSIS.

To the solution containing all, or practically all, of the molybdenum, there is added sufficient ferric sulphate to provide 10 times as much iron as there is arsenic present;
from 0.3 to 0.4 gram is usually ample. The acid solution is then nearly neutralized with ammonia (addition of a sufficient amount to impart a red tint to the clear yellow solution is to be avoided), heated nearly to boiling, and poured very slowly and with vigorous stirring into 75 c. c. of nearly boiling 15 per cent ammonia water contained in a 250 c. c. beaker. When it has settled, the ferric hydroxide (which will carry down quantitatively all arsenic in the ore) is filtered and washed thoroughly with hot water; it is then dissolved in a slight excess of hot dilute (1:4) sulphuric acid and the resulting solution is again heated to boiling and poured into 75 c. c. of boiling 15 per cent ammonia water. The two filtrates, which will contain all of the molybdenum, are collected in a 500 c. c. beaker. It is essential that arsenic, which is usually present in these ores, be eliminated, and the method described furnishes a simple and effective way for accomplishing this. Attempts to remove the arsenic by reduction with sulphurous acid and volatilization as trichloride, AsCl₃, by boiling with concentrated hydrochloric acid, have been unsuccessful, considerable arsenic always remaining with the molybdenum. The addition of ferric sulphate should be omitted only in case arsenic is known to be absent.

To the combined ammoniacal filtrates there are added 3 grams of tartaric acid, and when the acid has dissolved the warm liquid is thoroughly saturated with hydrogen sulphide. The presence of tartaric acid is absolutely necessary in order to prevent precipitation of vanadium and tungsten along with the molybdenum. If these elements are known to be absent its use may be dispensed with. Under these conditions the molybdenum remains in solution as ammonium thiomolybdate, (NH₄)₂MoO₄, which imparts a deep red color to the solution. If a small precipitate of insoluble sulphides separates out, it is filtered off and washed with hydrogen sulphide solution; if the solution remains clear, this step is omitted. Copper, in the amounts usually present, remains entirely in solution at this point and is reprecipitated with the molybdenum when the solution is subsequently acidified. The thiomolybdate solution is then made slightly acid with sulphuric acid (1:1). This results in the precipitation of the molybdenum as trisulphide.

The cessation of effervescence on addition of more acid, the absence of the odor of ammonium sulphide, and the disappearance of the red color of the ammonium thiomolybdate, mark the point where sufficient acid has been added to complete the reactions.

After heating for a short time, the precipitate is allowed to settle and filter on an 11-cm. paper and washed thoroughly with hydrogen sulphide water containing a small amount of sulphuric acid.

The filtrate from the molybdenum sulphide sometimes contains appreciable amounts of molybdenum; addition is made to it of 15 c. c. of nitric acid (sp. gr. 1.42) and the solution is evaporated to fumes of sulphur trioxide, more sulphuric acid is added if sufficient is not already present. After allowing it to cool, 5 c. c. of concentrated nitric acid are added and the solution is again evaporated to fumes. The addition of nitric acid and evaporation to strong fumes is repeated once more to insure the destruction of all organic compounds. After allowing to cool, sufficient water is added to dissolve all salts, 2 grams of tartaric acid are added, and after addition of an excess of ammonia (sp. gr. 0.90), the warm liquid is thoroughly saturated with washed hydrogen sulphide and filtered. The filtrate is acidified with sulphuric acid (1:1) and if, after standing for 15 to 30 minutes in a warm place, any molybdenum trisulphide has separated out, it is filtered, washed well with hydrogen sulphide water containing a small amount of sulphuric acid, and combined with the main precipitate. The precipitation of the molybdenum as sulphide, when carried out as described, effects the separation and removal of tungsten, vanadium, and chromium, and all other elements likely to be present.

The molybdenum sulphide precipitate and paper, or precipitates and papers, are put into a 250 c.c. beaker and treated with 6 c. c. of sulphuric acid (sp. gr. 1.84)
and 10 c. c. of nitric acid (sp. gr. 1.420) and the liquid is cautiously boiled until dense fumes of sulphur trioxide are freely evolved. After allowing it to cool somewhat, 5 c. c. of nitric acid (sp. gr. 1.42) are added and the evaporation is repeated. The evaporation with 5 c. c. portions of strong nitric acid is repeated several times until the filter paper has been completely destroyed and every trace of yellow color due to carbonaceous matter has disappeared. When this has been accomplished, the solution is fumed strongly for a short while, cooled, 5 c. c. of water are added, and the liquid is again taken to fumes of sulphur trioxide in order to insure the expulsion of every trace of nitric acid. When cool, addition is made of approximately 75 c. c. of water and the contents of the beaker are boiled for a few minutes, which should give a perfectly clear solution. Five grams of pure shot zinc (0.002 per cent iron or under) are then added and the solution boiled until most of it has dissolved; this results in partial reduction of the molybdenum and complete precipitation of the copper which is usually present. The liquid is then filtered on an asbestos or "aluminum" filter to remove the undissolved zinc and the copper.

The next step consists in reducing the molybdenum from the sexivalent to the trivalent conditions by passage through a zinc reductor in the following manner: The reductor being clean and in good condition from previous treatment with dilute (2.5 per cent) sulphuric acid and water, and the flask being attached to a filter pump regulated to give gentle suction, 35 c. c. of ferric phosphoric acid per liter are introduced into the suction flask. When the flask is connected to the reductor, the end of the reductor tube should dip into the ferric phosphate solution. Next, 106 c. c. of warm 2.5 per cent sulphuric acid are poured into the funnel which forms the top of the reductor tube, the stopcock being open and the flask under medium suction. When only a little of the acid remains in the funnel, the warm molybdenum solution is transferred to it. The beaker is rinsed several times with hot water, the rinsings also being added to the funnel. When only little solution remains in the funnel, 200 c. c. of warm 2.5 per cent sulphuric acid are added and this is finally followed with 50 c. c. of warm distilled water. At no time is the funnel permitted to become entirely empty, and the stopcock is closed while some of the wash water still remains above the surface of the zinc. By working in this way, no air can pass through the reductor. The molybdenum solution is green as it passes through the lower part of the reductor, but on coming in contact with the ferric phosphate it is changed to a bright red, due to its immediate partial oxidation, which is, of course, accompanied by reduction of a corresponding amount of the ferric salt to the ferrous condition. While still hot, the solution is transferred to an 80 c. c. battery jar and titrated with a standard, approximately 0.1 N solution of potassium permanganate until a permanent faint pink color develops. The reactions which occur are shown in part by the following equations:

\[
2\text{MoO}_3 + 3\text{Zn} + 6\text{H}_2\text{SO}_4 = 5\text{MoO}_4(\text{SO}_4)_2 + 3\text{ZnSO}_4 + 6\text{H}_2\text{O}.
\]

\[
5\text{MoO}_4(\text{SO}_4)_2 + 6\text{KMnO}_4 + 24\text{H}_2\text{SO}_4 = 10\text{MoO}_4(\text{SO}_4)_2 + 3\text{K}_2\text{SO}_4 + 6\text{MnSO}_4 + 24\text{H}_2\text{O}.
\]

Working under the conditions described, complete reduction from MoO₃ to MoO₂ is obtained, none of the MoO₃ being reoxidized by the air after passage through the reductor.

Since zinc always contains some iron, a "blank" is run on the 5 grams used for precipitating the copper and also on the reductor. This is done by dissolving 5 grams of the zinc in 75 c. c. of 6 per cent sulphuric acid, filtering on an asbestos or aluminun filter, and putting the solution through the reductor in exactly the same way as the molybdenum solution. The amount of permanganate required to impart a pink tint to the liquid constitutes the "blank" which must be deducted from the burette reading of every analysis.

The number of cubic centimeters of permanganate, less the "blank," multiplied by the Mo liter, divided by the weight of ore taken and multiplied by 100, gives
the percentage of molybdenum in the ore; the percentage of molybdenum multiplied by 1.5000 gives the molybdenum trioxide.

The reductor is filled by placing some glass beads at the point of construction of the tube; on top of this there is placed a plug of glass wool several centimeters thick and then a layer of acid-washed asbestos several millimeters in thickness. The tube is filled for about 28 cm. with 20-mesh amalgamated zinc, which should contain not more than 0.002 per cent iron. Amalgamation of the zinc is effected by treating it with a 2 per cent solution of mercuric chloride for a few minutes and then washing it thoroughly by decantation with distilled water. When idle, the reductor should always be kept full to above the top of the zinc with distilled water.

PREPARATION AND STANDARDIZATION OF SOLUTIONS.

FERRIC PHOSPHATE SOLUTION.

The ferric phosphate solution contains 100 grams of ferric sulphate, 150 c. c. of phosphoric acid (sirup, sp. gr. 1.725), and several cubic centimeters of sulphuric acid (1:1) per liter.

POTASSIUM PERMANGANATE, APPROXIMATELY 0.1 N.

Prepared by dissolving 3.18 grams of pure KMnO₄ in boiling distilled water, cooling to room temperature, filtering on asbestos, and making up to 1 liter and mixing thoroughly. The solution is standardized as follows: Exactly 0.3000 gram of pure sodium oxalate (equals 0.14328 gram Mo), obtained from the Bureau of Standards, is dissolved in 250 c. c. of hot water (80 to 90° C.), 10 c. c. of sulphuric acid (1:1) are added, and the hot solution is titrated with the permanganate to the first permanent pink color, care being taken not to permit the temperature to fall below 60° C. The excess of permanganate used to cause an end-point color is determined by matching the color in another beaker containing the same amounts of acid and hot water. By dividing the number of cubic centimeters of the permanganate required into 0.14328, the molybdenum value of each cubic centimeter is obtained.

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Compiled by J. P. Bonardi.


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MOLYBDENUM.


PART IV.—TUNGSTEN.

By C. W. Davis.

INTRODUCTION.

Tungsten has been important commercially for a long time, especially in high-speed steel. This use has stimulated the search for tungsten minerals throughout the world. The following are the principal tungsten minerals:

Scheelinite—a tungstate of calcium; specific gravity, 5.9 to 6.1.

Ferberite—a dark, grayish-black mineral; specific gravity, 6.8. It consists principally of tungstate of iron, but may contain small traces of manganese.

Wolframite and hübnerite—tungstates of iron and manganese. The percentage of manganese practically determines the mineral, although there are gradations that make classification difficult under either head. Typical hübnerite carries about 20 per cent manganous oxide, and typical wolframite 5 to 7 per cent.

Scheelite is found mainly in the Atolia district of California; the largest deposits of ferberite in the United States are in Boulder County, Colo. Small deposits of hübnerite, wolframite, and ferberite are scattered through New Mexico, Arizona, Nevada, and South Dakota. Tungsten deposits occur also in Burma, China, Queensland, Portugal, New South Wales, Argentina, and Bolivia. In China ferberite has been found in placer deposits associated with small quantities of tin.

Apart from the ores, the products that have to be analyzed are metallic tungsten and ferrotungsten, intermediate products, and the various tungsten steels. Metallic tungsten is obtained by the reduction of the oxide, and may contain different tungsten oxides due to incomplete reduction, as well as other impurities. Ferrotungsten carries from 50 to 80 per cent metallic tungsten; high-speed steels contain as much as 16 or 17 per cent metallic tungsten; self-hardening steels, or those requiring no tempering after forging, contain as little as 2½ or 3 per cent, with 6 or 7 per cent chromium. Extremely pure tungsten is used in filaments for incandescent lamps after repeated swaging and heating has made the metal ductile and fibrous.

The chief analytical methods for the determination of tungsten are described and discussed in the following pages.
SOLUTION OR DECOMPOSITION OF ORES AND METALS CONTAINING TUNGSTEN.

GENERAL SOLUBILITY.

Different tungsten-containing materials have different properties, and the method of attack is determined by their composition.

It is highly important that a sample of a tungsten ore be ground to an impalpable powder to aid disintegration; half an hour's work with mortar and pestle saves time in the end. A high-tungsten steel is so hard that it is impossible to get borings without contaminating the sample with the cutting tool unless the latter be annealed at 750° C. for two hours. (See Johnson (57).) The steel may be prepared for analysis by hammering it to a coarse powder in a steel mortar; pestles operated by air drills have been used advantageously in this work.

A brief statement of the effect of reagents on different materials containing tungsten gives an outline of the methods used in decomposition. Ores and minerals are decomposed by treatment with a mixture of acids, HF being a constituent. They may be fused with alkalies or alkaline carbonates or heated with H₂SO₄ and Na₂SO₄; low-grade ores may be treated with an alkaline leach.

WO₂ is soluble in hot HCl and readily soluble in KOH or hot H₂SO₄.

WO₃ is slightly soluble in acids, but is readily soluble in KOH, K₂CO₃, NH₄OH, (NH₄)₂CO₃, and (NH₄)₂S₂O₃.

Most of the orthotungstates are only slightly soluble in water or acids, whereas the metatungstates are easily soluble in water.

Tungsten metal is practically insoluble in HCl and H₂SO₄, and is slowly attacked by HNO₃, aqua regia, and alkalies. It is strongly attacked and readily soluble in a mixture of HF and HNO₃, forming WF₆ or WOF₆.

Tungsten alloys are decomposed by mixed acids or fusions, depending on the composition.

The following methods have proved satisfactory for the solution or decomposition of various substances containing tungsten. If desired, the WO₃ left as a residue in any of the methods may be dissolved by a KOH solution or by fusing with KNaCO₃ and leaching with water.

ORES AND MINERALS.

Ores high in sulphur should be roasted before applying the following methods:

1.—One gram of ore is digested with 40 c. c. of HCl for a half-hour and 5 to 10 c. c. of HNO₃ is added with stirring; it is then taken to dryness at not over 95° C.; baking at a higher temperature renders the WO₃ insoluble in NH₄OH solution. The residue is treated with
20 c. c. of HCl and 3 c. c. of HNO₃, and again taken to dryness. To remove the HNO₃, 5 c. c. of HCl is added, and the material is taken to dryness for the third time, after which 1 c. c. of HCl and 150 c. c. of water is added. The tungstic acid is then filtered and dissolved with NH₄OH. (See Ledoux & Co. (70).)

2.—One gram of ore is treated with 100 c. c. of HCl, heating one hour just below boiling; then 200 mg. of KClO₃ is quickly added to the covered casserole. After the violent action has ceased, the material is stirred and digested another hour, when 200 mg. of KClO₃ is added as before. This procedure is repeated until 2 grams have been added and the ore is completely decomposed. (See Johnson (57).)

3.—One gram of ore is treated with 10 c. c. of HF, 25 c. c. of HCl, and 10 c. c. of 25 per cent H₂SO₄ and heated until the solution is complete; an additional quantity of each acid except H₂SO₄ is added if necessary. (See Ledoux & Co. (70) and Scott (102).) Evaporate to fumes, add 100 c. c. of aqua regia, and evaporate to 20 c. c.

4.—One-half gram of ore is heated with equal parts of HF and HCl, with the addition of more acid if necessary. (See Low (76).)

5.—Less than 30 per cent ore is treated with 40 c. c. of aqua regia and evaporated to dryness. More concentrated ore is first digested with 40 to 50 c. c. of HCl until the volume is 15 c. c., then 25 c. c. of aqua regia added, and the solution again evaporated to 15 c. c. (See Low (76), p. 358.)

6.—One-half gram of ore is heated with 10 to 15 c. c. of liquid bromire, then 30 c. c. of HCl added and the bromine boiled off. More bromine is added if necessary. (See Fieber (32).)

7.—Five grams of low-grade ore is treated with HF, evaporated to dryness, warmed with 5 c. c. of HNO₃, diluted, filtered, and ignited, the residue being fused with a mixture of Na₂O₂ and NaOH, and extracted with water. (See Low (76).)

8.—Ore is fused with 5 to 10 times its weight of Na₂CO₃, K₂CO₃, or a mixture of both and the melt is extracted with water. (See Low (76), and Scott (102).)

9.—When tin is present, 1 gram of ore is fused with a mixture of 4 grams of Na₂CO₃, 2 grams of K₂CO₃, and 2 grams of NaHSO₄. (See Blanc (9).)

10.—One gram of ore is heated with 4 grams of Na₂SO₄ and 4 c. c. of H₂SO₄; this is heated until the flask is red hot, cooled, and 25 c. c. of HCl and 10 c. c. of HNO₃ added and boiled to 20 c. c. (See Low (76).)

11.—Five grams of a low-grade ore is digested with 20 c. c. of a 25 per cent KOH or NaOH solution for one-half hour on a water bath, then diluted and a little Na₂O₃ added. The decomposition is rapid, 98 per cent being decomposed in 15 minutes. (See Hutchin
Hutchin says that for satisfactory use this method depends on the fineness of the ore, and that KOH is to be preferred to NaOH.

12.—One gram of ore is fused with 8 grams of Na₂O₂, with or without NaOH, cooled, and extracted with water. (See Angenot (1–2) and Bullheimer (13).)

13.—One gram of ore is roasted with 1.2 grams of equal parts of CaCO₃ and NaCl, and digested with 40 c. c. of HCl. (See Foote and Ransom (33).)

14.—The ore is mixed with sulphur and heated for 20 minutes in a closed crucible, then brought to red heat for five minutes with the cover removed, cooled, and heated with 4 parts of HCl and 1 part of HNO₃ for about an hour. (See Sheda (104).)

15.—The ore is fused with K₂S₂O₇ and extracted with HCl and water. (See Cremer (20).)

16.—CCl₄ is passed over the heated ore to volatilize the tungsten as the oxychloride. (See Jannasch and Leiste (56).)

**TUNGSTEN POWDER.**

1.—A 1-gram sample is warmed with 10 c. c. of HF in a platinum dish and HNO₃ added drop by drop, keeping the dish covered, until the violent action ceases; then 10 c. c. of concentrated H₂SO₄ is added and taken to fumes. (See Johnson (58), and Scott (102).)

2.—Tungsten powder is readily soluble in a mixture of NH₄OH and H₂O₂ or (NH₄)₂S₂O₇; the coarse powder is treated with HNO₃ and then with NH₄OH and H₂O₂; large pieces are dissolved electrolytically with NH₄OH and 1 to 2 grams of (NH₄)₂S₂O₇ as the electrolyte. (See Arnold (3).)

3.—0.6 gram is fused with 10 grams of Na₂CO₃ and 2 grams of KNO₃, the melt being dissolved in water. (See Johnson (57) and Weiss (120).)

4.—The metal is roasted to the oxide and fused with Na₂CO₃. (See Preussier (91).)

5.—Chloroform is passed over the red-hot metal, forming the volatile oxychloride. (See Mennicke (80).)

**FERROTUNGSTEN.**

The metal is treated first with HCl, then with HNO₃, and the residue is fused with Na₂CO₃ or extracted with NH₄OH. (See Scott (102).) See also paragraph 6 under “Ores and minerals,” and paragraph 1 under “Tungsten powder.”

**TUNGSTEN STEEL.**

1.—A 5-gram sample is digested with 50 to 100 c. c. of HCl just short of boiling, HNO₃ is added, a few drops at a time, and the metal dissolves completely. (See Scott (102), and Lord and Demorest (75).)
2.—A low-tungsten steel is treated with HCl or dilute H$_2$SO$_4$, and the residue fused with Na$_2$CO$_3$ and extracted with water. (See Scott (102) and Von Knorre (115).)

3.—Two grams of low-tungsten steel is treated with 30 c. c. of (1:3) H$_2$SO$_4$. After the action has stopped, 60 c. c. of (1:20) HNO$_3$ is added and the sample digested just below boiling until the residue is a clear yellow, free from black particles. (See Johnson (59).)

4.—Two grams of a high-tungsten steel is heated with a mixture of 30 c. c. of HCl and 30 c. c. of HNO$_3$, heating until the action ceases and repeating the treatment until the tungsten residue is a clear yellow. (See Johnson (60).)

5.—The steel is digested with double chloride of copper and ammonium, dissolving the iron and leaving the tungsten. (See Bagley and Brearley (6).)

6.—One-half gram of a high-tungsten steel is heated with 10 times its weight of KHSO$_4$ over a low flame, the melt is cooled slightly, and 5 grams more of KHSO$_4$ is added, the treatment being repeated with a third addition of KHSO$_4$. The fusion is then brought gradually to a cherry red until all the black particles are gone. The melt is cooled and boiled with 50 to 75 c. c. of water, 20 c. c. of HCl added, and the residue filtered, washed with 10 per cent NH$_4$NO$_3$, and dissolved in hot NH$_2$OH. (See Scott (102).)

7.—Wolter (121) states that a high-tungsten steel is not readily attacked by treatment with dilute or concentrated acids or by fusion with Na$_2$CO$_3$ and KNO$_3$ or Na$_2$O$_2$ but yields to a fusion with KHSO$_4$.

**TUNGSTEN-CHROMIUM STEEL.**

1.—See paragraph 3 under "Tungsten steel."

2.—One gram of metal is treated with 60 c. c. of (1:4) HCl and 2 or 3 c. c. of HNO$_3$; the WO$_3$ remains as a precipitate and the Fe and Cr go into solution. (See Zinberg (124).)

**TUNGSTEN-MOLYBDENUM STEEL.**

1.—One gram of metal is treated with 50 c. c. of HNO$_3$ and evaporated to dryness, then taken to dryness twice with HCl. (See Johnson (61).)

2.—One gram of metal is treated with 90 c. c. of HCl and 10 c. c. of HNO$_3$ and evaporated to pastiness, then treated with (1:4) HCl; the Fe and Mo go into solution, leaving the WO$_3$. (See Scott (102).)

**TUNGSTEN-NICKEL STEEL.**

See paragraph 1 under "Tungsten steel," and Mennicke (80).

**TUNGSTEN-MOLYBDENUM-NICKEL STEEL.**

Treat with aqua regia. (See Mennicke (80).)
TUNGSTEN BRONZES.

One-half gram of the powder is fused with 2 grams of alkali-free \((\text{NH}_4)_2\text{SO}_4\) and 2 c. c. of \(\text{H}_2\text{SO}_4\), with the addition of 1 gram of \((\text{NH}_4)_2\text{SO}_4\) and 1 c. c. of \(\text{H}_2\text{SO}_4\); then the mixture is heated further. The melt is cooled, moistened with water, and digested with 50 c. c. of concentrated \(\text{HNO}_3\). (See Scott (102) and Treadwell and Hall (111).)

SLAG (FROM MANUFACTURE OF TUNGSTEN STEELS).

See paragraphs 8 and 12 under “Ores and minerals,” paragraph 3 under “Tungsten powder,” and paragraph 6 under “Tungsten steel.”

QUALITATIVE ANALYSIS.

DETECTION OF TUNGSTEN.

DETECTION IN GENERAL.

Hartmann and Runner (97) have selected the following tests which, properly performed, are useful in the detection of tungsten in most minerals and alloys:

Tungsten may ordinarily be detected in minerals by boiling the finely powdered material with concentrated hydrochloric acid until insoluble yellow tungstic acid is formed. Zinc or tin is then added and if tungsten is present in appreciable amounts a blue color forms in the solution or the yellow residue turns blue, due to reduction by the nascent hydrogen.

If only small amounts of tungsten are present, a larger portion (about half a gram) of the finely powdered material may be thoroughly mixed with 4 grams of sodium carbonate and fused. The fused or well-sintered mass is dissolved by boiling water in the crucible. The aqueous solution is next acidified with an equal volume of concentrated hydrochloric acid, a small piece of tin added, and the solution warmed gently if necessary. The volume of the solution should not be over 10 to 20 c.c. A fine blue color in the solution or a blue residue indicates the presence of tungsten. In either case, if reduction is continued long enough, a brown color is obtained.

These tests, if properly used, will show the presence of tungsten in materials as low as 2 per cent, and, by using special precautions, will detect tungsten in even lower grade materials. Tin is preferred to zinc for the reducing action, because if only a small quantity of tungsten is present, the zinc reduces it very quickly to the brown oxide, and the blue color may be unnoticed. The action of tin is slower but much more certain. If much tungsten is present, either tin or zinc gives good results.

Columbium is the only element at all likely to give a blue color followed by a brown color under the conditions of this test. The columbium blue is not so brilliant and can be distinguished from the blue of tungsten oxides by the fact that it disappears when the blue solution is diluted with water. Vanadium also gives a blue color when solutions of its salts are reduced, but tartaric acid also will cause this reduction, whereas it will not reduce tungstic oxide. Molybdenum on reduction goes through a series of color changes from violet to blue to black. Titanium gives a violet color. No other elements will interfere with the reduction test for tungsten.

The following procedure (see Scott, 102) will remove the above elements which if present may obscure the tungsten blue color. The solution obtained by extracting the
sample after fusion with sodium carbonate (or caustic alkali) is acidified with hydrochloric acid and boiled. The precipitate, which may contain antimony, molybdenum, columbium, silica, tantalum, tin, and tungsten is filtered off and the moist residue treated with a solution of yellow ammonium sulphide. Antimony, molybdenum, tin, and tungsten pass into the filtrate, columbium and tantalum remain in the filter. The ammoniacal sulphide extract is acidified with hydrochloric acid and boiled. The precipitate is filtered and washed with a little hydrochloric and nitric acid. Antimony, molybdenum, and tin pass into the filtrate, while sulphur and tungsten, as tungstic acid, remain on the filter. Tungsten is now confirmed as follows, portions of the precipitate being taken:

1. The residue is suspended in dilute hydrochloric acid and a piece of zinc, aluminum, or tin placed on the solution. A blue colored precipitate or solution indicates tungsten.

2. A portion of the precipitate is warmed with ammonium hydroxide and the extract absorbed with strips of filter paper. A strip of this paper is moistened with dilute hydrochloric acid and warmed. A yellow coloration is produced in the presence of tungsten. Another strip is moistened with a solution of stannous chloride, which produces a blue color in presence of tungsten. A third strip dipped into cold ammonium sulphide remains unchanged until warmed, when the paper turns green or blue if tungsten is present.

The following test for tungsten in steel is given by Johnson (57).

Dissolve 0.2 gram of the sample with 5 c. c. sulphuric acid (1:3) in a test tube * * *. If the steel has 0.1 to 0.3 per cent of tungsten, a black insoluble residue will be found in the bottom of the tube. This black sediment forms also with small amounts of molybdenum and phosphorus. But on addition of 1 c. c. of nitric acid (1.20 sp. gr.) to such a solution the black entirely disappears if due to the presence of the two last-named elements. The black precipitate, if caused by a small quantity of tungsten, on addition of the nitric acid, changes to a yellow. If the amount of the latter is small, it is better to put the test tube back on the water bath and permit the tungstic acid to settle for two hours, when it can be seen plainly as a yellow spiral thread rising up through the solution by giving the test tube a rotary motion.

CHARACTERISTIC REACTIONS.

The following characteristic reactions of tungstate solutions have been used for the detection of tungsten:

HCl, HNO₃, and H₂SO₄ produce, in the cold, a white amorphous precipitate, H₁₂WO₄. H₂O, which is prevented by tartaric acid. Boiling changes it to the yellow anhydrous acid, H₂WO₄. The latter is nearly insoluble in dilute acids, but is soluble to an appreciable extent in HCl (concentrated) and forms a pseudosolution with pure water. (See Treadwell and Hall (112).)

Phosphoric acid produces a white precipitate, Na₅PO₄.12WO₄, which is soluble in excess of phosphoric acid as well as in other acids (112).

Boiling a solution of Na₅WO₄ with H₂WO₄ produces a metatungstate, Na₅W₂O₁₃, from which acids cause no precipitation. Boiling with an excess of acids produces the H₂WO₄ again which is precipitated.

(NH₄)₂S gives no precipitate from an alkaline tungstate solution, but if acidified afterwards, the light-brown WS₃, which is insoluble in
HCl, comes down but redissolves in ammonium sulphide, and forms pseudosolutions in pure water.

When reducing agents—such as Zn, Al, Sn—are added with HCl to a tungstate solution, they cause the reduction of WO₃ first to blue and then to brown.

SnCl₂ produces a yellow coloration at first, but on the addition of HCl and warming, the blue color is formed.

Zinc subsulphide (formed by treating a sulphite with zinc) reduces tungstates to a deep brown compound, a deep blue being produced when small quantities are present. (See Ohly (85).)

When a few drops of a saturated solution of HgNO₃ solution, 1 c.c. of HCl, and an excess of KI are added to a neutral tungsten solution a blue color is produced, the test being of the same order of delicacy as the ordinary SnCl₂ test. (See Kafka (62).) Pozzi-Escot (90) has disputed the delicacy of this test.

HgNO₃ precipitates white mercurous tungstate from neutral solutions.

Lead acetate precipitates white lead tungstate from neutral solutions.

TiCl₃ reduces tungstic acid, giving a blue oxide that remains in colloidal suspension in dilute acid solutions. The presence of V, P, or Mo interferes. (See Travers (108).)

Heath (42) gives the following test:

Add 5 to 10 c.c. of glacial acetic acid to 15 c.c. of the acidified tungstate in a test tube and then add slowly down the side of the tube 8 to 12 c.c. of the test solution made by mixing 5 grams CuSO₄ in 15 c.c. H₂O, 5 grams SnCl₂ in 10 c.c. H₂O and 2 grams KI in 10 c.c. H₂O, and dissolving the precipitate formed in NH₄OH (100 c.c. or more). A blue-white precipitate is formed. If tungsten is present a characteristic red ring will appear below the precipitated solids. The usual metals present in tungsten ores do not interfere.

Certain organic compounds—cinchonine, quinine, benzidine hydrochloride, etc.—precipitate tungsten from slightly acid solution.

The finely powdered ore gives the following tests:

Salt of phosphorus bead: Colorless in oxidizing flame, blue in reducing flame, becoming red on the addition of a little FeSO₄. On long blowing or with tin on coal it becomes a dark green.

Borax bead: Colorless to yellow, hot; colorless, cold in the oxidizing flame; colorless to yellow, hot; yellowish-brown, cold in the reducing flame; it can be flamed opaque-white.

Boiled with HCl and tin or zinc, the blue color is formed.

WO₃ (free from MoO₃) is mixed with a few crystals of uric acid and a few drops of NaOH solution added, a blue color shows the presence of tungsten. (See Frabot (34).)

A phenol solution added to a solution of H₂SO₄ containing tungsten develops a red color, whereas a quinol solution gives a violet color under the same conditions. (See Defacqz (24).)
SEPARATION OF TUNGSTEN FROM THE ELEMENTS FOUND OR ASSOCIATED WITH IT IN ORES OR COMMERCIAL ALLOYS.

GENERAL SEPARATIONS.

A method of separating tungsten which holds good in most cases is as follows:

The material to be examined is treated by one of the methods given in "Method of solution or decomposition of ores and alloys" (p. 132). Twenty-five c. c. of HNO₃ or HCl is added and the material evaporated to pastiness. A little acid is added and then 50 c. c. of water, after which the WO₃ is filtered off and washed with acidulated water. To recover tungsten from the filtrate, it is heated nearly to boiling and 5 to 6 c. c. of cinchonine solution—25 grams of cinchonine dissolved in 200 c. c. of 1:1 HCl—is added. After settling overnight the precipitate is filtered off, washed with dilute cinchonine solution, and ignited to WO₃. In dilute acids WO₃ is somewhat soluble, and with phosphorus, arsenic, or silica forms compounds that are readily soluble in acid solution. Cinchonine removes tungsten under these conditions.

As the above process sometimes fails to give a quantitative separation, the following methods may be required for the isolation of tungsten:

ARSENIC AND PHOSPHORUS.

The oxides of arsenic and tungsten are treated with 15 grams of CuCl and 150 c. c. of HCl and distilled, with the addition of more HCl; distillation is repeated; 10 grams of KOH is added and the material is heated and cooled; more HCl is then added and another distillation conducted. (See Hilpert and Dieckmann (45).)

Phosphoric acid (D. 1.7) is added to a solution containing the arsenic and tungsten to form a tungsten complex, and CuBr and KBr or CuCl and KBr are added as a reducing agent, the arsenic being removed in one distillation. (See Hilpert and Dieckmann (46).)

Hinrichsen (47) precipitated phosphorus from a solution containing tungsten by the addition of tartaric acid and ammonium molybdate. Von Knorre (116) obtained a perfect separation of tungsten from phosphorus by adding HCl to 300 to 400 c. c. of the solution until acid to methyl orange and 3 c. c. in excess, then precipitating the tungsten in boiling solution with toluidine hydrochloride, cooling, filtering, and igniting to WO₃, which is fused with Na₂CO₃, extracted with water, acidified and precipitated as before, the WO₃ being free from phosphorus.

Both arsenic and phosphorus may be precipitated away from tungsten by cold magnesia mixture in an ammoniacal solution. (See Scott (102), Gooch (38), Gibbs (37), and Kehrmann (65).)

Dewar (26) used the above method in his quantitative scheme by precipitating the tungsten and phosphorus from neutral solution with
HgNO₃, igniting to the oxides (by the addition of HNO₃); then fusing with Na₂CO₃, leaching with water, making acid with HCl, boiling off CO₂, neutralizing with NH₄OH, and precipitating with magnesia mixture.

**SILICA.**

Silica is removed from WO₃ by heating the mixture in a platinum dish with H₂SO₄ and HF, volatilizing the silica. To remove the last traces of H₂SO₄ from this treatment the dried residue is again ignited with ammonium carbonate. Although Corti (19) says that WO₃ is volatilized by the action of H₂SO₄ and HF, Arnold (2) has shown that the loss is not due to volatilization, but to a mechanical driving off of the fine particles of WO₃, which can be prevented by the use of tall, well-covered crucibles for the ignition. The WO₃ left after the removal of SiO₂ by treatment in the HF is appreciably soluble in dilute acids. This prevents washing the WO₃ residue in the acid solutions. (See Hutchin (51).)

The WO₃ is dissolved in NH₄OH or (NH₄)₂CO₃ solution, leaving the SiO₂ behind. Corti finds that this does not eliminate all the silica.

**TIN.**

After the silica has been removed from the tungstic oxide residue, six to eight times its weight of ammonium chloride (free from nonvolatile matter) is mixed with it and the chlorides driven off by heat. This is repeated three times, and the residue of WO₃ weighed, after which more ammonium chloride is added, and the ignition is repeated. This procedure is continued until there is no further loss in weight. (See Scott (102) and Rammelsberg (92).)

Talbot (106) removed tungsten from tin and antimony by fusing the mixed oxides with 12 times their weight of KCN in a porcelain crucible, the soluble tungstic being leached out with water, boiled with HNO₃ (in a hood) to drive off the cyanogen compounds, and precipitated by the usual methods. Tin and antimony remained in the melt as metals. The KCN fusion may be leached with iron sulphate and the tin removed. (See Setlik (103).)

Treadwell (110) removed tin free from tungsten electrolytically from a NaOH-Na₂S solution with a current density of 1.7 to 0.5 amperes and a voltage of 1.7 to 2.3 and a temperature of 50 to 60°.

Dittler and Von Graffenried (27) precipitated tin free from tungsten by passing H₂S through a hot acid solution containing sodium phosphate, washing with ammonium acetate. The tungsten went into the filtrate as soluble phosphotungstic acid.

Travers (109) fused the mineral with Na₂SO₃, took it up with water, diluted it, and made it slightly acid, the tin then coming down, free from tungstic., as the sulphide. Another method used by him was to fuse with Na₂SO₃ and extract with aqua regia, leaving most of the tungsten
as WO₃ and recovering the rest free from tin, but with a trace of iron, by adding enough NH₄OH to precipitate the iron, but not an excess. If no iron was present, 10 per cent was added. The tungsten is entrained with the Fe(OH)₃, which is removed by dissolving the washed precipitate with 50 per cent HCl, evaporating to dryness, and taking up with HCl.

Powell (89) fused the ore with bisulphate and extracted the tungsten with tartaric acid solution.

Donath and Müllner (28) fused with zinc dust strongly, igniting in a covered crucible for 15 minutes, boiling with dilute HCl, oxidizing with KClO₃, and diluting with water. After standing over night the WO₃ is filtered, leaving the tin in solution.

Campredon (14) dissolves tin with ferric chloride solution, leaving the tungsten.

**MOLYBDENUM.**

Hommel’s method is to digest the moist oxides of tungsten and molybdenum with concentrated H₂SO₄ and a few drops of dilute HNO₃ over a free flame for one-half hour, cool, dilute with three times its volume of water, filter, wash with 1:20 H₂SO₄, and then with alcohol. The residue is ignited as WO₃. (See Scott (102), and Ruegenberg (95).)

Rose (94) precipitated molybdenum by H₂S, keeping the tungsten in solution with tartaric acid.

The oxides of the two metals are heated to 250 to 270° C. in a porcelain boat with dry HCl gas passing over them; in from one and one half to two hours the molybdenum will have passed off as MoO₃·2HCl, leaving the tungsten in the residue. (See Pechard (87) and Debray (21).)

To a boiling solution of tungstate and molybdate add 20 c. c. of Mdivani’s solution—50 grams SnCl₂·2H₂O in 200 c. c. of HCl—for every 0.15 gram of WO₃ present, boil 3 minutes, filter, and wash with hot 5 per cent HCl solution free from molybdenum. Ignite to WO₃. (See Markbaker (78).)

Tungsten in the presence of MoS₂ is roughly separated by roasting gently for 10 minutes and extracting the MoO₃ with weak NH₄OH, leaving the tungsten, which is removed by a Na₂CO₃ fusion. (See Trautman (107).)

Most of the WO₃ is precipitated free from MoO₃ by boiling with HNO₃ and the filtered solution is evaporated and ignited, the mixed oxides being completely separated by boiling with a mixture of one part H₂SO₄ and five parts SeOCl₂, which dissolves the MoO₃ and leaves the WO₃. (See Merrill (82).)

(See paragraph 2 under “Tungsten-molybdenum steel”.)
VANADIUM.

Tungstic and vanadic acids are precipitated with HgNO₃ and HgO; the moist precipitate is dissolved in HCl, and the solution largely diluted; WO₃ is precipitated free from vanadium. (See Friedheim (36).)

Treat as by Pechard’s and Debray’s method under “Molybdenum” on page 141

TITANIUM.

The material is heated with K₂CO₃ and KNO₃; tungsten is dissolved out with water and precipitated with HgNO₃. (See Defacqz (22).)

The material is fused with Na₂O₂, and the tungsten is extracted with water, the titanium being insoluble. Small amounts of vanadium do not interfere, but larger quantities contaminate both portions. (See Fenner (31).)

CHROMIUM.

In mixtures of tungstates and chromates a quantitative separation is effected by acidifying slightly with HCl, boiling, cooling, reducing the chromate with SO₂, and precipitating the tungsten with benzidine hydrochloride. (See Von Knorre (117).)

MISCELLANEOUS.

Arnold (3) removed the H₂S metals in acid solution with H₂S, keeping the tungsten in solution as Na₂WO₄·C₂H₄O₄ by means of 3 or 4 grams of tartratic acid. The precipitation took place slowly in hot solution.

Tin and iron are removed as by Dittler and Von Graffenried on page 140. (See also Mdivani (79a).)

Iron, beryllium, aluminum, thorium, and lanthanum are removed by fusing with Na₂CO₃ and extracting the tungsten, the first three with boiling NH₄NO₃ and the others with boiling water. (See Wunder and Schapiro (122).)

Tungsten is separated from the bases by the distillation of tungsten chloride compounds formed by mixing the substance with KCl, heating to a dull red, and passing CCl₄ and CO₂ over it. The volatile part is collected in dilute HNO₃. In the presence of lead, glass wool prevents the passage of PbCl₂ into the receiver. (See Jannasch and Leiste (56).)

Bourion (11) passed chlorine with a little sulphur chloride over the substance, catching the volatile oxychlorides in water. He heated 45 minutes at 180 to 190° C.; 45 minutes at 220 to 250°; and then 5 to 15 minutes at 500° C.

Defacqz (23) heated the material to 600 to 900° C. in a current of hydrogen to complete reduction, and passed dry chlorine gas to
volatilize the chlorides of tungsten which were condensed and dissolved in weak NH$_4$OH.

McCay and Furman (79) separated elements from tungsten electrolytically, whereas Treadwell (110) outlines conditions for the separation of copper and tin from tungsten by similar means.

Hutchin (50) concluded that the precipitation of tungsten from slightly acid solutions with cinchonine separated it from arsenic and phosphorus but not from molybdenum.

**QUANTITATIVE ANALYSIS.**

**PROPOSED METHODS FOR DETERMINATION OF TUNGSTEN.**

In this section are included abstracts of most of the methods that have been proposed for the analysis of different materials for their tungsten content. These methods are not all recommended, but some may prove valuable. Selected methods are given below in full (pp. 156 to 167).

**GENERAL.**

**GRAVIMETRIC METHODS.**

The following methods have been used for the quantitative determination of tungsten:

**PRECIPITATION OF TUNGSTEN AS TUNGSTIC ACID.**

This method depends on the fact that tungstates change to tungstic acid on boiling with mineral acids. The precipitated tungstic acid is not completely insoluble in dilute acids, but if the filtrate be boiled again most of the tungsten will be thrown out of solution; sometimes a repetition of the treatment removes it all, but occasionally—as when silicic acid is present—the tungsten is not all precipitated by this method.

An equal volume of concentrated HCl is added to the tungstate solution obtained by one of the methods described on page 132 under the topic, “Method of solution or decomposition of ores”; the mixture is evaporated to dryness, heated at 120° C., and the residue treated with dilute HCl, boiled with water, filtered, washed with 5 per cent HCl or ammonium nitrate. The precipitate is ignited and weighed as WO$_3$; the filtrate contains some tungsten, which is removed by repeating the evaporation and acid digestion. Silica is nearly always found as a contaminant and is removed as indicated under “Separation of tungsten from silica” (p. 140); that is, ignition with HF and H$_2$SO$_4$, or extraction with NH$_4$OH. This method has been recommended by Setlik (103), Helmhacker (43), Fieber (32), Pfordten (88), Hutchin (50), Scott (102), Low (76), Mennicke (81), and others, and has been used as a basis for other methods.
PRECIPITATION OF TUNGSTEN AS MERCURIC TUNGSTATE.

Twenty-five c. c. of the alkaline tungstate solution is made neutral to litmus with HNO₃, boiled to remove the CO₂, and an excess of a solution of HgNO₃ containing precipitated HgO in suspension is added, the precipitated HgWO₄ being washed with a weak solution of HgNO₃, dried, ignited, and weighed as WO₃ (1 gr. WO₃ = 0.792 gr. W). This method has been advocated by Pfordten (88), Defacqz (22), Desvergnes (25), and Watts (118), and is included in many textbooks.

Berzelius (8) stated that the precipitation of tungsten as mercuric tungstate by the addition of mercuric nitrate to a neutral solution was complete. Johnson (57) refused to use this method for the determination of tungsten, because phosphorus, aluminum, molybdenum, or vanadium were precipitated under the same conditions; and when a sodium carbonate fusion was used to decompose the ore it was difficult to wash the sodium salts from the mercuric tungstate. The presence of tin interfered also. Guglialmelli and Hordh (39) stated that HgNO₃ failed to precipitate the tungsten completely from a solution of wolframite on account of the formation of silico tungstic complexes, the mercury salt formed with silica and tungsten being soluble in warm slightly acidulated water.

PRECIPITATION OF TUNGSTEN AS TUNGSTATES OF OTHER METALS.

Brearley (12) added 2 to 3 grams of NH₄NO₃ to the alkaline tungstate solution, made it slightly acid with HNO₃, boiled, added a slight excess of NH₄OH and lead acetate, boiled briskly, filtered, and weighed as lead tungstate. Isbotson and Brearley (54) changed the lead tungstate to WO₃ by boiling with HNO₃ and weighed as WO₃.

Smith and Bradbury (105) suggested the use of barium, lead, and cadmium to precipitate the tungstates. These tungstates are easily washed.

PRECIPITATION OF TUNGSTEN WITH ORGANIC REAGENTS.

The first record of the use of cinchonine in the analysis of tungsten ores is credited to Cremer (20). He dissolved the material as in paragraph 15, “Ores and minerals” (p. 134), heated the solution, and added an excess of a solution of cinchonine in HCl (1:1), boiled, filtered, washed with a dilute cinchonine solution, dried, ignited, weighed, dissolved the WO₃ with NH₄OH solution, and weighed the residue. The difference in weight gave the WO₃. Forty-eight hours was required for the cinchonine precipitate to settle.

Hutchin (50) found the best conditions for the precipitation of tungsten with cinchonine to be a minimum of acidity, a volume of 100 to 200 c. c., a warm solution, and standing overnight. The precipitate should be washed with a weak solution of cinchonine in
HCl. Molybdenum is precipitated under the same conditions, but arsenic and phosphorus do not interfere. The precipitation of tungsten from the iron liquors of an acid attack is seldom complete.

Jannasch and Bettges (55) precipitated tungsten from a solution containing free HCl with hydrazine chloride, or with an ammoniacal solution of hydrazine sulphate at 70 to 80° C.

Von Knorre (116) made the solution neutral to methyl orange with HCl and added 3 c. c. in excess. He then precipitated the tungsten with an excess of benzidine hydrochloride or toluidine hydrochloride in the boiling 300 to 400 c. c. solution, cooled, filtered, ignited, fused with Na₂CO₃, extracted with water, acidified, and precipitated the tungsten as before. The second precipitation removed traces of phosphorus, if any was present in the material examined.

Tschilkin (113) added the solution containing tungsten to a slightly acidified HCl solution of alphanaphthylamine, precipitating 2(C₁₆H₁₈N).5WO₃.3H₂O. After three hours this precipitate was filtered, washed, and ignited to WO₃.

Kafka (63) precipitated tungsten with cumidine.

Gutbier and Weise (40) dissolved the WO₃ obtained by other methods in the smallest quantity of NaOH solution, diluted to 150 c. c. with boiling water, made acid with CH₃COOH, heated to boiling, stirred vigorously, and added an excess of Busch's nitron acetate solution. When cooled and settled, the material was filtered and washed with 4 per cent nitron solution, then dried and ignited to V₂O₅ at 800° C.

Lefort (72) precipitated tungsten from a tungstate solution acidified with HNO₃, with quinine sulphate or acetate; the precipitate was allowed to settle, filtered, washed with cold water, and ignited to WO₃ with the addition of HNO₃ to complete the ignition.

Mdivani (79a) precipitated tungsten as WO₃ by the addition of a solution of stannous chloride (5 grams stannous chloride in 20 c. c. HCl), boiled two minutes, washed, dried, and ignited to WO₃. The precipitate is absolutely free from tin, and iron does not interfere.

**Miscellaneous.**

Although gravimetric methods are preferable for exact results, the following volumetric methods have been used for the determination of tungsten.

Freih (35) described Zimmermann's method: A solution containing tungsten was heated, and 70 to 80 c. c. of HCl (27 per cent) and 14 to 15 grams of zinc was added. When the reduction was completed, and a red color appeared, the solution was cooled, and an excess of KMnO₄, manganese sulphate, and H₂SO₄ was added. An excess of
standard ferrous sulphate was introduced, the excess being titrated with KMnO₄. He obtained 78.93 per cent WO₃ as compared with 78.91 per cent by other methods, and 6.89 per cent instead of 6.886 per cent.

Knecht and Hibbert (67) reduced in the same manner to WO₂ and after passing CO₂, titrated with a standard iron alum solution, using KCNS as an indicator; the disappearance of the blue color may also be taken as the end point. Good results were obtained in the presence of large quantities of iron. The reactions were as follows:

\[ \text{WO}_3 + 4\text{HCl} + \text{H}_2 = \text{WCl}_4 + 3\text{H}_2\text{O}. \]
\[ \text{WCl}_4 + 2\text{FeCl}_3 = \text{WCl}_6 + 2\text{FeCl}_2. \]

Kuklin (69) reduced as above and titrated with KMnO₄.

Hundeshagen (49) separated the WO₃ by the usual manner, dissolved in an excess of normal NaOH, and titrated the excess with standard acid, using phenolphthalein as an indicator.

Schmidt (99), however, stated that the results were uncertain, changing with the conditions. Nevertheless, Lind and Trueblood (74) used the same method for the determination of tungsten in steel; and Herting (44) suspended the WO₃ in hot water and titrated directly with a standard alkali. Both used phenolphthalein as the indicator. Bartonec (7) used Lind and Trueblood's method.

Kanchew (64) titrated the precipitate of benzidine tungstate, suspended in water, with a standard NaOH solution, starting at 60° C. and at the end heating to 100° C., using phenolphthalein as the indicator. He claimed this method to be within 0.1 per cent.

Ekeley and Kendall (29) dissolved the isolated WO₃ with C₂H₅NH₂ of known strength, and titrated back with oxalic acid, using phenolphthalein as an indicator; or an excess of oxalic acid was added and this was titrated with C₂H₅NH₂.

\[ 2\text{C}_2\text{H}_5\text{NH}_2 + \text{H}_2\text{O} + \text{WO}_3 \rightarrow (\text{C}_2\text{H}_5\text{NH}_3)_2\text{WO}_4. \]

COLORIMETRIC METHODS.

No colorimetric method has been thoroughly tested, but Travers (108) gave a tentative scheme. The reduction of H₂WO₄ by TiCl₃ gave a blue oxide which was held in suspension under certain conditions. This might be used as a method for the determination of tungsten. Vanadium, phosphorus, and molybdenum interfere and must be removed.

Schoeller and Powell (100) outlined a tentative method. The solution freed from metals of the (NH₄)₂S and the H₃S groups should be reduced to form the blue oxide.

NEW METHODS.

The following new methods have not been tried out at the Bureau of Mines laboratories:

Erlich (30a) treats W with HCl and FeCl₃ followed by NH₄NO₃. The weighed residue is fused with NaHSO₄, the melt is treated
TUNGSTEN.

with a mixture of \((\text{NH}_4)_2\text{CO}_3\) solution and bromine, and the residue is weighed. The difference between the weights of the residues gives, by calculation, the \(\text{WO}_3\) in the sample.

Löwy (77a) analyzes ferrotungsten by a modification of Low’s method, decomposing the sample by heating with \((\text{NH}_4)_2\text{SO}_4\) and \(\text{H}_2\text{SO}_4\) following by extraction with water; precipitation of \(\text{H}_2\text{WO}_4\) by boiling with \(\text{HCl}\); removal of \(\text{Fe}\) by \(\text{NH}_4\text{OH}\) followed by fusion with \(\text{Na}_2\text{CO}_3\) and removal of \(\text{SiO}_2\) by treatment with \(\text{HF}\).

Enos (30) uses a modification of Zimmermann’s volumetric method, reducing by means of a Jones reductor.

Fiorentine (32a) determines \(\text{W}\) volumetrically by adding a known excess of standard acid-lead acetate solution to the hot tungstate solution that has been acidified with acetic acid and neutralized with \(\text{NH}_4\text{OH}\) and then determining the excess of lead in the solution by means of a standard ammonium molybdate solution, using a fresh tannin solution as an outside indicator.

Lavers (69a) developed a volumetric method very similar to the one given by Fiorentine. He dissolved cinchonine tungstate in ammonium acetate, added a known volume of lead acetate solution, and titrated the excess with standard ammonium molybdate solution.

The colorimetric method outlined by Schoeller and Powell (100) has been developed by Heath (41a) who reduces a \(\text{H}_2\text{SO}_4\) tungstate solution by the addition of a “test solution” containing \(\text{SnCl}_2\), \(\text{SnCl}_4\), \(\text{H}_2\text{PO}_4\), and \(\text{CH}_3\text{COOH}\) and compares its color with that obtained from a standard \(\text{W}\) solution.

Lavers (69a) has also experimented with this method, removing \(\text{Mo}\) with \(\text{H}_2\text{S}\) because it interferes with the color reaction.

ORES AND SLAGS.

GRAVIMETRIC METHODS.

PRECIPITATION OF TUNGSTEN AS TUNGSTIC ACID.

Rusag (98) treated the ore with \(\text{HCl}\) and \(\text{HF}\) as described under “Ores and minerals,” paragraph 4 (p. 133). The \(\text{H}_2\text{WO}_4\) was extracted with \(\text{NH}_4\text{OH}\) and \(\text{NH}_4\text{Cl}\), filtered, taken to dryness, and ignited three times with \(\text{NH}_4\text{Cl}\) to remove any tin, the residue being weighed as \(\text{WO}_3\).

Coblentz (18) treated the ore by the method discussed under “Ores and minerals,” paragraph 1 (p. 132), the ammoniacal tungstate solution being evaporated and ignited to \(\text{WO}_3\).

Watts (118) used a similar method, but extracted the tungsten with 15 c. c. of an ammonia solution—400 c. c. of \(\text{NH}_4\text{OH}\), 2,000 c. c. of \(\text{H}_2\text{O}\), and 20 c. c. of \(\text{HCl}\)—instead of using \(\text{NH}_4\text{OH}\) alone.

Robinson (93) decomposed the ore as described in paragraph 4 under “Ores and minerals” (p. 133), then filtered and removed the
HF by boiling to 10 c. c. with HNO₃ and HCl, the WO₃ being recovered by dilution, filtration, and ignition.

Hutchin (51) treated the ore in a manner similar to that described in paragraph 4 under “Ores and minerals;” the filtrate being evaporated, ignited to WO₃, and weighed. The residue of silica was extracted with NaOH; then the solution was filtered, neutralized with HNO₃, and the tungsten precipitated with HgNO₃, filtered, washed, ignited, and weighed as WO₃.

Chesnau, Bourion, and Nicolardot (16) heated the ore with NaOH solution, added bromine water, neutralized with HCl, filtered, passed H₂S through the slightly acidified filtrate, filtered, and recovered tungsten from the filtrate by boiling with HNO₃ to throw down H₂WO₄.

Bornträger (10) gave a rough rapid method. He fused with Na₂CO₃, extracted with water, and then dried and weighed the residue. The difference, he says, "gives the tungsten within 5 per cent." For a more accurate method he treated as did Cobenzl (p. 147), but precipitated H₂WO₄ from the ammoniacal solution with acid, filtered, ignited, and weighed as WO₂.

Sheda (104) treated the ore with sulphur as in paragraph 14 under "Ores and minerals;" evaporated to 3 c. c., extracted with dilute HCl (the H₂WO₄ being filtered off and dissolved with a solution containing 30 c. c. of NH₄OH, 7 grams (NH₄)₂CO₃, and 250 c. c. of water), evaporated to dryness, ignited, and weighed as WO₃.

Footo and Ransom (33) decomposed high-grade ores by heating with CaCO₃ and NaCl as in paragraph 13 under "Ores and minerals" (p. 134), digested with HCl, HNO₃, etc., dissolving the H₂WO₄ in NH₄OH, evaporating, igniting, and weighing as WO₃.

Low (76) gives several methods. In one method he treats the ore with HCl and HF until decomposed, filters, and precipitates H₂WO₄ by boiling with HCl and HNO₃, extracts the tungsten with NH₄OH, filters, evaporates, ignites, and weighs as WO₃. In another process the ore is fused with Na₂CO₃, extracted with water (the fusion being repeated until the disintegration of the ore was complete) evaporated repeatedly with HNO₃ to throw down the H₂WO₄, filtered, washed with NH₄NO₃, ignited, and the SiO₂ removed with HF. The method used in Low's laboratory is a modification of the ordinary tungstic acid precipitation. For ores and siliceous material, he heats with Na₂SO₄ and H₂SO₄ as in paragraph 10 under "Ores and minerals;" the cooled melt is treated with 25 c. c. of HCl and 10 c. c. of HNO₃ and boiled to 20 c. c.; 50 c. c. of hot water is added, and, after boiling and settling, the H₂WO₄ is filtered off and washed with 1:10 HCl; the filtrate is reserved. The H₂WO₄ on the filter is dissolved with a mixture of 2 parts of wood alcohol and 1 part of NH₄OH, washing several times,
the filtrate is evaporated to dryness and ignited to WO$_3$; the residue is ignited, and extracted with strong NaOH solution, heating for a short time. This solution is dilute, filtered, acidified with HCl, and added to the reserved filtrate from the first procedure. The combined filtrates are heated, and 5 to 6 c.c. of a solution of 25 grams of cinchonine in 200 c.c. of 1:1 HCl is added. After digesting some time, hot, the cinchonine precipitate is filtered, washed with weak cinchonine solution, and ignited to WO$_3$. To remove the silica, the combined WO$_3$ residues are treated with HF.

Calcium tungstate and high-grade scheelite are treated by a slightly different method. The ore is fused with NaKCO$_3$, extracted with water, and the H$_2$WO$_4$ precipitated by boiling with acid, the residue is filtered off, washed with dilute acid, and ignited to WO$_3$. The tungsten is removed from the filtrate by precipitation with cinchonine as before, and the silica is removed by treating with HF.

Mennicke (81) gave the method of Margeritte. This method uses H$_2$SO$_4$ as the precipitant for H$_2$WO$_4$, which is washed with alcohol and ignited to WO$_3$.

Johnson (57) treated the ore with HCl and KClO$_3$ as given in paragraph 2, under "Ores and minerals" (p. 132), extracted with dilute HCl, recovering the tungsten in the filtrate with cinchonine, treated the residue with HF and H$_2$SO$_4$, ignited, and weighed. This residue was fused with Na$_2$CO$_3$ and extracted with water; when the filtrate was green, a little alcohol was added, and the solution warmed to precipitate manganese. After filtration the residue was ignited and its weight deducted from that of the previous ignition. To correct for aluminum or tin, the filtrate from the Na$_2$CO$_3$ fusion was acidified with HCl, then made alkaline with NH$_4$OH, warmed, filtered, washed with NH$_4$NO$_3$ solution, ignited, and weighed. Tantalum and niobium are removed and hence do not interfere.

Ledoux & Co. (70) give two methods, which are described in full under "Ammonia solution of tungstic acid" and "The hydrofluoric difference method," on pages 156 to 164.

**Precipitation of Tungsten as Mercurous Tungstate.**

Bullnheimer (13) fused a low-grade ore with Na$_2$O$_2$ and NaOH as in paragraph 12, under "Ores and minerals" (p. 134). To the water extract was added NH$_4$NO$_3$ to precipitate the silica or tin and Mg(NO$_3$)$_2$ to precipitate arsenic or phosphorus, and after settling and filtering the tungsten was recovered from the filtrate with HgNO$_3$. After igniting to WO$_3$, the residue was ignited with NH$_4$Cl, to remove any molybdenum that might be present.

Dewar (26) roasted the ore to remove sulphur, if present, then treated with HF and H$_2$SO$_4$, the residue being fused with NaKCO$_3$,
leached, and filtered. The filtrate was neutralized with HNO₃, boiling off CO₂, and the tungsten was precipitated with HgNO₃ together with phosphorus, if any was present. The precipitate was filtered, washed, ignited, fused with Na₂CO₃, extracted with water, and boiled with HCl, the phosphorus was removed with magnesia mixture, and the tungsten was precipitated from the filtrate again with HgNO₃, filtered, ignited to WO₃, and weighed.

Hutchin and Tonks (52) give four methods for the determination of tungsten in high-grade ores, all depending on the precipitation of tungsten with HgNO₃. The first method decomposes the ore with acids, extracts with NH₄OH, evaporates to dryness, ignites to WO₃, and weighs. The residue from the NH₄OH leach is extracted with NaOH solution, and the tungsten in this neutralized filtrate is precipitated with HgNO₃, filtered, ignited, and weighed as WO₃. The second method treats with acids, extracts the residue with NaOH, and recovers the tungsten from the neutralized extract with HgNO₃. The third method digests the ore with NaOH and proceeds as above. The fourth method fuses with NaOH and Na₂O₂, extracting with water and recovering the tungsten with HgNO₃.

Low (76) gives a method in which the ore is treated with HF, evaporated to dryness, and digested with dilute HNO₃. The ignited residue is fused with Na₂O₂ and NaOH, extracted with water, acidified with HNO₃, made alkaline with NH₄OH to precipitate the silica, filtered, and the tungsten precipitated with HgNO₃ from the neutralized solution.

**PRECIPITATION OF TUNGSTEN WITH ORGANIC REAGENTS.**

Guglielmelli and Hordh (39) recommend the process of von Knorre (116) for the analysis of wolframite. He precipitates the tungsten from a slightly acid (H₂SO₄) solution of tungsten with benzidine hydrochloride at ordinary temperature, ignites to WO₃, and removes silica by treating with HF and H₂SO₄. This precipitation is quantitative even in the presence of silicotungstic complexes, but molybdenum is precipitated at the same time.

**SPECIFIC GRAVITY METHODS.**

Whenever the ore is fairly uniform and the gangue of nearly constant composition, the approximate quantity of tungsten present can be determined by the specific gravity method. This method was originated by the Wolf Tongue Mining Co. and was used successfully in the Boulder district of Colorado; a similar scheme was utilized at Atolia, Calif.

The specific gravity of an ore is determined quickly by dividing the weight of a quantity that will displace a certain amount of water—200 grams is satisfactory—by the weight of the water. Knowing the
specific gravity and composition of several samples, a table may be made that will give the quantity of tungsten for each specific gravity determined. This table is dependent, of course, on the individual ore examined. Runner (96) gives a detailed treatise on this subject, showing the ratio of specific gravity to composition in different ores.

STEEL, METALLIC TUNGSTEN, AND ALLOYS.

GRAVIMETRIC METHODS.

PRECIPITATION OF TUNGSTEN AS TUNGSTIC ACID.

In tungsten powder.—Arnold (3) treated tungsten powder or tungsten metal as given in paragraph 2 under "Tungsten powder" (p. 132); that is, with a mixture of NH₄OH and H₂O₂, etc., throwing out the H₂S metals in the presence of tartaric acid; this required heating and continued action of H₂S for some hours. The solution containing tungsten was filtered off, made alkaline with NH₄OH, and poured slowly into a boiling HCl solution. The H₃WO₄ settled out and was washed by decantation. The filtrate and washings were evaporated to dryness; the residue was partly ignited with the addition of HNO₃ and KClO₃, and the tungsten was extracted with water as K₂WO₄. The tungsten was recovered as H₂WO₄ by boiling with acid, and was freed from silica with HF and H₂SO₄, or by fusing with KHSO₄ according to the method of Berzelius (8).

Johnson (58) gives two methods for the determination of tungsten in tungsten powder. The rapid method is a modification of one given by Arnold and Ibbotson (4). A gram sample is dissolved in HF and HNO₃ as shown in paragraph 1 under "Tungsten powder" (p. 134); then 10 c. c. of H₂SO₄ is added and evaporated to fumes, cooled, 10 c. c. of HCl and 10 c. c. of water is added, and then the material is boiled, filtered, and washed free from iron with 1:10 HCl. The residue is ignited, weighed, fused with KHSO₄, cooled, and extracted with (NH₄)₂CO₃, filtered, and washed with (NH₄)₂CO₃, and ignited. Its weight is then taken from that of impure WO₃. If the amount of SiO₂ is large or of a yellow tinge, it is fused again with KHSO₄, extracted with (NH₄)₂CO₃, etc., as before. The results are 0.1 to 0.2 per cent lower than those obtained by the following method:

In his second method Johnson fuses with Na₂CO₃ and KNO₃ as indicated in paragraph 3 under "Tungsten powder" (p. 134), the water extract is acidified with HCl, evaporated to dryness, treated with 10 c. c. of 1:10 HCl, and warmed to dissolve the iron; 200 c. c. of water is added and heated for 30 minutes; and the H₂WO₄ is filtered and washed free from iron with dilute HCl. The filtrate is evaporated to dryness, digested, filtered, and washed as before. To the second filtrate and washings a solution of cinchonine in 1:1 HCl is added; and after settling, the tungsten precipitate is filtered, washed, ignited, and
added to the other tungsten precipitates. The impurities are removed, as in the previous method, by fusion with KHSO$_4$ and extraction with (NH$_4$)$_2$CO$_3$.

Ibbotson and Brearley (54) oxidized the tungsten powder by heating in platinum and treated it with HF, the residue being boiled with NaOH. HCl was then added and the solution was largely diluted to precipitate the H$_2$WO$_4$.

In tungsten steel.—Van Duin (114) used the method of Ziegler as modified by Classen (17). The sample is treated with HNO$_3$, and the iron salts filtered off. The filtrate is taken to dryness several times with HCl on a water bath, the final dried residue being taken up with dilute HCl, filtered, and washed. The combined residues are ignited and treated with HF and H$_2$SO$_4$ for the removal of silica.

M’Kenna (83) and Zinberg (124) used substantially the same method.

Kern (66) treated with aqua regia, took to dryness, and extracted with HCl and water. The residue was extracted with NH$_3$OH and then boiled with NaOH and filtered. HCl was added to the filtrate and the H$_2$WO$_4$ precipitated by boiling was filtered off, ignited, and weighed as WO$_3$.

Bartonec’s method (7) differed in that the first evaporation was not taken to dryness, and the WO$_3$ was dissolved with (NH$_4$)$_2$CO$_3$ instead of with NH$_3$OH.

Lehalleur (73) changed Kerr’s method by adding a separation of silica by means of HF after the final recovery of the WO$_3$.

Parry and Morgan (86) treated the steel with aqua regia, evaporating to dryness, but not heating. The residue was extracted with NH$_3$OH, filtered, evaporated, ignited, and weighed as WO$_3$.

Wolter (121) fused the metal with KHSO$_4$, as shown in paragraph 6 under “Tungsten steel” (p. 135), extracted with water, boiled with HCl to throw down the tungsten, filtered, washed with NH$_3$NO$_3$, evaporated to dryness, and ignited to WO$_3$. The tungsten was recovered from the filtrate by evaporating to dryness, heating at 120° C., extracting with dilute HCl, filtering, washing, and igniting. The silica was removed from the combined precipitates by treating with HF.

Fieber (32) used the methods of Fresenius. He treated the metal with HCl, fused the residue with NaKCO$_3$, and extracted with water. This filtrate with the HCl solution was evaporated to dryness, extracted with dilute HCl, and the tungsten recovered from the filtrate by repeated evaporations with HCl. The WO$_3$ thus obtained was fused with Na$_2$CO$_3$, leached with water, neutralized with HNO$_3$, and the tungsten precipitated with HgNO$_3$. The ignited WO$_3$ was treated with HF to remove silica.
Herting (44) treated the steel with aqua regia, evaporated twice with HNO₃, dehydrated at 120° C., and took up with dilute HNO₃. The residue was fused with Na₂CO₃, extracted with water, filtered, evaporated to 2 c. c. with HNO₃, taken up with HNO₃ and water, and filtered. The silica was removed by treating the ignited residue with HF.

Carnot and Goutal (15) dissolved the iron away from the tungsten with cupric potassium chloride in an atmosphere of CO₂, the residue being treated by the usual methods.

Johnson (59), (60) gives three methods for the determination of tungsten in steel. The first is for a high-tungsten steel containing manganese, chromium, phosphorus, and sulphur. The sample is treated with a mixture of HCl and HNO₃ as given in paragraph 4 under "Tungsten steel" (p. 135), and evaporated to 15 c. c.; then 50 c. c. of HNO₃ is added and evaporated to dryness, followed by ignition at a dull-red heat. Fifty cubic centimeters of HCl is added to the cooled residue and the substance boiled to 15 c. c. After diluting with 30 c. c. of water, the H₂WO₄ is filtered off and washed with 1:20 HCl, the filtrate and washings being reserved. The residue is ignited, treated with 2 or 3 drops of H₂SO₄ and HF, evaporated again, and ignited, leaving WO₃, Fe₂O₃, and Cr₂O₃. The reserved filtrate is evaporated until basic iron forms on the margin of the solution, 20 c. c. of water is added, and the substance is filtered and washed free from iron with 1:20 HCl. This residue is added to that of the WO₃, Fe₂O₃, and Cr₂O₃, ignited, and weighed. This is then fused with Na₂CO₃, extracted with water, washed, and the weight of the ignited residue deducted from the weight of the combined oxides. If the filtrate from this fusion is yellow, chromium is determined in it volumetrically, and the weight of the crude WO₃ corrected for its Cr₂O₃ content. The SiO₂, Fe₂O₃, and Cr₂O₃ may be removed as given in the method for the determination of tungsten in tungsten powder. The second method, to be used for low tungsten-chromium steel, evaporates 3 grams of the steel with 60 c. c. of HNO₃ to dryness, ignites, treats with HCl, and finishes as in the preceding method. The third method is for use when tungsten and chromium only are to be determined. The metal is treated with H₂SO₄ and HNO₃ as given in paragraph 3 under "Tungsten steel" (p. 135), diluted to 200 c. c., boiled, filtered, and washed free from iron with dilute H₂SO₄. Cinchonine is added to the hot filtrate and washings and, after settling, the tungsten precipitate is filtered off, ignited, and with the main residue freed from impurities with bisulphate or carbonate fusions as in the method for high-grade steel.

Lord and Demorest (75) use a method which is a combination of several others. The sample is dissolved in HCl and HNO₃ as described in paragraph 1 under "Tungsten steel" (p. 134), 5 c. c. of HNO₃.
is added, and the material evaporated to 10 c. c. Fifty cubic centimeters of water is then added and after boiling the residue is filtered off and washed free from iron with 5 per cent HCl. The filtrate is evaporated to hard dryness, heated with 15 c. c. HCl, diluted to 50 c. c., filtered, and washed. The two residues are ignited at a dull-red heat, treated with H₂SO₄ and HF to remove silica, weighed, and fused with Na₂CO₃. The melt, extracted with water, is filtered, and the weight of the ignited impurities deducted from that of the impure WO₃.

Auchy (5) called the quantity of iron carried down by the H₂WO₄ a constant for tungsten steels which have approximately the same content of tungsten, thus saving time in the analysis.

Kuczynski (68) treated steel with 5 c. c. of HNO₃, 2 c. c. of water, 5 grams of NH₄F and 2 to 3 drops of H₂SO₄, heating to a clear solution. Two or three c. c. of H₂SO₄ was then added, and the HF removed by evaporation. The tungsten was then recovered by evaporation with acids, and the WO₃ dissolved in NH₄OH, evaporated to dryness, and ignited.

In ferrotungsten and alloys.—Ibbotson and Brearley (54) dissolved in HCl and HNO₃, evaporated till the H₂WO₄ began to separate, and diluted to twice the volume. When boiled, the H₂WO₄ precipitated and was filtered off and purified.

Fieber (32) in his short method decomposed the metal with bromine as in paragraph 6 under “Ores and minerals” (p. 133), driving off the bromine by boiling with acid (the tungsten was removed by evaporating with HCl), and extracting the iron with dilute HCl. The residue, moistened with NH₄NO₃, was ignited and weighed as WO₃, silica being removed by treatment with H₂SO₄ and HF.

Namias (84) oxidized the alkaline or carbonate solution with bromine and evaporated several times with HCl. The precipitate was dissolved in NH₄OH and again precipitated with HCl, washed with NH₄NO₃, ignited, and weighed as WO₃.

Preusser (91) oxidized the metal by heating and then treated repeatedly with aqua regia, evaporated, heated at 120°C., extracted with dilute acid, and filtered off the residue. This was fused with Na₂CO₃, extracted with water, acidified, evaporated to dryness, washed with NH₄NO₃, extracted with NH₄OH, filtered, evaporated, ignited to WO₃, and weighed.

Ziegler (123) improved the preceding method by first roasting with NH₄NO₃ to expedite the oxidation.

Wdowiszewski (119) fused with borax and NaKCO₃, extracting the tungsten with water, the tungsten being recovered as WO₃ by acid evaporation and purified by solution with NH₄OH.

Kuczynski (68) passed chlorine over the heated metal, catching the chlorides in water, and washing the apparatus with hot dilute HCl
and then with NH₄OH. The tungsten was then precipitated by acid evaporation and the WO₃ dissolved in NH₄OH, evaporated to dryness, and ignited.

In tungsten bronzes.—Brunner (111) fused with (NH₄)₂SO₄ and H₂SO₄ as given under “Tungsten bronzes” (p. 136); the analysis proceeded as in the analysis of ores.

Precipitation of Tungsten as Mercurous Tungstate.

Schöffel (101) treated steel with double chloride of copper and ammonia, dissolving most of the iron. The residue was fused with Na₂CO₃, leached with water, neutralized with HNO₃, and the tungsten precipitated with HgNO₃, filtered, ignited, and then fused with KHSO₄ and leached in the (NH₄)₂CO₃ to separate the WO₃ from silica.

Bagley and Brearley (6) dissolved the iron by the same method, but precipitated the tungsten as H₂WO₄ by heating with acid.

Hinrichsen and Wolter (48) evaporated several times with dilute HNO₃, ignited, fused with Na₂O₂, extracted with water, filtered, and washed. The filtrate was acidified with HNO₃ and part of the silica thrown down by adding NH₄OH. The tungsten, together with Cr₂O₃ and some silica, was precipitated by HgNO₃ solution. The silica was removed by treating with HF and the weight of Cr₂O₃ determined volumetrically was deducted from the weight of the impure WO₃.

Hinrichsen (47) in the above method removed phosphorus with magnesia mixture.

Von Knorre (116) acidified the solution of tungstates, chromates, etc., boiled, cooled, reduced with SO₂, added benzidinehydrochloride, and recovered the tungsten free from chromium.

Volumetric Methods.

The following volumetric methods for the determination of tungsten in steels have been suggested:

Lind and Trueblood (74) separated the WO₃ in the usual way and dissolved it in an excess of normal NaOH, titrating back with standard acid, using phenolphthalein as the indicator. If impure with iron, the end point was unsatisfactory. This method was proposed by Hundeshagen (49) and criticised by Schmidt (99), who stated that the results were uncertain, depending on the conditions. Bartonec (7) used this method, and it is given in Lord and Demorest (75).

Kuklin (69) dissolved steel in sulphuric and phosphoric acids, oxidized with KMnO₄, and treated half the solution with zinc; the resulting liquid was titrated with KMnO₄. In the other half of the solution he determined iron by stannous chloride and iodine. From the different results the quantity of tungsten was calculated.
SELECTED METHODS.

GENERAL.

Of the many methods proposed for the determination of tungsten in various materials, no method can be selected that will be suitable for all analyses. The ideal method of quantitative analysis would be both rapid and accurate. These opposing qualities are the variables which become fixed for any one method and determine its sphere of usefulness. The technical laboratory requires speed, and the research laboratory, where the time element is not so important, does not object to it. In both, the degree of accuracy required must be the deciding factor in choosing a method for the analysis of each material.

The following methods have been selected because they have given satisfactory results in the field for which they were devised.

ORES AND SLAGS.

For the satisfactory analysis of ores and slags a method must be used which first of all breaks up the gangue and then completely removes and separates the metal sought from all other metals present.

AMMONIA SOLUTION OF TUNGSTIC ACID.

After long experience with gravimetric methods, Ledoux & Co. (71) are now using one that may be termed the ammonia solution of tungstic acid method. It is satisfactory for the analysis of ores and concentrates. The authors gratefully acknowledge the courtesy of Ledoux & Co. in supplying it.

RÉSUMÉ OF PROCESS.

The sample is digested with HCl for an hour below 60° C., the temperature raised, and the solution evaporated to half the original volume. HCl and HNO₃ are then added, and the whole is evaporated to a small volume with the addition of more HNO₃. After dilution and heating, cinchonine solution is added to precipitate the tungsten still remaining in solution. After filtering, the tungsten is removed from the insoluble matter with warm NH₄OH. The residue is ignited, then fused with a mixture of Na₂CO₃ and KNO₃, leached with water, filtered, the filtrate acidified, and the CO₂ boiled off. Cinchonine solution is added to the diluted solution to recover the last traces of tungsten. If a precipitate forms, it is leached with NH₄OH, and the two ammoniacal solutions containing all the tungsten are boiled to remove excess ammonia, acidified, diluted, and the tungsten precipitated again with cinchonine. The ignited WO₃ is treated with H₂SO₄ and HF to remove silica, and is further examined for other impurities.
TUNGSTEN.

RECTIONS INVOLVED.

The recovery of the main portion of the tungsten by this method depends on the formation of a yellow anhydrous acid, $\text{H}_2\text{WO}_4$, slightly soluble in mineral acids. The addition of a cinchonine solution precipitates the last traces of tungsten as cinchonine tungstate. Both tungsten precipitates are soluble in $\text{NH}_4\text{OH}$, forming ammonium tungstate in solution and cinchonine as a precipitate. The final cinchonine tungstate precipitate is converted to $\text{WO}_3$ by ignition. The silica is volatilized as $\text{SiF}_4$ when it is heated with HF.

METHOD OF PROCEDURE.

"Ores should be ground in an agate mortar to pass a 200-mesh screen; double screening is recommended to insure perfect fineness.

"Weigh one gram into a 350 c. c. beaker, add 5 c. c. of water, and shake to spread the ore evenly over the bottom of the beaker. Add 100 c. c. of strong HCl, cover the beaker, and set it to warm gently for an hour. The temperature should not exceed 60° C., as heating higher expels HCl gas. The ore is decomposed slowly, and most of the tungsten is held in solution by excess HCl, leaving the undecomposed ore exposed to further attack by the HCl.

"Stir the solution with a glass rod once or twice during this digestion to prevent the formation of crusts or cakes on the bottom. The glass rod may be left in the beaker.

"After an hour, increase the heat and boil until the solution is evaporated one-half or thereabouts. The cover may be removed after boiling begins, or, better, it may be supported over the beaker on three glass hooks. After the liquid is reduced in volume to 50 or 55 c. c., scrape the bottom of the beaker thoroughly with a glass rod to detach all caked ore and residue; this step is very important, otherwise complete decomposition by the acid treatment is difficult if not impossible to accomplish. Add 40 c. c. more strong HCl and 15 c. c. $\text{HNO}_3$; replace the cover and boil until all danger of spattering (owing to the rapid expulsion of chlorine) is past, remove the cover and evaporate to a volume of 50 c. c., then add 5 c. c. more $\text{HNO}_3$, replace cover and continue boiling, finally remove cover, and evaporate to a volume of 15 c. c. or less. Boiling and evaporation require about an hour. Occasional stirring is recommended to break up crusts, especially when fresh additions of acid are made.

"Add 200 c. c. of hot water to the concentrated solution, stir well, and simmer gently just at the boiling point for half an hour. Nearly all of the tungstic acid is separated after the addition of nitric acid, and during the subsequent simmering and boiling after dilution, but a little may remain in solution. Add 6 c. c. of cinchonine solution,
stir well, and let stand for half an hour or longer, if convenient, thus precipitating all tungsten.

“Cinchonine solution is made by dissolving 100 grams of the alkaloid in dilute HCl—1 part acid to 3 parts water—and diluting to 1,000 c. c. with HCl of the same strength.

“This method of attack is preferable to that formerly employed, wherein less acid was used and HNO₃ was added earlier in the digestion. Most ores are completely decomposed, so far as tungsten minerals are concerned, but it is unsafe to assume that this is the case unless the residue is pure white silica.

“After the tungstic acid residue has settled well and has stood for half an hour, filter the solution through a 9-cm. paper, using a little paper pulp in the filter. Wash the residue well, first by decantation in the beaker, and afterwards on the paper with a dilute solution of cinchonine and HCl.

“Cinchonine wash solution is made of 30 c. c. cinchonine solution, 30 c. c. strong HCl to 1,000 c. c. of water.

“It is unnecessary to detach the tungstic acid which adheres to the sides of the beaker, but the washing should be thorough to remove all iron, manganese, lime, etc., from the residue and filter paper. Finally, wash both beaker and filter once with cold water to displace most of the dilute cinchonine washing solution.

“Wash the tungstic acid and residue back from the filter into the original beaker with a fine jet of water (25 c. c.) from a wash bottle; the residue washes out easily because the paper pulp prevents adherence. Add 6 c. c. of strong NH₄(OH), cover the beaker, and warm it gently for about 10 minutes. Tungstic acid dissolves readily; stir well, and wash down the sides of the beaker with dilute ammonia, make sure that all the yellow tungstic acid has dissolved, then filter the warm solution through the filter paper that was first used, thus dissolving the small quantity of tungstic acid that adhered thereto. Collect the filtrate in a 400 c. c. beaker, wash the original breaker and the filter paper thoroughly with dilute ammonia—1 part strong NH₄(OH) and 9 parts H₂O. The filtrate should be clear or only slightly cloudy. The addition of one gram of NH₄Cl to the solution before filtering, and a little of the same salt in the wash solution will insure a perfectly clear filtrate, though its use is not recommended unless a large amount of the silicious residue tends to pass the filter. The residue insoluble in ammonia is usually free from tungsten; it may consist of tin oxide—cassiterite—silica, and undecomposed silicates, titanium minerals, or columbite. To make sure that no tungsten is present, the residue must be fused as described below.

“Cover the 400 c. c. beaker and boil it until free ammonia is expelled. The object of boiling off the free ammonia is to minimize ammonia salts, as the cinchonine tungsten compound to be precipi-
tated comes down more quickly and completely in solutions free
from ammonium salts. Dilute the solution to 200 c. c. with hot
distilled water, acidulate with 3 c. c. HCl, and add 6 to 8 c. c. of
cinchonine solution. Stir very briskly for half a minute, thus caus-
ing the flocculent precipitate to agglomerate. It will then settle
rapidly, leaving a clear supernatant liquid. Let it stand until cold,
filter on an 11-cm. weightless ash filter (B. & A.—A grade) which
has been treated to a copious dose of paper pulp. If ammonium
chloride is used in the prior operation, the solution should be allowed
to stand for several hours—preferably over night—after adding cin-
chonine. Wash well with dilute cinchonine solution (the wash solu-
tion described above), policing the beaker with a rubber-tipped rod.
Then wash once with cold water, transfer the filter to a small weighed
platinum dish or large crucible, dry by heating on the hot plate,
then burn the filter slowly over a Bunsen burner, or in a muffle,
following by strong ignition until all the carbon is consumed.

"The use of paper pulp in the filter promotes ignition, and leaves
the ignited precipitate as a porous, friable mass; otherwise the
ignited precipitate is dense, and it is sometimes difficult to burn
the carbon completely. After the carbon is practically all consumed,
brake down the residue with a glass rod flattened at one end, wipe
off the end of the rod with moistened filter paper, adding it to the
dish. Any remaining carbon and the small piece of filter paper
are quickly burned, leaving a pure yellow residue.

"Moisten the residue with three drops of strong H₂SO₄, add 5 c. c.
of HF, and evaporate slowly on the hot plate until the HF is ex-
pelled. Heating on the hot plate should be continued until the
H₂SO₄ is expelled also, to eliminate danger of spitting. Ignite the
dish cautiously at first, finally at full red heat for 10 minutes, cool
in a desiccator, and weigh as WO₃.

"The residue left after the ammonia treatment should always be
examined; it may contain WO₃, although with scheelite and with
most pure ores and concentrates it does not. In treating impure
ores containing much insoluble residue, the residues from duplicate
determinations should be examined separately. When the residue
is small and light colored, the duplicates may be united for this
determination.

"Ignite the filter containing the residue in a small crucible of porce-
lain, as tin may be present, which would be reduced by the filter
paper and ruin the platinum. Mix the ignited residue with five or
six times its weight of sodium carbonate—1 gram being the mini-
"mum—plus a very little KNO₃. Transfer the mixture to a platinum
crucible and fuse for 5 or 10 minutes. Leach the fusion with 50 c. c.
of hot water in a small beaker, filter, acidulate slightly with HCl,
and boil to expel CO₂. Add 5 c. c. cinchonine solution. Let the beaker stand for several hours, preferably over night; long standing is essential as small quantities of tungsten are slowly precipitated by cinchonine in the presence of alkaline chlorides.

"If any tungsten precipitate appears, filter it off on a 7-cm. paper and wash it with dilute cinchonine solution, followed by one wash with cold water, dissolve on the filter in warm dilute ammonia, collecting the filtrate in a small beaker, boil out the excess of ammonia, make slightly acid with HCl, and reprecipitate the tungsten with cinchonine. This reprecipitation is done in a very small volume of liquid practically free from salts, so the tungsten comes down quickly; let it stand for an hour, filter on a small weightless ash filter containing a little pulp, wash with dilute cinchonine solution followed by one wash with water, ignite, cool, treat with a drop of H₂SO₄ and 1 c. c. of HF, evaporate, ignite, and weigh. Add to the principal amount the percentage of WO₃ thus found."

NOTES ON THE METHOD.

1. The WO₃ residue may still be contaminated with traces of other substances which may be corrected by the following treatments:

The residue is fused with Na₂CO₃ and extracted with water, filtered, and washed thoroughly with hot water. If the solution is greenish, a few drops of alcohol are added, and the solution is warmed to precipitate the manganese. Any precipitates formed are ignited, and their weights deducted from the previous weight of the WO₃ residue. (See Ledoux & Co. (70).)

The filtrate from this last treatment is examined for possible contamination with Al, Ta, Nb, Sn, etc. The filtrate is acidified with HCl, 5 grams of NH₄Cl is added, and the solution is made just alkaline with NH₄OH, followed with 5 c. c. in excess. The solution is heated to coagulate any precipitate formed, which is then filtered off, ignited, and its weight deducted from the weight of the WO₃ previously found. (See Ledoux & Co. (70).)

If molybdenum is present in the original ore it will contaminate the cinchonine precipitate of tungsten. (See Hutchinson (50).) The second precipitation of cinchonine reduces the quantity of molybdenum in the final residue, but does not remove it completely; it may be removed by the method of Rose (94). The oxides are fused with Na₂CO₃, leached with water, and 2 grams of tartaric acid and a drop of methyl-orange indicator are added. HCl is added until one drop turns the solution pink, then H₂S is introduced, and a few drops more of HCl are added. When the solution is saturated with H₂S, the molybdenum will be completely precipitated. The molybdenum sulphide is filtered and washed free from tungsten with H₂S water. The tungsten may be recovered from the filtrate
with cinchonine solution after boiling off the $\text{H}_2\text{S}$, or the residue may be examined for molybdenum and the tungsten separated by Markbaker's method (78). The oxides are dissolved by fusing with $\text{Na}_2\text{CO}_3$ and leaching with water. The solution is acidified with HCl, heated to boiling, and 20 c. c. of Mdivani's solution—50 grams of $\text{SnCl}_2\cdot 2\text{H}_2\text{O}$ in 200 c. c. of HCl—added for every 0.15 gram of $\text{WO}_3$ present. After boiling the solution for three minutes the tungsten precipitate is filtered off, washed with 5 per cent HCl solution, and the residue, free from molybdenum, is ignited and weighed as $\text{WO}_3$. The filtrate is examined for molybdenum by the addition of ammonium thiocyanate and zinc, after having previously oxidized the solution with $\text{H}_2\text{O}_2$, a red color showing the presence of molybdenum.

A third method of treatment is to heat the oxides at 250 to 270° C., passing dry HCl gas over them. The molybdenum goes off in about two hours as $\text{MoO}_2\cdot 2\text{HCl}$, leaving the tungsten as a residue. (See Pechard (87) and Debray (21).)

2. Corti (19), Johnson (57), and Lord and Demorest (75) make statements to the effect that $\text{WO}_3$ is volatilized by the action of $\text{H}_2\text{SO}_4$ and HF. Arnold (3) has shown, however, that the loss is due not to volatilization but to a mechanical driving off of fine particles of the oxide. This loss can be prevented by the use of tall, well-covered crucibles for the ignition.

3. For the analysis of tailings or other very low-grade material a larger sample is desirable.

4. Hutchin (50) has shown that synthetic samples where iron has been added gave low results when the cinchonine precipitation was used. This is true if the cinchonine be added to the tungsten-iron solution without previous treatment. If the solution is evaporated with HCl and HNO$_3$, however, as is done in the process of analysis, no loss of tungsten will result, but the time of settling in the presence of considerable iron should not be less than 12 hours.

5. Concerning the time required for analysis by the preceding method and its limit of accuracy, Ledoux & Co. (71) make the following statement:

The time required to get results is approximately 36 hours, although this may be shortened if the decomposition is so perfect that no tungsten remains in the insoluble residue.

Long experience with the gravimetric methods for tungsten leads us to believe that the limit of accuracy is approximately 0.2 per cent, which is about one part in 300 on a 60 per cent ore. Duplicate determinations carried on side by side usually agree much closer than this, but the same sample analyzed by the same operator using the same details will give results varying to this extent, when duplicates are made at different times.

6. One gram of $\text{WO}_3 = 0.7931$ gram of tungsten.
Another method given by Ledoux & Co. (70) designated as "the hydrofluoric difference method" is more rapid than the preceding one, and is as follows:

**HYDROFLUORIC DIFFERENCE METHOD.**

**RÉSUMÉ OF PROCESS.**

The ore is treated with HF, HCl, and H₂SO₄, then diluted, and the tungsten precipitated with cinchonine solution. The precipitate is filtered, ignited, and treated with HF and H₂SO₄, and again ignited and weighed. This residue is fused with Na₂CO₃, extracted with water, ignited, and the weight deducted from that of the impure WO₃. Impurities in the filtrate obtained from the Na₂CO₃ fusion are removed by acidifying with HCl, making alkaline with NH₄OH and heating at 60° C. The precipitate is filtered and ignited. Its weight also is deducted from the weight of the impure WO₃.

**REACTIONS INVOLVED.**

The reactions involved in this method are the same as those given in the preceding method, and need not be repeated.

**METHOD OF PROCEDURE.**

Treat 1 gram of the finely ground ore in a platinum dish with 10 c. c. of HF, 25 c. c. of HCl, and 10 c. c. of 25 per cent H₂SO₄. Heat gently until the solution is complete, adding more of each acid except H₂SO₄ if necessary. Evaporate to fumes of SO₃, dilute with water, transfer to 400 c. c. beaker, and add 100 c. c. aqua regia. The WO₃ can usually be completely removed from the platinum dish by rubbing with a finger cot, but if any stain adheres it can be removed with ammonia and added to the solution. The aqua regia solution is evaporated to 20 c. c., diluted to 250 c. c. with cold water, 10 c. c. of cinchonine solution added, and the beaker set aside for two hours to allow the precipitate to settle. Filter, wash with water containing cinchonine, and ignite residue at a dull red. Treat with HF and H₂SO₄ and ignite, repeating the treatment to constant weight.

This residue is purified by the treatment given in paragraph 1 under "Notes on the method" (p. 160). The other notes in that section apply here also.

**LOW'S METHOD.**

The following method has been used regularly in Low's laboratory (77) for the technical analysis of ores, and has proved accurate enough for this type of work. It is not only rapid but has also the added feature—which is often essential in this class of work—that the analysis may be conducted without using platinum utensils the results being but slightly vitiated.

**RÉSUMÉ OF PROCESS.**

The ore is heated with Na₂SO₄ and H₂SO₄, cooled, treated with aqua regia, diluted, and filtered. The tungsten in the filtrate i
recovered with cinchonine, whereas that in the residue is extracted
with NH₄OH, filtered off, evaporated to dryness, and ignited to
WO₃. The combined tungsten residues are treated with HF and
ignited to remove silica.

REATIONS INVOLVED.

There are no new reactions involved, those given in the "ammonia
solution method" applying in this method.

METHOD OF PROCEDURE.

Weigh 1 gram of the agate-ground ore into an 8-ounce copper flask. Add 4 grams
of sodium sulphate (dry) and 4 c. c. of strong sulphuric acid. Heat on heavy wire
gauze over Bunsen burner with hottest possible flame until decomposition is as com-
plete as possible. This may take 15 minutes, more or less, with the sulphuric acid
boiling strongly. Heating over a free flame will greatly shorten the time. Finally,
finish over a free flame with the flask in a holder so as to expel most of the free sul-
phuric acid, with the bottom of the flask nearly red hot. Do not carry the heating
too far, or the cooling melt may subsequently break the flask. Rotate the flask as
the melt cools so as to distribute the cake over the sides near the bottom. When
cold, add 25 c. c. strong HCl and 10 c. c. strong HNO₃ and boil the mixture down
to about 20 c. c. Now add 50 c. c. of hot water, heat to boiling, and allow to stand
on the hot plate for perhaps 20 minutes. Filter through a 9-cm. filter and wash
10 times with hot dilute HCl (1:10).

Remove the filtrate, add to it 5 to 6 c. c. of cinchonine solution (25 grams of cin-
chonine dissolved in 200 c. c. 1:1 HCl). Heat to boiling and allow to stand, hot,
during subsequent operations on the residue on the filter. Remove filter and con-
tents to a small beaker, and add 25 to 30 c. c. of ammonia solution. (Watts's solution,
consisting of 1,000 c. c. water, 200 c. c. strong ammonia, and 10 c. c. strong HCl is ex-
xcellent.) Heat the mixture in the beaker nearly to boiling and stir the filter about
until it is nearly disintegrated. The ammonia solution used should first be poured
into the flask in several portions to dissolve any tungstic acid adhering therein. Filter
off the filter pulp and undissolved gangue with a 9-cm. filter and wash 10 times
with ammonia solution, cold or slightly warm. Allow to run through completely
each time. Receive the filtrate in a platinum dish. When the dish is partly full
it may be replaced by a small beaker and set on a water bath while the washing is
being finished. This saves much time. Finally, transfer the washings to the plat-
ium dish and continue the evaporation to complete dryness. Ignite the residue,
gently at first, to expel the ammonia, etc., and then with the full power of a Bunsen
burner. During the evaporation filter the cinchonine mixture (which has stood, hot,
perhaps 15 to 20 minutes) through an ashless filter and wash filter and precipitate
10 times with hot dilute cinchonine solution (100 c. c. water to 5 to 6 c. c. of the above
cinchonine solution). Add this filter and precipitate to the above ignited residue
(it is best to dry the filter first) and ignite again until all carbon is consumed. Cool,
add 1 to 2 c. c. of hydrofluoric acid, evaporate to dryness on the water bath, ignite
again, cool, and weigh as WO₃.

NOTES AND REMARKS.

1. In most cases the residual silica will amount to only about 0.0008 gram. It
will therefore frequently suffice to dispense with the platinum dish and hydrofluoric
acid, making the evaporation in a large porcelain crucible and allowing for the above
correction. See Low (76).
If the final ignited tungstic acid shows fused salts, due to incomplete washing with very dilute hydrochloric acid to dissolve everything soluble, filter through an ashless filter, washing with hot, dilute HCl, and precipitate any tungstic acid in the filtrate with cinchonine, as described above. Filter this through a second filter, washing with the dilute cinchonine solution, and finally reignite both filters and residues together to constant weight.

3. Molybdenum, if present in the sample, would contaminate the final tungstic oxide as explained in paragraph 3 of note 1 on the "Ammonia solution of tungstic acid" method (p. 160).

4. 1 gram of $\text{WO}_3 = 0.7931$ gram of tungsten.

STEELS AND ALLOYS.

An accurate determination of tungsten in a metal depends, as in ores, on the thorough disintegration or solution of the sample and the recovery of the tungsten free from contaminants. After the metals have been treated by one of the methods given in the discussion, "Solution or decomposition of ores and metals" (pp. 132 to 136), the tungsten is determined by one of the following methods.

TUNGSTEN POWDER, FERROTUNGSTEN, FERROTUNGSTEN ALLOYS, AND ALL LOW-TUNGSTEN STEELS WHEN TUNGSTEN ONLY IS REQUIRED.

Tungsten powder, ferrotungsten, ferrotungsten alloys, and all low-tungsten steels may be analyzed by the same method when tungsten only is required.

JOHNSON’S METHOD.

This method is essentially that of Johnson (57), a few minor changes having been introduced.

Résumé of method.—The sample is fused with $\text{Na}_2\text{CO}_3$ and $\text{KNO}_3$, extracted with water, acidified with HCl, evaporated to dryness, treated with HCl, warmed, diluted, heated, and the $\text{H}_2\text{WO}_4$ filtered off, and washed with (dilute) HCl. The filtrate is evaporated to dryness, digested, filtered, and washed as before. To the second filtrate and washings a solution of cinchonine is added, and after settling, the tungsten precipitate is filtered, washed, ignited, and added to the other tungsten precipitates. The impurities are removed by fusion with KHSO$_4$ and extraction with (NH$_4$)$_2$CO$_3$.

Reactions involved.—The reactions involved are the same as those given under “Ores and slags” (pp. 155 to 160) for the ammonia solution of tungstic acid method, the evaporation to dryness causing the formation of insoluble tungstic acid.

Method of procedure.—A 1-gram sample is fused with a mixture of 10 grams of $\text{Na}_2\text{CO}_3$ and 2 grams of $\text{KNO}_3$ for about 20 minutes, or until the fusion is complete, then extracted with water and acidified with HCl in a covered dish, care being taken that nothing is lost through effervescence. The dish is heated until all danger from loss is over,
then the cover is removed and the contents evaporated to dryness. (See Note 3, following.) Ten c. c. of 1:1 HCl is then added, and after warming to dissolve the iron, 200 c. c. of water is added and the solution heated 30 minutes to dissolve the sodium salts. The precipitated tungstic acid is filtered off and washed thoroughly with dilute HCl to remove all the iron. The filtrate and washings are again evaporated to dryness, dissolved, filtered, and washed as before. The second filtrate and washings, which should have a volume of about 200 c. c., are heated and 5 to 6 c. c. of cinchonine solution—prepared as given in the ammonia solution method for the analysis of ores—added and the precipitate allowed to settle over night. The precipitate is filtered and washed with dilute cinchonine solution. The three tungsten precipitates are then ignited together at a low red heat until bright yellow, then weighed and fused with 10 grams KHSO₄ until the fusion is clear and transparent, the mixture being carefully warmed for about half an hour, then the heat gradually raised until the fusion reaches a bright red heat. At no time should the flux spatter against the lid of the covered crucible. The melt is extracted with a solution containing 15 grams of (NH₄)₂CO₃, warmed gently to hasten the solution, and the heat removed at once when solution of the fusion has started. The residue of iron and silica is filtered out and washed free from the sulphate test with (NH₄)₂CO₃ solution. The residue is ignited and its weight deducted from that of the impure WO₃. If the silica residue is large or has a yellowish color, another fusion with bisulphate is necessary to recover all the tungsten.

Notes on Johnson's method.—1.—The resulting WO₃ may be examined for other contamination by the methods given in Note 1 under the "Ammonia solution of tungstic acid" method for the analysis of ores and slags (see p. 160), and in the presence of molybdenum this procedure is essential for correct results.

2.—When the first bisulphate fusion is being dissolved, if the heating is continued after the action starts, tungsten will be precipitated.

3.—Ferrotungsten alloys and low-tungsten steels may best be attacked by an acid treatment, after which the above method is to be used. (See "Decomposition or solution of ores and metals containing tungsten" (pp. 132 to 136).)

4.—One gram of WO₃ = 0.7931 gram of tungsten.

Rapid method.

This method is a modification of one given by Arnold and Ibbotson (4) and that given in Johnson (57).

Résumé of method.—A sample is dissolved in HF and HNO₃ and 10 c. c. of H₂SO₄ is added and evaporated to fumes; then 10 c. c. of HCl and 10 c. c. of water are added, and the material is boiled, filtered, and
washed free from iron with dilute HCl. The residue is ignited, weighed, fused with KHSO₄, extracted with (NH₄)₂CO₃ solution, and the ignited weight of the residue deducted from the first weight of the WO₃.

Reactions involved.—No new reactions involved.

Method of procedure.—One gram of the metal is treated in a covered platinum dish with 10 c. c. of HF. To the warmed contents, HNO₃ is added drop by drop—letting the violent action stop before a new addition of acid—until there is no further action. About 5 c. c. of HNO₃ is required to accomplish this. The lid is removed and rinsed into the dish, 10 c. c. of H₂SO₄ is added, and the contents is evaporated to copious fumes of SO₃. The cooled material is treated with 10 c. c. of HCl, then 10 c. c. of water is added, and after boiling, with constant stirring to prevent bumping, the cooled tungsten precipitate is filtered and washed free from iron with 1:10 HCl. The last traces of tungsten are then removed from the washings and filtrate with cinchonine solution as in the previous method, the combined precipitates being ignited, weighed, and purified by the KHSO₄ fusion and (NH₄)₂CO₃ leach as given in that determination also.

Notes on the rapid method.—This scheme gives results one or two tenths of 1 per cent lower than the longer method.

One gram of WO₃ = 0.7931 grams of tungsten.

TUNGSTEN STEELS.

A method for the determination of tungsten in steels where silica and chromium are to be estimated also has been used extensively.

METHOD OF LORD AND DEMorest.

The method of Lord and Demorest (75) has been drawn from various sources, namely, Johnson (57), Wolter (121), Zinberg (124), Bartonec (7), Arnold and Ibbotson (4), and McKenna (83).

Résumé of process.—The sample is dissolved in HCl and HNO₃, evaporated to a small volume, diluted, boiled, filtered, and washed with dilute HCl. The filtrate is evaporated to hard dryness, heated with HCl, diluted, filtered, and washed. The two residues are ignited at a dull-red heat, treated with HF and H₂SO₄ to remove silica, weighed as WO₃, and purified by fusing with Na₂CO₃, the melt being extracted with water, filtered off, and its ignited weight deducted from that of the impure WO₃.

Reactions involved.—The section entitled "Ammonia solution of tungstic acid" (p. 156) includes most of the reactions involved here. The evaporation to dryness in this method is used to render the tungsten insoluble by the formation of anhydrous tungstic acid.

Method of procedure.—Place 2 grams of the drillings in a 200 c. c. casserole and add 40 c. c. of HCl, sp. gr. 1.19, and heat nearly to boiling. When action ceases, add
from time to time a few drops of HNO₃ until the steel is entirely decomposed. In this way the sample is dissolved without the separation of WO₃. When decomposition is complete, add 5 c. c. of HNO₃, boil the solution down to about 10 c. c., add 50 c. c. of water, boil for several minutes, and filter. Wash well with hot 5 per cent HCl solution until all ferric chloride is removed. Evaporate the filtrate to hard dryness, add 15 c. c. of strong HCl, and heat until all iron salts are dissolved, dilute to 50 c. c. heat to boiling, and filter; wash well to wash out all iron. Ignite the two papers and their contents in a platinum crucible until all paper is burned off, but do not heat the WO₃ hotter than a dull red. Cool in a desiccator and weigh.

Add 3 drops of H₂SO₄ and 5 c. c. of HF and evaporate off the acids under a good hood, finally driving off the H₂SO₄ by heating the crucible near the top. Heat to a dull red and weigh. The loss in weight is silica.

The residue of tungstic acid always contains some ferric oxide and possibly some chromic oxide. To obtain these, fuse the residue with 5 grams of Na₂CO₃ until all tungstic anhydride is dissolved, dissolve the cold cake with hot water, and filter off the residue of ferric oxide. Wash well with hot water, burn off the paper, and weigh the residue. Subtract the weight so obtained from the weight of the impure WO₃ after the silica was driven off and the difference is the weight of the pure WO₃. Multiply this by 79.31 and divide by the weight of the sample to obtain the percentage of tungsten in the sample.

Notes on method of Lord and Demorest.—If the leach from the Na₂CO₃ fusion shows a greenish tinge, a few drops of alcohol are added and the solution is warmed to precipitate the manganese; if the filtrate is yellow, chromium may be determined in the oxidized solution by titration with ferrous sulphate; the oxides of these elements are then deducted from the weight of WO₃ previously found.

For methods of sampling tungsten steels see “Tungsten steel” (pp. 134 to 135).

The above method dissolves the steel before the precipitation of tungstic acid starts, thus preventing much contamination with iron.

Any tungstic acid adhering to dishes may be removed by filter paper moistened with NH₄OH, the filter paper being immediately placed in the crucible in which the WO₃ is to be ignited.

Lord and Demorest (75) make the following assertion: “A fairly accurate determination of tungsten may be made by omitting the evaporation to dryness.” This omission would materially shorten the analysis for rough work.

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PART V.—RADIIUM.

By S. C. Lind.

INTRODUCTION.

In addition to uranium and thorium, the only radioactive elements that have hitherto proved to be of commercial importance are radium and mesothorium and some of their disintegration products.

Ores containing radioactive substances differ in one important respect from all other ores and minerals. On account of the radiations that they emit they can be detected and even approximately estimated without being attacked by any chemical reagent. Radioactivity often can be easily detected without even grinding the mineral specimen. In this part of the bulletin, the arrangement of other sections will, therefore, be reversed, and the methods of detecting the radioactive elements will be described before methods of bringing the ores into solution are discussed.

The radiations emitted by radioactive substances have the following properties: (1) They affect a photographic plate like light; (2) they discharge electrostatically charged systems as do X-rays; (3) they produce scintillations and luminescent effects on certain bodies; (4) they produce chemical change in many substances; and (5) they produce color in or change the color of glass, many minerals, and some gems.

The first of these properties, that of affecting the photographic plate, is now mainly of historical interest, since through it Becquerel (3) first discovered the property of radioactivity in a uranium salt. This method has also been very extensively recommended and used for detecting radioactivity in mineral substances. It has one advantage, that its sensitiveness can be greatly increased by prolonging the exposure; but it has the serious disadvantage of giving little insight into the quantity of the radioactive material encountered; moreover, when the method is not properly applied, very misleading results can be obtained. The usual method involves wrapping a photographic plate in black paper and exposing it to the material to be examined for radioactivity, but the novice frequently makes the mistake of placing the mineral or other substance suspected of radioactivity directly upon the plate or upon the paper in which it
measured by the telescope containing an eyepiece with a micrometer scale, and electrometers in which the quantity of electrical discharge is actually measured. The comparison with the electroscope can be made without any reference to electrical units. If it is required to know the actual quantities of electricity involved in the discharge, this may be done by standardizing the instrument in terms of voltage and by determining its electrical capacity. Usually, however, if such a knowledge is required, it is more convenient to use an electrometer which can be standardized in terms of current or used in connection with the Curie piezo-electrique. (See Curie (5), p. 95.) In both methods of measurement it is important to employ a voltage sufficiently high to produce saturation current. Although electrometers and the piezo-electrique are invaluable for purposes of research, they are not necessary for the practical measurements of radioactivity. The Bureau of Mines has, therefore, confined itself to the use of the electroscope entirely, adopting the general type devised by C. T. R. Wilson. Gold and aluminum leaves have been employed with equally good results. The greater ease with which aluminum foil can be handled makes it preferable for most purposes.

In devising an electroscope for the use of the Bureau of Mines, accuracy and economy were kept equally in mind. It was sought as far as possible to combine the advantages of the types already in use in a single instrument. Three types of instrument were necessary: An alpha-ray electroscope with an open chamber into which solid substances could be introduced on plates or shallow trays for alpha-ray comparisons (see the following section); an emanation chamber, which must be gas tight and provided with two suitable stopcocks; and a gamma-ray instrument. These instruments have now become thoroughly standardized, are manufactured by the Sachs-Lawlor Co. of Denver, and are distributed through the Denver Fire Clay Co. of Denver.

As an emanation chamber can be used only once a day, it is necessary to have one ionization chamber for each determination to be made on the same day. If each chamber constituted part of a complete electroscope, the equipment necessary for 10 or 12 determinations a day would therefore be very expensive. However, by arranging the emanation chamber so that it can be detached from the head carrying the leaf system and telescope, the ionization chamber can be inexpensively duplicated as many times as necessary. This feature of employing an interchangeable head for a number of ionization chambers was first used by Ebler (6) in connection with the Exner type of double-leaf electroscope. Instead of the latter, it was thought preferable to use the simpler single-leaf Wilson type with extensive modifications. The highly advantageous feature of having the reading microscope firmly fixed to the electroscope...
head so that there could be no chance of accidentally changing the relative positions of the leaf and micrometer scale was adapted from the Wulf (22) "electrometer," thus providing rigidity while preserving complete visibility of the leaf system, an advantage not possessed by the Wulf instrument.

Figure 1 is a cross section of the instrument. The emanation chamber $a$ is a gas-tight brass cylinder 4 inches high and $3\frac{1}{2}$ inches in diameter, with a volume of about $\frac{1}{4}$ liter. The ionization chamber is provided at $o$ with two metal stopcocks (not shown in the diagram) which must, of course, be gas tight. The insulation at $d$ and $g$

![Figure 1.—Cross section of electroscope.](image)

in the latest type of instrument is provided by amber or amberoid plates. As the insulation at $d$ closes the emanation chamber, it must also be gas tight. This has been accomplished without the use of any binding material by an ingenious arrangement developed by Mr. P. F. Elzi of the Sachs-Lawlor Co. Figure 2 illustrates its construction.

*Special collar with amberoid insulation made gas tight without binding material.*

The brass collar $a$ is threaded into the lower chamber (not shown) at $b$, and made gas tight by a lead washer, $c$. The collar $a$ is hollow and provided with an interior projecting shoulder, $d$, on which rubber washers rest at $f$ and $f'$ above and below. On $f$ and $f'$ rest amberoid disks $g$ and $g'$, pierced by the rods $h$ and $h'$, both of which
are threaded into the connector \( i \). The holes through \( g \) and \( g' \) are made tight by small rubber washers, \( j \) and \( j' \): \( h \) terminates above in a shoulder, \( k \), resting on the washer \( j \) and a tip \( l \), to make electrical contact with the spring \( s \) attached to the leaf system above. Below, \( h' \) is provided with a similar shoulder, \( k' \), resting on the washer \( j' \) and leads below, to the electrode \( e \). By screwing \( h \) and \( h' \) into the common connector \( i \) tension is applied on the washers \( f \) and \( f' \) and \( j \) and \( j' \), thus making the lower chamber gas tight without binding material. This simple device has proved eminently satisfactory, usually holds gas tight for a year or more, and can be readily tightened or, if necessary, taken apart to renew the washers. Much labor in recalibrating the instrument is avoided in this way.

\[\text{Figure 2.—Cross section of ameboid insulation.}\]

In Figure 2, the electrode \( e \) in the latest construction is made much smaller than is indicated in the figure, at present about \( \frac{1}{3} \) inch in diameter. It extends to within about \( \frac{1}{4} \) inch of the bottom and has an upper shoulder about the same distance below the insulation at \( d \). Insulations \( n \) and \( k \) in connection with the charging rod are of hard rubber. The entire cap \( g \) supporting the leaf system \( i \) can be unscrewed so that the leaf system may be removed if necessary without disturbing the rest of the instrument.

Plate I, \( A \), shows the arrangement by which the telescope is held fixed, yet with the leaf system remaining visible from both sides. In order that the telescope may be set to observe the leaf at any part of its arc, the front plate carrying the electroscope sets into the head in a \( \vee \) groove. By loosening the three screws shown in
the photograph, the plate may be turned to bring the telescope to view the leaf at any angle desired. The mica windows which close the leaf chamber are held in place by circular steel wire which springs into place in a groove, thus securing the window and the wire gauze screen by means of which stray charge is prevented from accumulating on the nonconducting mica.

The same interchangeable electroscope head can also be used in connection with an open alpha-ray chamber, or with any other type of discharge chamber, as for the direct examination of the radioactivity of natural waters by the “fountactometer” method.

USE OF THE OPEN ALPHA-RAY CHAMBER FOR THE EXAMINATION OF ORES, TAILINGS, AND OTHER SOLID MATERIALS.

The alpha-ray method of comparison consists in comparing a known and an unknown substance under like conditions as regards degree of fineness, area, depth of layer, etc. Details of the measurement will be described in a later section. (See p. 182.)

USE OF INTERCHANGEABLE ELECTROSCOPE IN THE EMANATION METHOD.

The principle underlying the use of the emanation electroscope is that, in a given discharge chamber containing at two different times different quantities of radium emanation, the ionization and consequent rate of discharge will be proportional to the quantity of emanation present. If in one test this quantity is known, the unknown quantity can be determined by a direct comparison of the two rates of discharge. The principle seems simple and with the observation of a few essential precautions is so in application.

Owing to the rapid decomposition of radium emanation into the series of elements, radium A, B, and C, each of which deposits as a solid “active layer” on the walls of the chamber and contributes materially to the activity, it is necessary to wait three hours after the introduction of the emanation for the active deposit to have reached a maximum. This maximum is maintained with little change between the third and fourth hours, hence the measurement of the rate of discharge may be made during this period.

These active decomposition products of radium emanation, however, carry a positive electrical charge when formed; hence the position at which they are deposited in the chamber will depend somewhat on the electrical field to which they are exposed during deposition and in turn the ionization and rate of discharge will be influenced.

It seems simple to allow the deposition of the active layer always to take place with no electrical field, but the difficulty here is that as soon as the field is made for measuring the rate of discharge, a shift in the position of newly formed Ra A takes place so rapidly
A. ALPHA-RAY ELECTROSCOPE.

B. GAMMA-RAY ELECTROSCOPE.
that even in the few minutes necessary for measurement, the rate of
discharge may change considerably, increasing or decreasing according
to whether the new position of Ra A is more or less favorable to
ionization.

To overcome this difficulty, one practice is to keep the electroscope
charged during the entire three hours of activation, but this pro-
cedure may be inconvenient if different instruments are being used
on the same charging line, and it has been found more satisfactory
in the laboratory to charge for 15 minutes before the measurement.
Any shift of Ra A can be practically completed, and any shift of Ra C
(through Ra B, a product without alpha rays) will not have proceeded
to any considerable degree.

The measurement itself consists in determining with a stop watch
the time elapsing during the passage of the leaf over a certain part
of the scale, the reading being made always between the same scale
divisions. Two or three closely agreeing measurements suffice, but
if the deviations are greater than 1 per cent, an average of 10 measure-
ments is taken. The discharge is then reckoned in terms of scale
divisions per second. From the result is subtracted the "natural
leak" of the instrument, which is determined before the introduction
of emanation. Even with a double contact of amberoid insulation,
the natural leak should maintain a low value of about 0.003 to 0.005
division per second.

Another source of error is the so-called "electrical soak" of the
insulator, meaning that a certain time is necessary for the insulator
to become fully charged. Unless sufficient time is allowed (not less
than 15 minutes) for this process to complete itself, the rate of dis-
charge is erratic.

The procedure in the use of the electroscope is, then, as follows:
1. Set up the electroscope as shown in Plate I, A, and charge for
15 minutes from a battery with voltage just sufficient to hold the
leaf on the part of the scale to be used later.
2. Observe the natural leak during 15 or more minutes.
3. Detach the top and evacuate the lower chamber to the desired
vacuum.
4. Pass the emanation-air mixture through a H₂SO₄ drying tube
into the evacuated chamber and restore normal pressure.
5. Allow the emanation to stand in the discharge chamber for
three hours.
6. Charge for 15 minutes as before.
7. Take three readings, if agreements are good, or ten if deviations
are greater than 1 per cent.
8. Clean out the emanation chamber by drawing dry, dust-free
air through it for some time (over night if convenient).
9. Calculate the discharge and subtract the natural leak, expressing both in divisions per second.

10. Compare the corrected discharge with the calibration of the instrument to determine the quantity of radium under measurement, taking time corrections into consideration.

**CALIBRATION OF EMANATION ELECTROSCOPE.**

The calibration of the electroscope is carried out in exactly the same way as in ordinary measurement, except that a known quantity of emanation is introduced. This known quantity may be obtained in one of two ways as follows:

1. Air may be passed through a standard solution of some radium salt until its emanation is all transferred into the electroscope. This practice has two disadvantages, the necessity of taking care of the standard solution, and the uncertainty attaching to the quantity of radium emanation removed from it, because of the tendency of radium in such a small quantity to be precipitated out in part. The latest practice in the employment of radium solutions as a standard indicates that when the radium is properly protected in solution by a large excess of barium and by at least 5 per cent of halide acid, corresponding to the employment of the halide salt of radium, there is no diminution in the quantity of emanation that can be extracted from it. Instead of the employment of aspiration at ordinary temperature to remove emanation, the standard solution may be boiled. The large quantity of steam thus formed sweeps the emanation out thoroughly in a short time. If this practice is employed, an amount of the standard solution sufficient to produce a convenient rate of discharge is introduced into a 1:1 HNO₃ solution, boiled to reduce the initial emanation to zero, and then sealed for a few days before again boiling to remove the accumulated emanation. The standard solution is preferably used only once in this way, a fresh portion being taken for a new determination. The authors believe, however, that the preferable practice is as follows:

2. A suitable quantity of high-grade analyzed pitchblende is dissolved for each standardization, and the quantity of radium is calculated from the uranium analysis. The quantity of radium emanation obtained when the pitchblende is dissolved will not correspond exactly to the radium content because a small fraction (2 to 5 per cent) of the gas diffuses from the ore; this fraction, termed the "emanating power," must be determined by sealing a quantity of the ore in a tube for a month or more, and drawing off the emanation into an electroscope by the passage of air. The emanating power thus determined in the standard sample is used as a subtractive correction. Convenient quantities of radium emanation are those that will produce a discharge of the order of one to two scale divisions per second.
Example.—Given a standard pitchblende containing 60 per cent U metal and having an emanating power of 3 per cent:

If the Ra/U ratio is $3.40\times10^{-7}$, 1 mg. of pitchblende contains $2.04\times10^{-10}$ grams of Ra but as only 97 per cent of this Ra can give off emanation, 1 mg. of pitchblende on being dissolved will furnish emanation equivalent to $1.98\times10^{-10}$ grams of Ra. For the electroscope herein described, use 20 to 40 mg. of high-grade pitchblende.

Contamination of the discharge chamber may come about through the gradual accumulation of active deposit on the inner walls, which results in the increase of the natural leak of the instrument. For this reason more emanation than is necessary for a measurement is never introduced. The emanation should be moved from the chamber immediately after the completion of the measurement. To avoid the introduction of any emanation that may be present in the laboratory air, air is drawn from the outside, being passed through sulphuric acid and a train of cotton batting to remove moisture and dust. Should the discharge chamber become contaminated in spite of all precautions, the chamber is opened and the walls thoroughly washed with dilute (1:3) HNO₃, followed by washing with distilled water and drying. This is repeated until the natural leak is sufficiently reduced. Contamination of the insulation itself usually necessitates its complete removal.

In measurements of great accuracy it is desirable to calibrate each discharge chamber separately, but by taking greater precaution in the construction and position of the electrode each chamber can be made to have the same electrical capacity, hence one calibration will serve for all. It seems practicable to reproduce chambers that shall have the same calibration value within 1 per cent.

The convertible electroscope may also be used with other forms of discharge chamber than that for emanation. For example, it may be utilized in water analysis by attaching it to a water chamber of the fontactometer type, or it may be attached to an open alpha-ray chamber such as is employed for the cursory examination of ores, or to any other desired form of discharge chamber.

ACCESSORIES FOR ELECTROSCOPE.

Accessories for the interchangeable electroscope include a wrench for removing the collar carrying the insulation when the gas leak or the electrical leak has become unduly high; and hard-rubber caps with brass binding-screw head, used in charging additional chambers while the regular top is being used on another chamber.

When great accuracy is desired, two interchangeable heads, which have been standardized in connection with a given chamber, may be used in reading it in order to eliminate as far as possible the error of electroscopic determination.
METHODS OF MEASUREMENT.

In general, three methods of measurement will serve for the estimation of radioactive substances of commercial importance.

1. ALPHA-RAY METHOD FOR SOLIDS.

The material in which radioactivity is to be detected or measured is introduced into the charged chamber, in lumps, if detection alone is sufficient, or ground. The degree of comminution is not of great importance, if the material is fine enough to be spread conveniently in an even layer. In general, if an unknown substance is being compared with one of known radioactivity, both should be of about the same degree of fineness. The material to be examined is usually spread over a plate a few millimeters deep. If the activity of the total surface exposed by the plate is too great for convenient measurement, the active area may be reduced by placing metallic plates over the surface with smaller openings of different diameters in the center. When the bare surface of any radioactive substance is thus exposed in a discharge chamber, the nonpenetrating or alpha radiation is mainly responsible for the discharge produced. This can be readily proved by placing over the plate a sheet of the thinnest paper, which will be found to reduce the rate of discharge to a small percentage of its former value.

As alpha radiation is extremely nonpenetrating, it is effective only from particles on the surface or at a very slight depth from the surface. For this reason the depth of the layer on the plate makes very little difference after a certain minimum—a fraction of a millimeter—is exceeded. If the substance is porous, the diffusion of gaseous emanation from within may produce an additional effect when the depth of the layer is further increased. The course of procedure in merely detecting the presence of radioactivity is to observe the rate at which the leaf is discharged, first in the absence and then in the presence of the active material. If the material in question produces any increase in rate above the natural electrical leak of the instrument, it may be said to be active.

RATE OF DISCHARGE.

The simplest method of gaining a rather rough idea of the radioactive content of a powdered solid is to compare its rate of discharge in terms of divisions per second or per minute, after deducting the natural leak in the same units, with that of an equal area and depth of some powdered solid of known radioactive content.

SOURCES OF ERROR.

On account of the simplicity and ease of application of this method, it has been quite extensively used for determining radium in ores
and other solid substances of not too high activity. It is subject, however, to several serious sources of error which may sometimes entirely vitiate the quantitative aspect of the results obtained. In attempting to measure the radium content of uranium ores by this method, the three main sources of error possible are as follows:

1. Abnormal value of the radium-uranium ratio.—This source of error is relatively unimportant. It is met only in small hand specimens of radioactive ores of secondary nature, such as carnitite, and sometimes in autunite of rather recent formation. (See Lind and Whittemore (16).)

2. The emanating power.—By emanating power is meant the percentage loss out of the total emanation which should be in equilibrium with the radium content, which loss varies considerably in different minerals, and in carnitite varies between quite wide ranges—16 to 50 per cent. This entails the loss not only of the alpha radiation from the emanation lost, but also from its alpha-ray decay products, namely, radium A, radium C, and radium F. It is evident that this might become a source of error. In a recent publication the writer had occasion to compare several samples of carnitite by the alpha-ray method. (See Lind (14).) After correction was made for both the sources of error just mentioned, there was little or no improvement in the variation between uranium content and activity observed. The discrepancy in some cases amounted to 200 or 300 per cent by the alpha-ray method. It was, therefore, found that the final source of error now to be described may frequently become the controlling factor.

3. The position of the radioactive material relative to the surface.—In a primary uranium mineral like pitchblende this source of error does not seem to be serious. As mentioned above (14) it was shown that the alpha radiation from the surface of ground pitchblende agrees relatively—within about 3 per cent—with the uranium content for different grades of ore. With a secondary mineral like carnitite, however, very much larger deviations are encountered, as has been stated, which must be attributed to differences in the depth of the radioactive material in different samples of the ore. The unreliability of the alpha-ray method, therefore, for strictly quantitative purposes, is too evident to need further discussion.

COMMENT ON METHOD.

Its unreliability, however, does not prohibit entirely the use of the alpha-ray method. Under suitable conditions it may be employed to much advantage. For example, in sorting ore at the mine, it has proved of great service in determining whether the ore was sorted into a grade suitable for shipment. The method may also be used
conveniently in comparing an ore with its tailing after some extraction process. Under such circumstances, if the extraction is good, even a large percentage of error in determining the radium content of the tailing will not produce a great error in the computed recovery.

Alpha-ray measurement of radium, however, can not take the place of uranium analysis. Hitherto all uranium ores have been bought and sold on the uranium content, a constant uranium-radium ratio being assumed. This practice relieves the assayer from the necessity of making an actual radium determination, but is open to the objection that an unscrupulous ore seller might introduce into his ore uranium from which the corresponding radium had already been extracted. This fraudulent practice, that has actually come to the author's notice at least twice, can only be detected by an actual measurement of the radium content by the emanation method.

2. GAMMA-RAY METHOD OF MEASURING RADIUM.

Radium itself emits alpha rays only, but both Ra B and Ra C emit gamma rays which present the most convenient means of measuring radium in quantities above 0.1 mg. and of not less than 0.05 per cent purity. Since Ra B and Ra C are products resulting from the decay of radium emanation, a gas, it is necessary to confine radium preparations in a closed vessel to prevent the escape of the gas before its activity is measured. The measurement may be made after the sample has been closed for a month or more, when the gamma radiation will have reached a constant maximum and no time-correction will be necessary. The gamma radiation will then have become directly proportional to the quantity of radium present, as is true of all standard tubes of radium salt that have been sealed for more than a month. If the measurement is made prior to this period, a correction must be made for the unelapsed time. This correction is readily made from the Kolowrat table, as described in the writer's article on radium measurement by the emanation method (13).

In order that the accumulation of emanation shall have taken place over a definite period of time, the starting point must be rendered exact by sealing the radium salt in a glass tube as soon after crystallization as possible. It is first necessary, however, to dry the salt thoroughly by raising the temperature for 20 minutes or more to 250° C., or higher; otherwise, decomposition by the alpha rays of any water remaining, even as water of crystallization, would generate a dangerous gas pressure in the small tube. If the zero period is indefinite or unknown, a series of measurements must be made at different intervals, from which the final maximum value can be calculated by comparisons with the Kolowrat table. Dorsey (5a) has given a formula and a graphical method to facilitate this calculation.
The measurement itself consists simply of comparing the rate of discharge produced by a tube with known radium content and that of the unknown, each tube being placed successively in the fixed position at a suitable distance from the discharge chamber. Almost any type of electroscope may be used by placing a lead screen, $\frac{1}{4}$ to $\frac{3}{4}$ inch thick, between the instrument and the tube containing the radium. A special gamma-ray electroscope used in the United States Bureau of Mines is shown in Plate I, B (p. 178.)

An accuracy of about 1 per cent in the gamma-ray measurement can be readily attained with ordinary precautions by the use of the simple aluminum or gold-leaf electroscope.

Radium salts are bought and sold in the United States almost entirely on the certificate of the United States Bureau of Standards. The measurements are made electroskopically by the gamma-ray method, using standards that have been compared with the international standard in Paris. Every radium laboratory should have at least one secondary standard that has been certified by the Bureau of Standards.

Radium emanation, which is now quite largely used therapeutically instead of radium itself, may be measured by the gamma-ray method exactly as radium, and is expressed in equivalent units, 1 curie being that amount of emanation in equilibrium with 1 gram of radium element. It is only necessary to allow the emanation to remain in a closed vessel for four hours before the measurement is made. One additional correction is necessary in measuring. On account of the short life of radium emanation (3.85 days half period) Ra C lags behind in decaying by 0.8 per cent; and as it is Ra C, not emanation, that furnishes the principal gamma rays, this correction must be deducted from the gamma-ray indication to give the true quantity of emanation. If one wishes to know simply the gamma radiation and not the actual quantity of radium emanation, this correction is not necessary.

V. F. Hess has recently proposed the extension of the gamma-ray method to materials very much lower in radium content than those already mentioned in this section. The method consists simply in using larger quantities of the material to be examined. For radium-barium sulphate (8b), the material is placed in a semicircular container near the electroscope. For ore (8a), quantities up to 200 or 300 pounds are inclosed gastight in a wooden container with an inset projecting toward the center, into which the gamma-ray electroscope is placed in order to receive radiations from five sides.

3. EMANATION METHOD OF MEASURING RADIUM.

A very fortunate circumstance in more ways than one is that the first decay product of radium happens to be a gas. Radium
emanation, or rad, as it is now called, is a member of the inert series of gases represented by helium, argon, and others. Although the quantity associated with radium is minute, the gas can nevertheless be collected and handled conveniently as any other gas. When separated from the parent radium, the emanation decays rather rapidly, in proportion to the amount present, always losing one-half of its initial quantity in 3 days and 21 hours. The rate of its decay as a factor of time can be readily obtained by consulting the Kolowrat table. (See Curie (5) pp. 361–362; Kolowrat (12); and Rutherford (19).)

Radium at minimum activity, that is to say, radium that has just been deprived of all of its emanation by fusion or solution, regains its emanation content (if held in a closed vessel) at the same percentage rate as the emanation itself decays when separated from radium. The laws that govern this action can be mathematically demonstrated, but it will suffice here to say that either the decay of emanation when separated from radium or its growth in contact with radium can be obtained directly from the Kolowrat table just cited. The measurement of the discharge produced by radium emanation, when introduced in suitable quantity into a gastight discharge chamber of an electroscope, constitutes the most convenient and accurate method of measuring radium in small quantities.

RECOMMENDED METHODS.

The methods to be presented here are suited for ores and the various products that accompany the production of radium on a plant scale. Their applicability has been tested by many determinations made during several years of actual plant operation. Three methods will be described, but the reader should remember that before finally adopting any one method for a given substance it will always be wise to try others, and then select the one that seems by comparison to give satisfactory results with the least expenditure of effort.

The underlying principle of the determination of radium by the emanation method is the separation of radium emanation as gas from its parent radium in order to measure its quantity in a gastight electroscope previously standardized with a known quantity of radium emanation. Analyzed pitchblende or standard radium solutions may be employed to furnish known quantities of emanation for standardization purposes. One of the three following general procedures may be employed:

1. Liberate and measure electroskopically the emanation from a substance in which equilibrium exists between radium and radium emanation. This condition of equilibrium will not be fulfilled except
in substances that have been inclosed for a month or more in a
gas-tight container. When this condition is not fulfilled, more or
less emanation diffuses away spontaneously even from a solid and
thus lowers the expected content of emanation. As an exceptional
condition, radium might be contained in a solid of such compact
structure that no spontaneous loss of emanation could take place;
but even in pitchblende the loss of emanation (called emanating
power and expressed in terms of per cent of the total possible eman-
ation) amounts to a few per cent.

2. When the condition of complete retention of the emanation has
not been met by retaining the sample in a closed vessel for more
than one month, the following procedure may be used: Liberate and
measure the amount of emanation retained in the solid substance
and apply as an additive correction the emanating power, which
should be determined separately by measuring the emanation diffus-
ing from the radioactive substance when retained in a closed vessel.
This is Boltwood’s method (4). Procedures 1 and 2 have been
described by Lind and Whittemore in detail (16). In practice these
involve rather long delays, and though suited to scientific investiga-
tion are not adaptable to purposes of plant control, for which rapidly
obtainable results are essential. Whenever possible, it is preferable
to use the shorter procedure below:

3. By means of some suitable operation (see p. 194) remove the
emanation completely from the substance to be analyzed for radium,
close the stopped substance in a gas-tight vessel, and allow the
emanation to accumulate for a convenient period (one to four days
or longer), then collect and measure it. A time correction must be
applied to ascertain the maximum amount that would be obtained
after equilibrium had been reached with the radium content. The
regeneration of radium emanation takes place according to the
logarithmic law,

$$E = 1 - e^{-\lambda t}$$

where $E$ is the percentage of regeneration at any time, $t$, $e$ is the
base of Napierian logarithms, and $\lambda$ is the time constant for radium
emanation ($=0.0075$ hour$^{-1}$). The solution of the function $e^{-\lambda t}$
for intervals of time from one hour to 30 days will be found in
the Kolowrat table already cited (12).

DEÉMANATION.

To liberate emanation from a radioactive substance, the latter
must be put into a state either of solution or of fusion. Some sub-
stances, like carnotite, can be deémanated by heating to a high tem-
perature without fusion, but are so changed physically that a second
ignition does not remove all the emanation. It is, therefore, evident
that direct ignition can be used only in connection with procedures
1 and 2 above, not for procedure 3.
The removal of emanation from solution may be accomplished by aspiration, or preferably by boiling. Only the latter method has been used and will be described here. Emanation is removed from a fusion by passing air or some other gas over the fused mass. When possible, it is better to bubble air through the mass or to produce evolution of gas in it to insure the complete removal of emanation. Another procedure that has been found useful for carbonate fusions, in the absence of much SiO₂, consists in dissolving the cold fusion in 1:1 HNO₃ with evolution of CO₂, followed by boiling. A further elaboration of this procedure is given in the following sections.

PROCEDURE FOR RADIIUM IN SOLUTION OR IN A SOLUBLE FORM.

The direct determination of Ra in solution can usually be made without difficulty; if certain precautions are carefully observed. These precautions are necessitated by the oft-repeated observation that Ra solutions tend to lose Ra from solution on standing, as manifested by the decrease in the successive quantities of emanation that can be liberated from the solution. This loss of radium from solution is to be attributed to the precipitation or adsorption of Ra from solution in a form that will not readily give up its emanation. As only minute quantities of Ra are used in analysis, the loss of a very small absolute quantity represents a large relative loss.

The presence of precipitates or suspensions in solution should, in general, be avoided, although this source of error has been overestimated. According to the latest views on adsorption of the radionelements, there is need of guarding against only those adsorbents, the negative radical of which would form with the radionelement in question a compound insoluble in the given solution. (See Paneth (18) and Horowitz and Paneth (9).) Accordingly, the loss of radium by the action of small quantities of sulphate originating in the glass of the container or in the reagents should be carefully avoided by the addition of a considerable excess of "protective barium" and the maintenance of a fairly high concentration of HNO₃.

The protective action of an excess of Ba in Ra solutions depends on the chemical similarity of the two elements, due to which any precipitant, such as sulphate, that would remove Ra will be removed by the excess of Ba, or rather Ra and Ba will be precipitated in the same proportion in which they occur in solution, and hence the greater the excess of Ba the more insignificant becomes the loss of Ra. HNO₃ increases the solubility of radium sulphate and prevents the formation of any basic salts of Ra which are formed by the action of the alpha radiation and which would be precipitated in neutral solution. The solubility of Ba(NO₃)₂ in concentrated HNO₃ is not very great, hence care must be taken that the two shall not exceed the
solubility product of Ba (NO$_3$)$_2$ in boiling solution. The two important factors in dealing with Ra solutions analytically consist, then, in maintaining an excess of Ba and a rather high concentration of HNO$_3$. All solutions will fall into one of the three following classes, and the reasons for the treatment prescribed for each will be clear from the foregoing discussion:

1. SOLUTIONS CONTAINING BARIUM IN LARGE EXCESS OF THE RADIUM.

Take a suitable portion of the solution (to contain about $1 \times 10^{-8}$ grams of Ra) and add it to HNO$_3$ in a small pyrex flask, adding sufficient water to make a 1:1 HNO$_3$ solution. Add a few glass beads and boil for 5 to 10 minutes to remove all emanation. Allow to cool slightly before closing tightly with a one-hole stopper provided with a glass tube drawn out to a capillary at the upper end. Seal off the capillary while some steam is still in the flask in order to produce a partial vacuum, which should be retained until the flask is again opened, thus affording a proof that no outward leak of gas has taken place. Note the exact time and date of closing the flask, and hold for accumulation of emanation. When using a rubber stopper to retain emanation in the flask, especial care is needed to keep it gas tight. A rubber stopper of a size to make a snug fit should be used and the surface of the stopper should be carefully scraped with a sharp knife or razor blade to make its surface as smooth as possible. Rather heavy rubber cement should then be rubbed into the surface of the stopper, which should be forced into the neck of the flask very firmly. If possible, it is preferable actually to draw out the neck of the pyrex flask, making a complete seal in glass. Under all circumstances, a partial vacuum should be retained until the flask is reopened.

2. SOLUTIONS CONTAINING LITTLE OR NO BARIUM.

Add a suitable portion of the solution to 1:1 HNO$_3$ saturated with Ba (NO$_3$)$_2$ and proceed as in method 1.

3. SOLUTIONS CONTAINING NO BARIUM BUT AN EXCESS OF A BARIUM PRECIPITANT, SUCH AS SULPHATE OR CARBONATE.

Solutions containing no barium but an excess of a barium precipitant are usually filtrates from a radium-barium precipitation, and require especially careful treatment to avoid erroneous results, either high or low. If such solutions were boiled off and sealed directly, the results might be low as much as tenfold, because of a decreasing emanating power, and continue to become lower as long as the solutions remain sealed. This behavior has suggested that the precipitation of Ra at very low concentrations, or at any rate its removal,
whatever the process, is a progressive time reaction. This same circumstance may, on the other hand, lead to high results through incorrect sampling, even in the use of a correct chemical procedure, when, for example, too much of the fine (frequently invisible) precipitate may have been included in a given volume of liquid. This might easily occur in siphoning the liquid from above a sulphate precipitate if the sample were taken too near the end of the operation. It is preferable to take several samples at intervals and make a composite.

PROCEDURE FOR LIQUIDS OF THE THIRD CLASS.

Add a small sample of suitable volume to a solution containing an excess of Ba and filter off the precipitate after the solution has stood overnight. The filtrate containing an excess of Ba is made acid to the saturation point with HNO₃ and treated as in method 1. The precipitate, if BaSO₄, is fused with four to five times its weight of 1:1 molar Na₂CO₃-K₂CO₃ mixture and treated as described later for fusions. If the precipitate is BaCO₃, it is dissolved in HNO₃ containing enough H₂SO₄ to precipitate an amount of BaSO₄ convenient for fusion, which is filtered off, dried, and fused. The filtrate is combined with the original and treated as in method 1. All the radium is then contained either in the filtrate with an excess of protective Ba or in the fused precipitate; both of these fractions should be handled—before and after the accumulation of radium—as nearly simultaneously as possible, within 15 minutes, in order that both lots of emanation can be introduced into the same electroscope. Instructions on handling solutions for the final collection of emanation for introduction into the emanation chamber are given on page 194.

FUSION METHODS.

CARBONATE METHOD.

If radium is contained in a substance not soluble in aqueous or acid solutions, such as a radium-barium sulphate, a fusion method is used, which may prove even more convenient for soluble substances. Fuse a suitable quantity of the material in a small platinum or porcelain boat with a carbonate fusion mixture, noting the exact time of solidification. Close this boat at once in a glass tube of the type shown in Figure 3. The ends of the tube are drawn down to accom-

![Figure 3.—Fusion boat sealed in glass.](image-url)

modate rubber tubing and then to capillary tips to be broken inside the rubber on opening. Emanation is collected for one or more days. Connect the glass tube at one end by rubber tubing to a glass stopcock and at the other to the highly evacuated emanation chamber.
of the interchangeable electroscope. Break the glass tips inside the rubber connections and exhaust the air from the glass tube into the electroscope, refilling the glass tube with air several times by means of the stopcock but being careful to leave enough vacuum in the electroscope chamber to accommodate the gas to be introduced later from the further treatment of the fusion. Disconnect the glass tube, break it, remove the boat and its contents, wrap in a filter paper, and place in the neck of a pyrex flask (as shown in Fig. 4) which is half filled with 1:1 HNO$_3$.

After the flask is connected with the gas burette (as shown in Fig. 4), a little of the acid is brought into contact with the carbonate fusion, thus setting up an evolution of CO$_2$. The stopcock leading to the gas burette is immediately opened and the boat and its contents are thoroughly wet with acid, then shaken down into the body of the acid. With large fusions the evolution of CO$_2$ becomes very rapid and special precautions must be taken, but with small fusions, not exceeding 1 to 2 grams, the boat may be brought down at once into the acid, which is boiled as soon as the gas evolution begins to slacken. All of the CO$_2$ is of course absorbed by the NaOH solution in the burette. The boiling off of the emanation from this point on is identical with that of solutions to be described later. (See p. 194.)

For small fusions of substances containing radium in the order of one part per million, such as the usual crude Ba(Ra)SO$_4$ and high-grade pitchblende, of which a sample of 20 to 40 mg. would be fused, it has been found convenient to use small boats folded from a piece of platinum foil $\frac{1}{2}$ inches in length and $\frac{1}{2}$ inch broad, which makes a boat about 1 inch long and $\frac{1}{2}$ inch in cross section. Such foil is $\frac{1}{2}$ inch thick and has a rather long life if the substance fused does not contain much lead. For substances much poorer in radium, porcelain boats have been used, and flasks large enough to hold a liter are required to dissolve the fusion; a gas burette with a bulb enlargement at the top is used to hold enough NaOH solution. In this method the fusion should not be brought down into the liquid until a considerable part of the evolution has been conducted by manipulation of the flask.

**DIRECT-FUSION METHOD.**

Carbonate fusion may be employed both before and after collection of emanation if preferred, instead of dissolving the fusion in acid as just described. As soon as the initial fusion has cooled, it is removed from the boat by unfolding the platinum foil (for which purpose the thin foil is most convenient) and put into a pyrex glass tube of the form already described, where it is held in place by glass-wool plugs. The glass wool has the advantage of reacting with the carbonate.
during the second fusion to produce a vigorous evolution of CO₂, which aids in the complete removal of emanation. If the radioactive substance is free from thorium, air may be drawn directly over the melt into the electroscope. A solution of NaOH is interposed before the electroscope to prevent the introduction of any CO₂.

No gas except air should ever be introduced into the electroscope with emanation, because the specific ionization of the various gases differs from that of air, roughly in proportion to their densities.

It is well to place a sulphuric acid drying bulb before the electroscope and another with water at the entrance to the train for controlling the flow of gas and for drying it.

To produce the second fusion, the hard-glass tube, after being properly connected with asbestos protectors for the rubber tubing, is strongly heated with a Meeker burner while air is being drawn through to the electroscope. The heating is continued until the glass collapses completely, but this collapse should not be permitted until a large quantity of air has passed and the vacuum is nearly refilled. It may also be advantageous to allow the tube to bend into a U shape or to constrict itself so that air actually bubbles through the melt.

Both modifications of the fusion method are unfavorably affected by the presence of a high percentage of SiO₂, which increases the viscosity of the melt, thus rendering the removal of emanation by direct fusion difficult. Much SiO₂ also makes complete solution by the acid method impossible, by the separation of silicic acid gel on the surface preventing further attack of the acid and causing adsorption of radium and radium emanation. This point is more fully discussed under the method for carnotite and tailings. (See p. 196.)

**BISULPHATE-FUSION METHOD.**

Potassium or sodium bisulphate may be found preferable as a fusion agent. H. H. Barker (1) has described the procedure in detail. Briefly, it consists in using a hard-glass pyrex test tube of a size suitable for the amount of substance to be fused and 6 to 8 inches long. A layer of bisulphate is placed at the bottom of the tube, the radioactive material in which radium is to be determined is placed on top of it or, if desired, mixed with a charge of bisulphate, and, finally, a layer of bisulphate is placed over the charge. The material before fusion should more than two-thirds fill the tube. The mass is then heated directly over a free flame until thoroughly fused and a rapid evolution of gas begins; heating is continued for about five minutes, until all of the emanation has been swept out. Then the fusion is allowed to cool and the time of solidification is noted as the zero point for the accumulation of emanation.
The tube is closed with a two-hole stopper, which should be treated in the same way as has been described in a preceding paragraph to insure its being gas tight. As the fusion itself, however, retains the emanation almost completely, the same precaution is not necessary here as when the radium emanation is in solution and can diffuse more readily. The two-hole stopper is provided with two tightly fitting glass outlet tubes, both bent at a right angle to be horizontal just above the stopper. One of them projects immediately below the stopper and the other extends to just above the fusion; both are initially drawn to tips that can be broken off under the rubber connection.

After the bisulphate fusion has stood for a few days for the accumulation of radium emanation it is connected to a highly evacuated emanation chamber in the following manner:

Next to the chamber is a micro drying bulb (L, Fig. 4) containing concentrated sulphuric acid to dry the gases. Next to it and connected with the fusion tube itself is a similar micro drying bulb containing a rather concentrated solution of NaOH to retain any acid fumes that may come from the bisulphate fusion. On the inlet side of the fusion is a third micro drying bulb containing water simply as an indicator for the flow of gas. All connections are made with rubber tubing.

After breaking the glass tips inside the rubber connections the stopcock of the emanation chamber is opened to produce a slow inward flow of gas. The bisulphate fusion is then melted with a free flame. As soon as the fusion begins to evolve gases the stopcock to the emanation chamber is opened wider to sweep them readily through the solutions into the chamber. Fusion is continued until the vacuum in the emanation chamber has been depleted, when the stopcock is closed and the chamber is allowed to stand for equilibrium with induced activity to be attained in the usual way before making the electroscopic measurement.

This procedure of running the emanation directly into the emanation chamber is allowable only when thorium or any source of thorium emanation is not present in the fusion. If the presence of thorium emanation is suspected, the gases should first be run into a container, preferably over mercury, and allowed to stand for 10 minutes before introduction into the electroscope chamber. Underwood and Schlundt (21) have described an apparatus suitable for this purpose.

**Method and Apparatus for Boiling Off and Transferring Emanation from a Solution.**

Set up an apparatus as shown in Figure 4. Wire the rubber connections at A. Put into the leveling bulb C a stick of NaOH 2 to 3 inches long (use more if large quantities of CO₂ are to be absorbed).
Make sure that stopcock D is closed and E open. Pour boiling water in the leveling bulb, which rapidly dissolves the NaOH with evaporation of much heat. If the boiling becomes too vigorous place a one-ounce stopper in the mouth of the leveling bulb to prevent liquid from being thrown out. After the solution is complete, raise the level until the gas burette is filled to the upper stopcock; close this at once and lower the leveling bulb to its original position. If the volume of air to be introduced is small, some air may be left initially in the burette.

Break the glass tip F inside the rubber tubing and slowly open D to ascertain if there is vacuum remaining in the flask G. If so, close D again and begin to heat G over a wire gauze with a Bunsen burner. The glass tip F after being broken off tends to be carried upward by the current of steam and sometimes has lodged in the stopcock D, causing serious explosions. This may best be prevented by having a small glass trap sealed in at I with its point opening projecting in the direction of the flow of steam and gas. Such a trap prevents the passage of the glass tip or any other solid material to the stopcock and insures complete safety.

Test the vacuum every few seconds and as soon as the pressure is outward, open D and begin to boil vigorously. Boil 5 to 10 minutes, until live steam has raised the temperature of the liquid in the gas burette to boiling. After the boiling off is complete, remove the flame, and as soon as the liquid begins to draw back close D and remove the flask entirely. If desired, the flask may be closed again for a second accumulation of emanation, but usually, if duplicates are desired, two or more flasks are closed originally.

Evacuate the electroscope chamber to a suitable degree, either with a hand pump or with an aspirator. Connect a H₂SO₄ drying bulb to the evacuated chamber and to the gas burette, as shown in Figure 4. Be sure that stopcock J is closed. Open the stopcock K of the electroscope for a moment to produce vacuum in the drying bulb, reclose it, slowly open E to full width, and then again gradually open the stopcock of the electroscope to allow gas to pass through the drying bulb at a fairly rapid rate.
When the liquid in the gas burette has risen exactly to the stopcock, turn it to permit dry dust-free air taken from outside the laboratory to be drawn into the burette until the water level drops 6 to 8 inches from the top. Again turn the stopcock to pull this air into the chamber; turn the cock again to draw in about the same amount of air as before; when the water level has risen within 4 to 6 inches of the stopcock pour all of the solution out of the leveling bulb, thus pulling in air at the bottom of the burette. The air bubbles up through the hot solution and sweeps out any emanation that may have remained dissolved in it. The sweeping-out process is continued until the vacuum in the electroscope is exhausted. This precaution is perhaps unnecessary, for the hot solution of NaOH certainly does not dissolve much emanation during the limited exposure, but it is a precaution in the direction of accuracy and requires no additional effort.

The same procedure is followed in boiling off and in handling the solutions derived from dissolving any fusion or other solid material dissolved directly. For example, ground carnottite or pitchblende ores may be wrapped in filter paper and handled in the same way as shown for a fusion in Figure 3, the correction for emanating power being applied; or the ore may be sealed for a month in a thin glass bulb which is opened by crushing it against the bottom of the flask by tapping on the glass stem projecting above through a second hole in the rubber stopper closing the flask. (See Lind and Whittemore (16).) To economize time, two or three of the boiling and transferring operations can be carried on simultaneously by one operator.

After the emanation is collected in the gas burette, as just described, it is transferred to the emanation chamber and the determination with the electroscope is carried on, as already described on page 178.

**CHOICE OF METHOD**.

Some indications are given below as to the applicability of the various methods discussed to different products that frequently present themselves for radium analysis.

**PITCHBLENDE**.

High-grade pitchblende is low in SiO₂ and readily soluble in boiling 1:1 HNO₃. (See Becker and Jannasch (2).) Solutions as well as fusion methods are therefore available. Low-grade pitchblende with high SiO₂ content is subject to the same difficulties of analytical treatment as carnottite. (See p. 196.) Since the Ra/U ratio is constant and normal \((3.40 \times 10^{-7})\), in various pitchblendes, it may be used in calculating the radium from the uranium content. (See Lind and Roberts (15) and Heimann and Marckwald (8).) This statement also
applies to carnottite in large and well-sampled lots. (See Lind and Whittemore (16).)

CARNOTITE.

Carnotite, the principal American radium-bearing ore, is primarily a sandstone impregnated more or less with uranium vanadate. The latter is readily soluble, with the Ra, in an excess of boiling 1:1 HNO₃. One of the best methods for its radioactive analysis is solution from a sealed glass tube after a month’s accumulation, or ignition in a hard-glass tube sealed under the same conditions. Direct solution in hot 1:1 HNO₃ saturated with Ba(NO₃)₂, followed by accumulation in a closed flask for a few days without filtering, also gives approximately correct results, but is not to be so highly recommended as the two longer methods just mentioned.

On account of the high SiO₂ content of carnottite the carbonate fusion melt is very viscous at temperatures suitable for the use of pyrex glass, hence it is difficult for the radium emanation to be liberated. Higher temperature, or the direct bubbling of air through the melt, helps to obviate this difficulty, but experience in the Bureau of Mines laboratory has been generally unfavorable to the use of alkali fusion methods for carnottite. Dropping the carbonate fusion into acid fails completely for reasons already stated. (See Schlundt (20).) More recently it has been found that the bisulphate fusion method works admirably for carnottite and other radioactive materials high in SiO₂, and it is therefore the method recommended most.

CARNOTITE RESIDUES OR TAILINGS.

All the difficulties arising in the analytical treatment of carnottite are many times multiplied in analyzing its extracted residues, with the additional difficulty that, since the radium has already resisted solution, to apply solution methods is not permissible. Carbonate fusion methods may be applied only after the removal of all the SiO₂ with HF from at least a 10-gram sample. The bisulphate fusion method has also been found adapted to carnottite residues or tailings, and is recommended for their treatment. Usually the solid alpha-ray method has proved accurate enough for the residues, which are generally so low in radium that a large relative error produces but a small absolute error in estimating the percentage of radium extraction. (See Moore and Kithil (17).)

ACID FILTRATES FROM ORE EXTRACTION.

Acid filtrates from ore extraction (free from sulphates) can be boiled and sealed directly after the addition of a little Ba, as prescribed. Carnottite ore contains considerable Ba, so that little more need be added. This is not true for pitchblende, which contains little Ba.
RADIIUM.

BARIUM (RADIIUM) SULPHATES AND SULPHIDES.

Barium (radium) sulphates and sulphides are fused with carbonate mixture in platinum or porcelain boats (described under fusion method, p. 190), sealed in glass tubes for the accumulation of emanation, and either dissolved in acid or fused again to effect deemanation. The bisulphate fusion method may also be used for this class of substances.

FILTRATES WITH EXCESS OF SULPHATE OR CARBONATE.

Filtrates with excess of sulphate or carbonate must be treated with observance of all the precautions prescribed for liquids of this character. (See p. 189.)

BARIUM (RADIIUM) CHLORIDE (OR BROMIDE) LIQUORS OR CRYSTALS.

Barium (radium) chloride or bromide liquors or crystals may be treated after solution and suitable dilution according to method 1 for liquids. (See p. 188.) For solutions of fairly high-grade radium salts the necessary dilution becomes considerable, as much as 1 to 1,000,000 or even more. This dilution is carried out with pipettes and measuring flasks according to the usual procedures of volumetric analysis and with due regard for the principle of protective barium and acid throughout. Unusual care must be taken when rinsing the vessels in which such large dilutions are made. It is advisable to have sufficient pipettes and flasks to avoid using the same ones through too great a range of concentration.

BIBLIOGRAPHY ON RADIIUM.

PART VI.—URANIUM.

By C. W. Davis.

INTRODUCTION.

Uranium has had its importance greatly enhanced by its connection with radium. Uranium is now recognized as the "mother" of radium, and its ores are mined and treated mainly for their radium content. Because of the increasing recognition of the therapeutic value of radium in the treatment of cancer, radium-bearing ores are becoming more important each day. In many such ores the ratio of the radium to uranium is constant, and as this ratio is known it is possible to estimate the amount of radium by analyzing the ore for uranium; in fact, this is common practice in the sale of radium-bearing ores, an analysis for radium being very unusual. Accuracy in uranium analysis has, therefore, become very important owing to the fact that a small error on the uranium content means a corresponding error on the radium content, and the monetary values involved are thus much greater than if the ore were sold for its uranium only.

The two principal commercial ores of uranium are pitchblende and carnottite. The former is an impure oxide of uranium, the uranium being partly $\text{UO}_2$ and partly as $\text{UO}_3$. In addition, there are traces of iron oxide, $\text{Al}_2\text{O}_3$, and oxides of $\text{Mn}$, $\text{Ca}$, $\text{Mg}$, $\text{Pb}$, and sometimes $\text{Cu}$, $\text{K}$, $\text{As}$, and others. The chief impurities are generally oxides of $\text{Fe}$, $\text{Ca}$, and $\text{Pb}$. Carnottite is probably a potassium-uranil-vanadate, containing traces of $\text{Ba}$ and $\text{Ca}$. Its composition may be expressed roughly by the formula $\text{K}_2\text{O}.2\text{UO}_3.\text{V}_2\text{O}_5.3\text{H}_2\text{O}$. Pitchblende is a dark, bluish-black massive mineral found in igneous rock, principally at Joachimstahl, Bohemia; Cornwall, England; and in Gilpin County, Colorado, gold veins. Small deposits have been reported in Russia, Sweden, Norway, and North and South Carolina. At present a deposit of high-grade uranium ore, consisting mainly of pitchblende and its alteration minerals, is being developed in the Katanga district of the Belgian Congo, Africa. It is reported that the deposit is large enough to be an important source for the production of radium. Carnottite is a canary-yellow mineral of secondary origin found principally in sandstone deposits, notably in San Miguel and Dolores Counties, southwestern Colorado, and in eastern and southeastern Utah.
These have been considered the largest uranium, and therefore radium, deposits in the world, and during the last six years have yielded the larger part of the radium and uranium on the world's market. Of lesser importance are the minerals autunite (Ca(UO₂)₂ (PO₄)₂·8H₂O), the principal deposits of which are in Portugal and South Australia; and torbernite (Cu(UO₂)₂·P₂O₇·8H₂O) also found in those countries, and in Cornwall, Saxony, and other regions. Autunite is a yellow mineral crystallizing in orthorhombic plates or tabular crystals. Torbernite forms greenish-yellow tetragonal crystals.

Uranium is utilized mainly in the ceramic industry, and in making special steels. In ceramics, either the yellow oxide (sodium diuranate) or the green oxide (U₂O₅) may be used. By varying the composition of the glaze and controlling the conditions of firing, different colors may be obtained, such as yellow, orange, shades of brown, and even dark green. Uranium has been used in making steels high in uranium and sometimes carrying other elements, such as tungsten. It is claimed that uranium in place of tungsten will give a satisfactory high-speed steel, the former replacing two or three times its weight of the latter; but such steels have not come into general use.

Until the advent of the radium industry in the United States, methods of analysis for uranium were somewhat crude. In the early stages of the industry it was difficult to get commercial chemists to check each other on the uranium content of an ore, but as the importance of the problem became more and more appreciated, methods were worked out giving satisfactory results, and it is now possible to obtain check analyses with a reasonable experimental error. These methods are described in the following pages:

**METHOD OF DECOMPOSITION OR SOLUTION OF URANIUM ORES AND METALS.**

**SOLUBILITY.**

Decomposition of substances containing U and solution of the element sought is most easily accomplished if the properties of the material being examined are known.

UO₂ is soluble with difficulty in concentrated HCl, HBr, and H₂SO₄, but is readily soluble in HNO₃ or aqua regia. (See Ibbotson and Clark (35).) U₂O₅, when formed by the ignition of ammonium uranate, is soluble with difficulty in dilute HCl or H₂SO₄, and but slowly soluble in HNO₃. (See Treadwell and Hall (78).) Heated with H₂SO₄ (1:6) in a closed tube at 150 to 175° C. for a long time, U₃O₈ is completely dissolved, with the formation of uranous and uranyl sulphates. (See Hillebrand (32).)
The uranates are insoluble in water, but soluble in acids. Metallic U is soluble in concentrated H$_2$SO$_4$, HNO$_3$, and HCl, and slowly soluble in cold dilute H$_2$SO$_4$. Cl attacks it at 150° C. and Br at 240° C. Caustic alkalies have no apparent action on it. (See Browning (10).)

Metals containing U are treated with acids. Aqua regia or H$_2$SO$_4$ has been used frequently for the solution of alloy steels. (See Johnson (36) and König (43).)

U may be extracted from most ores (carnotite, autunite, pitchblende, etc.) by HNO$_3$ or aqua regia. (See Johnstone (38).) Some forms of thorite, however, require a fusion to effect their decomposition (a carbonate fusion followed by an acid leach). If, after an acid treatment, the residue still contains U, it may be treated with HF, taken to dryness, fused with Na$_2$CO$_3$, and extracted with HCl.

**QUALITATIVE ANALYSIS.**

**DETECTION OF URANIUM.**

There are two methods by which the presence of uranium in an ore may be detected, the radioactive and the chemical.

**RADIOACTIVE METHOD.**

Ra is always associated with U in an ore, and the rays given off by U, Ra, and their disintegration products cause effects that can be detected even though Ra is present in minute quantities. The disintegration products of Th are radioactive also; hence, if an ore shows radioactivity it is well to examine it chemically to determine its composition.

Of the three general methods employed for examining the radiations from radioactive bodies—the action of rays on a photographic plate, the ionizing action of the rays on the surrounding gas, and the luminosity produced by the rays on a screen of phosphorescent material—the first two have been used for the detection of radioactivity in ores.

A piece of radioactive ore placed on a photographic plate that has been covered with a light-tight wrapping and left for a day or more will darken the plate. As the effect may be produced in the absence of uranium, this test is not recommended. See under "Radium," page 173.

If ore containing U be placed in the chamber of an electroscope, the ionizing action of the rays from radioactive constituents will cause the charged leaf to fall more rapidly than it did before the introduction of the sample. The rate of fall of the leaf is a rough measure of the U content of the ore. The subject is treated more fully in the quantitative section of this chapter, "Radioactive method for ores," page 220, and in Part V on Radium (p. 182).
CHEMICAL METHOD.

Uranium may be detected by Scholl's rapid quantitative method (73). The sample, heated with 1:1 HNO₃, is diluted to 250 c. c. and filtered. Ferric chloride is added and the solution neutralized with Na₂CO₃, 1 gram being added in excess, and then heated at 90° for about 20 minutes and filtered. The filtrate containing the U is neutralized with HNO₃ and the CO₂ boiled off. NaOH is then added in excess and the U is precipitated, filtered, and dissolved in dilute HNO₃. NH₄OH is then added to the hot solution and a yellow precipitate of ammonium uranate settles out on heating for a short time. This may be filtered off and dissolved in acid and the U confirmed by K₄Fe(CN)₆.

CHARACTERISTIC REACTIONS.

Various chemical tests have been used to detect the presence of U. Solutions of uranyl compounds give the following reactions (see Treadwell and Hall (78)):

KOH, NH₄OH, etc., precipitate yellow amorphous uranates, uranyl hydroxide being formed first.

\[ 2\text{UO}_2\text{Cl}_2 + 6\text{KOH} \rightarrow \text{K}_2\text{U}_2\text{O}_7 + 4\text{KCl} + 3\text{H}_2\text{O}. \]

The alkali uranates are soluble in alkaline carbonates, especially in (NH₄)₂CO₃, with the formation of complex salts.

\[ (\text{NH}_4)_2\text{U}_2\text{O}_7 + 6(\text{NH}_4)_2\text{CO}_3 + 3\text{H}_2\text{O} \rightarrow 2(\text{NH}_4)_4(\text{UO}_2\text{CO}_3)_2 + 6\text{NH}_4\text{OH}. \]

Tartaric acid and other organic substances also prevent precipitation by alkali.

Na₂CO₃ produces in concentrated solutions an orange-yellow precipitate of sodium uranyl carbonate, soluble in the presence of considerable water, and still more soluble in an alkali carbonate solution. From such solutions NaOH precipitates sodium uranate, but ammonia produces no precipitation.

BaCO₃ precipitates the U completely in the cold, probably as barium uranyl carbonate (Ba₂(UO₂)(CO₃)₃). (NH₄)₂S precipitates brown uranyl sulphide (UO₂S), soluble in dilute acids and in (NH₄)₂CO₃; H₂S therefore causes no precipitation in acid solution. Na₂HPO₄ precipitates yellowish-white uranyl phosphate (UO₂HPO₄). In the presence of ammonium acetate, uranyl ammonium phosphate (UO₂·NH₄PO₄) is precipitated. Both precipitates are insoluble in acetic acid, but soluble in mineral acids.

K₄Fe(CN)₆ produces a brown or brownish-red precipitate, (UO₂)₂(Fe(CN)₆). On the addition of KOH the precipitate becomes yellow, owing to the formation of potassium uranate (difference from Cu); the solubility of the ferrocyanide in dilute HCl is another difference from Cu. The solution for this test should be made just acid with
HCl and a small amount of NaCl added to prevent the formation of a colloidal precipitate. (See Noyes, Bray, and Spear (58).) The test is delicate.

H₂O₂, added to a dilute nitrate or acetate solution of a U salt, forms a yellowish-white precipitate. The precipitation is complete in acetic acid and practically so in weak HNO₃ solutions. Excess salts of K, Na, Ba, Ca, and excess HCl, HNO₃, or H₂SO₄ prevent the precipitation. (See Fairley (18).)

HF added in slight excess to a reduced solution of U forms a heavy green precipitate (possibly UF₄), easily filtered and washed with water containing a little HF. On ignition in air the UF₄ (?) is changed to U₃O₈. (See Giolitti (29).)

Ethylendiamine in a 10 per cent solution, added to a solution of a U salt, gives a bright yellow precipitate which settles quickly and filters easily. It is insoluble in alcohol, ether, chloroform, etc. It is a delicate test, but other elements give precipitates under the same conditions. (See Siemssen (75).)

Methylamine gives a brown flocculent precipitate from H₂SO₄ solutions. It is readily soluble in dilute acids, but when washed and heated in water for some time becomes dense and very slowly soluble in acids. (See Oechsner de Coninck (59).)

Thiosinamine in alkaline solution gives a persistent yellow precipitate with U. No other alkaline earth or heavy metal, except cadmium, yields a precipitate with this reagent. (See Lemaire (47).)

Turmeric paper is colored brown by uranyl salts. The nitrate gives a much stronger reaction than the sulphate or acetate. The color becomes violet black when sprinkled with dilute Na₂CO₃ solution and the original yellow is obtained by the action of HCl. (See Zimmermann (82).)

If Zn be added to a HNO₃ solution of a uranyl salt a yellow coating, possibly UO₃·2H₂O, forms on the Zn. (See Buell (12a).)

With borax in the oxidizing flame, the bead is yellow when hot, colorless when cold, and can be flamed enamel yellow. In the reducing flame, the bead is bottle green and can be flamed black but not enameled. (See Moses and Parsons (56).)

With salt of phosphorus, the bead is emerald green in the reducing flame, and in the oxidizing flame is yellow while hot and yellowish green when cold. (See Moses and Parsons (56).)

**SEPARATION OF URANIUM FROM THE ELEMENTS FOUND OR ASSOCIATED WITH IT IN ORES OR COMMERCIAL ALLOYS.**

**GENERAL SEPARATIONS.**

Uranium sulphide, being soluble in acid solution, may be separated from metals of the second group in the usual manner. (See Gibbs
(28). Other members of its own group, Fe, Ni, etc., are precipitate by \((\text{NH}_4)_2\text{S}\) in the presence of an excess of \(\text{Na}_2\text{CO}_3\) or \((\text{NH}_4)_2\text{CO}_3\), leaving the U in solution. (See Kern (40).) It is separated from the alkalies and alkali earths by \((\text{NH}_4)_2\text{S}\) in the presence of \(\text{NH}_4\text{Cl}\) in slight excess, as uranium oxysulphide. (See Treadwell and Hall (78).)

**ALKALIES AND ALKALI EARTHS.**

Although a single precipitation with \(\text{NH}_4\text{OH}\) will carry down a portion of alkali or alkaline earth metals, several precipitations with \(\text{NH}_4\text{OH}\) will effect a separation. (See Fresenius and Cohn (24) and Hillebrand and Ransome (33).) Kern (40) found the separation complete in three precipitations in hot solution in the presence of \(\text{NH}_4\text{Cl}\).

Fouillon (22) found the separation of U from Ca by \((\text{NH}_4)_2\text{S}\) incomplete; however, repeated precipitation in the presence of \(\text{NH}_4\text{Cl}\) has effected a separation.

The separation of Ba, Ca, and Sr from U by \(\text{H}_2\text{SO}_4\) and alcohol was proposed by Frémy (23), and used by Rammelsberg (65) and others. Fouillon (22) separated the Ca as oxalate in the presence of excess \((\text{NH}_4)_2\text{CO}_3\). This method was criticized by Aliibegoff (1), who separated U by precipitating with HgO in the presence of \(\text{NH}_4\text{Cl}\), boiling, filtering, and washing with \(\text{NH}_4\text{Cl}\) solution. In the presence of Mg, the solution should be boiled with \(\text{NH}_4\text{Cl}\) before the addition of the HgO. Kern (40) finds this method deficient in a good separation of Ba.

A separation has been accomplished by heating the alkali uranates with \(\text{NH}_4\text{Cl}\) in a current of H. (See Rammelsberg (65).) The chlorides of the alkalies were extracted with water. The alkali earths were precipitated by \(\text{H}_2\text{SO}_4\) and alcohol.

Smith and Wallace (76) and Kern (40) advise the electrolysis of an acetate solution for a simple, complete, and rapid method of separation of U as the oxide from the alkali and alkaline earth metals.

Kern (40) found that the separation of U from the alkalies and alkali earths, by an excess of ammonium phosphate in the presence of ammonium acetate, was complete if the precipitation was effected in a hot solution which was then boiled for 15 minutes.

**IRON, ALUMINUM, NICKEL, ETC.**

Pisani's \((\text{NH}_4)_2\text{CO}_3\) method (63) and Patera's \(\text{Na}_2\text{CO}_3\) method (60) for the separation of Fe and U have given trouble, but Kern (40) states that the separation is complete in the presence of excess \(\text{Na}_2\text{CO}_3\) if the solution be boiled 15 minutes before filtration. No U remains with the Fe, which is completely precipitated, readily filtered, and washed.
Trautman (77) found Pisani’s method erroneous and advised a modification of Rose’s (NH₄)₂CO₃, (NH₄)₂S method (71).

König (43) removed Fe, Ni, and Co from U electrolytically in a solution of ammonium oxalate, the electrolysis being continued until the oxalate was all changed to carbonate.

Buckminster and Smith (12) separate Hg, Co, or Ni from U electrolytically.

Rheineck (70) separates Fe and U by nearly neutralizing the HNO₃ solution with Na₂CO₃, adding sodium acetate, diluting, and boiling. The Fe precipitate is contaminated with U unless heated with a large quantity of water.

Brearley (9) boils the phosphates of U and Al with an excess of Na₂CO₃ in the presence of NH₄Cl and filters off the U after two hours.

Walker (79) precipitates Fe with NaOH in the presence of considerable H₂O₂, the precipitation taking place in a hot dilute solution. The filtrate contains all the U.

Ditte (16) heats the oxides of Fe and U in a current of H, then in HCl gas at red heat, the Fe going off as the chloride.

Burcker (13) cites a method of Rose in which the oxides of U and Fe are reduced with H, and the Fe dissolved with dilute HCl, leaving the U.

Zimmerman (83) boils a hot solution with an excess of ammonium thiocyanate, and NaHCO₃ is then added until the red color disappears. The Fe is precipitated free from U.

Becker and Jannasch (3) lay much stress on the separation of Fe and U by hydroxylamine.

Kern (40) separates ferric iron from U by extracting with ether in HCl solution, three extractions removing all the Fe. The ether must be saturated previously with HCl. This method was suggested by Langmuir.

Rammelsberg (65) separates U from Mn, Zn, Ni, and Co by adding BaCO₃ (free from alkali carbonates) to the slightly acid solution containing NH₄Cl. (See the method of Rose (72).)

BERYLLIUM, CHROMIUM, AND ZIRCONIUM.

U has been precipitated free from Be by H₂O₂ in the heat, a second precipitation being required in the presence of considerable Be. (See Wunder and Wenger (80).)

Gibbs (28) removes Cr by adding NaOH and Br to the solution of U and Cr. On boiling, the Cr is oxidized and the sodium uranate filtered off.

Ditte (16) heats the oxides of U and Cr in H gas and dissolves the U with HNO₃, leaving the Cr.
Formánek (21) claims that Ditte’s method and the method which separates Cr by precipitation as mercurous chromate in the heat are inadequate.

Classen (15) separates U from Cr by electrolysis in an oxalate solution.

Walker (79) separates Zr from U by fusing with Na₂S₂O₇ and extracting with cold water. H₂O₂ and NaOH are added and the Zr is precipitated by heating, the U being left in solution.

Angelotti (1a) separates Zr from U by cupferron, the Zr being precipitated in H₂SO₄ solution and the U being left in solution.

PHOSPHORUS AND ARSENIC.

According to Girard (69), Reynoso removes P from a HNO₃ solution by the addition of metallic Sn at a boiling temperature, the excess Sn being removed by H₂S. (See Kern (40).) Hintz (34) found that a complete separation of U and P by this method could be made.

Reichardt (67) precipitates P with magnesia mixture, then boils off the CO₂ and precipitates the U with NH₄OH.

Lepierre and Carvalho (48) claim that the only satisfactory separation of P is obtained when the acidity of the solution is nearly neutralized with NaOH, sodium acetate added, and, in the presence of excess Fe, boiled to precipitate ferrous phosphate, the remaining Fe coming down as the basic acetate.

Fresenius and Hintz (25) precipitate the U with K₄Fe(CN)₆ in a faintly acid solution, in the presence of NaCl. The precipitate is decomposed by dilute KOH, the U precipitate being free from P and As.

Knopp (41) fused P₂O₅ and U₂O₃ with KCN and K₂CO₃, and extracted with water, the P being dissolved and the U left in the residue. Hintz (34) found that Na₂CO₃ in place of K₂CO₃ gave very satisfactory results.

Friedel and Cumenge (26) separated phosphoric acid from U by dissolving the substance in HNO₃ and precipitating the phosphoric acid with ammonium molybdate at 65°. This method was used at the University of Pennsylvania for estimating P₂O₅ in precipitates of uranous phosphate.

MOLYBDENUM AND TUNGSTEN.

Pierlé (62) has found that if a solution of W, Mo, and U is evaporated to dryness with HNO₃ on a water bath, and the residue moistened with HNO₃, the U, as uranyl nitrate, can be extracted completely with ether, leaving the Mo and W.
The separation of U from V has been discussed by Pierlé (62) as follows:

Friedel and Cumenge (26) separated uranium from vanadium by evaporating the nitric acid solution of these metals to dryness with an excess of HNO₃, and extracting the uranyl nitrate from the residue with a warm dilute solution of NH₄NO₃. Hillebrand and Ransome (33) failed to extract all the uranium from such a residue by this reagent because of the occlusion of uranyl nitrate in the vanadic oxide.

Kern (40) states that A. C. Langmuir used mercuric oxide and mercurous nitrate successfully for separating vanadium from uranium by precipitating vanadium as mercurous vanadate, and determining the uranium in the filtrate after removing the excess of mercury with hydrogen sulphide. This process seems questionable since Alibegoff (1) precipitated uranium, with mercuric oxide in separating it from the alkalies and alkaline earths.

Fritche (27) precipitated uranium from vanadium by NaOH in the presence of Na₂CO₃. This method is open to criticism, as uranium is not entirely precipitated by sodium hydroxide in the presence of alkaline carbonates.

In 1842 Peligot (61) found that uranyl nitrate dissolved readily in ether.

Pierlé (62) separates U from V by evaporating a solution of their salts to dryness on a water bath in the presence of excess HNO₃. The residue, moistened with HNO₃, is extracted with ether, dissolving the U and leaving the V. The U-V residue may also be extracted with glacial acetic acid (at least 95 per cent) to which HNO₃ has been added in a ratio of 100 c. c. acetic to 5 c. c. HNO₃ (1.42). The V is not attacked under these conditions.

Low (49) separates U from V by the addition of CH₃COONH₄, NaKHPO₄, and glacial acetic acid, and boiling. The V is precipitated, leaving the U in solution. A second precipitation is necessary to effect or to complete separation.

Hillebrand (32) removes V from U by treating with HNO₃ in a porcelain boat, evaporating to dryness, and passing HCl gas over the heated tube in which the boat is placed. The V goes off as oxychloride, leaving the U. The treatment with HNO₃ and evaporation may have to be repeated. Hillebrand also gives a separation by evaporating the HNO₃ solution to dryness and extracting with cold water; the V in solution is removed by a second evaporation with HNO₃, and the U in the precipitate extracted by a second treatment of the residue.

König (43) separates V from U by treating their solution with (NH₄)₂CO₃ and (NH₄)HS, followed by boiling with acetic acid.

Auger (1b) found that cupferron did not precipitate UO₂ but that when the acid solution was reduced with Zr the resulting uranous salt was quantitatively precipitated by cupferron. The precipitate is soluble in CHCl₃. U and V can be separated in this way.

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Hillebrand (32) precipitates the rare earths from a weakly acid solution with oxalic acid at 60° C. The oxalates are removed from the U solution by evaporation and ignition.

QUANTITATIVE ANALYSIS.

METHODS PROPOSED FOR THE DETERMINATION OF URANIUM.

The methods of quantitative analysis in this section have been used for the determination of U.

GENERAL.

GRAVIMETRIC DETERMINATION.

Several methods have been proposed for the gravimetric determination of U.

1. PRECIPITATION AS AMMONIUM OR SODIUM URANATE.

The precipitation of U by means of NH₄OH is one of the oldest methods for the determination of this element, being used by Peligot (61) in 1840. The precipitation is usually carried out in a solution which has been previously freed from interfering elements, the ammonium uranate being filtered off and ignited to U₃O₈ in the air, or reduced in a current of H and weighed as UO₂. Although some adverse criticism has been offered to this method, accurate results can be obtained by proper care in procedure.

Zimmermann (83) claimed that he could not get consistent results when weighing as U₃O₈ and advised reduction with hydrogen. Others have found no difficulty from this cause. (See Pierlé (62), Scott (74), and Treadwell and Hall (78).) Kern (40) considers the reduction with H unreliable, although better results are obtained with platinum than with porcelain crucibles. Kern's method was to ignite the ammonium uranate intensely either with or without the filter paper for about 10 minutes over a blast lamp, allowing the crucible, which is in a slanting position, to cool in the slowly decreasing flame. H₂O₂, CO₂, tartaric acid, oxalic acid, or nonvolatile organic substances prevent the precipitation of ammonium uranate, but the presence of NH₄Cl or NaNO₃ is desirable to secure complete precipitation of the ammonium uranate. Boiling causes the slimy precipitate to coagulate. (See Noyes, Bray, and Spear (58) and Kern (40).)

Bornträger (8) found that if the U be precipitated with NaOH, the sodium uranate was much more difficult to wash than the ammonium salt.

2. PRECIPITATION AS URANIUM PHOSPHATE.

Although the precipitation of U as the phosphate is generally used as a step in the volumetric estimation of U, the precipitate may be ignited and weighed as (UO₂)₂P₂O₇.
Leconte (45) has been given the credit of proposing the phosphate method. Pisani (63) used an alkali phosphate, precipitating uranyl hydrogen phosphate. Na₂HPO₄ has been found to give a precipitate hard to filter and difficult to wash free from Na. (See Pierlé (62).) Kern (40) used (NH₄)₂H₂PO₄ and boiled for half an hour, forming uranyl ammonium phosphate in crystals, which could be as easily handled as ammonium uranate. He advised that the phosphate should be ignited at a low red heat in a porcelain crucible, then moistened with HNO₃, and again ignited at low redness. Brearley (9) used microcosmic salt in the presence of sodium thiosulphate, obtaining a precipitate easy to filter and wash but hygroscopic after ignition, making it difficult to ignite to constant weight. Pierlé (62), using the method of Kern (40), experienced difficulty in filtering; the precipitate had a tendency to run through, and the ignited (UO₂)₂P₂O₇, absorbed moisture more rapidly than lime. His results, however, were good.

Noyes, Bray, and Spear (58) considered it desirable to precipitate the phosphate in the presence of ammonium salts to promote the formation of UO₂NH₄PO₄ as UO₂HPO₄ ran through the filter.

McCoy and Ross (52) have studied precipitation of U as the phosphate, which they dissolved and determined volumetrically.

3. Precipitation as the Sulphide.

Precipitation of U as the sulphide in the presence of NH₄Cl has generally been used to separate U from the alkalies and the alkaline earths. The determination of U by ignition of the sulphide to the oxide has been attempted. Berthier (6) is supposed to have been the first to use (NH₄)₂S in the estimation of U. The precipitation is complete if the solution has been neutralized with NH₄OH, and if no carbonates are present.

Rose (71) used ammonium polysulphide for the sulphide precipitation. Remelé (68) found that this precipitation was best effected by adding to the nearly neutral ammoniacal solution an excess of ammonium polysulphide, the solution being boiled one-half hour, filtered, washed, roasted free from sulphur, and ignited to U₃O₈. Although Zimmermann (81) found this method reliable when compared with the NH₄OH method, Pierlé (62) has always obtained results that are too high, owing to the presence of sulphates in his ignited U₃O₈.

4. Electrolytic Precipitation.

The electrolytic method for the analysis of solutions containing U was used by Classen (15). He precipitated U as the hydroxide in an oxalate solution. Smith and Wallace (76) and Kollock (42) precipitated U electrolytically from acetate, formate, nitrate, and sulphate solutions. In an acetic acid solution with a current of
N. D. = 0.18 ampere and 3 volts, at a temperature of 70° C., the U was precipitated; then it was ignited, and weighed as U₃O₈. The maximum error was 0.3 per cent. Kern (40) got excellent results by Smith's method. He found the best conditions for the precipitation in acetic acid solution were with 0.10 gram U₃O₈, 1 to 2 grams sodium acetate, 1 to 2 c. c. acetic acid (50 per cent), 150 to 200 c. c. volume, temperature about 65° C., current N.D. = 0.60 to 0.70 ampere and 6 to 8 volts, the U being completely precipitated in from five to seven hours; with 0.15 gram U₃O₈ the conditions are the same, except that a current of N.D. = 0.70 to 1 ampere is used, the temperature being kept up, after the start, by the current and no external heat being required; when more than 0.15 gram U₃O₈ is present a longer time is required with a current not to exceed N.D. = 1 ampere, since a greater current gives a spongy deposit which peels from the dish.

5. MISCELLANEOUS PRECIPITATIONS.

Fairley (18) used H₂O₂ as a precipitant for U. He found that in an acetate or dilute nitrate solution the U could be precipitated quantitatively with an excess of H₂O₂; excess of salts of Na, K, Ba, or Ca, and excess of HCl, HNO₃, or H₂SO₄, however, prevent complete precipitation.

Mazzucchelli (50), using the same method, found that UO₄ came down in a form more easily filtered if the solution had NH₄Cl present in approximately molar quantities. He also found that the temperature should not exceed 70° C., that H₂O₂ should be in excess, that 1/10N NH₄Cl solution should be used for wash water, and that while moderate amounts of alkali chlorides, sulphates, nitrates, or ammonia did not interfere, large quantities of these salts, as well as fluorides, acetates, oxalates, and tartrates, prevented the precipitation to some extent.

Wunder and Wenger (80) used this method for the separation of U and Be.

Blair (7) determined U in the presence of V as V₂O₅.2UO₃(NH₄)₂ O.H₂O. Ammonium acetate solution (30 per cent acetic acid added to strong NH₄OH until acid to litmus) was added to the faintly acid U solution which contained an excess of V. The ammonium uranyl vanadate was filtered off, washed, ignited at a low red heat, and weighed as V₂O₅.2UO₃.

Giolitti (29) precipitated the U from a solution, which had been reduced, by means of a slight excess of HF. The heavy green precipitate, possibly UF₄, was ignited and weighed as U₃O₈, then reduced with dry H and weighed as UO₂. The fluoride was readily filtered and washed with water containing a little HF. As an alternate method, instead of reducing the solution he electrolyzed it in a solution

* N. D. = signifies normal density per 40 sq. cm.
containing 4 to 5 c. c. of HF at a volume of 100 to 150 c. c., with a current density of 0.8 ampere per square centimeter. The green insoluble fluoride was loosely deposited and was easily transferred to the filter, and treated as in the previous method.

Siemssen (75) proposes the use of ethylenediamine as a precipitant for U. He found that a 10 per cent solution added to a U solution caused a bright yellow precipitate to form. This precipitate settled quickly, was readily filtered, washed easily with cold water, and on ignition formed $U_3O_8$. Various organic reagents were without effect on the precipitate, but other metals gave precipitates with the ethylenediamine.

Ditte (16) determined U in the presence of Fe and Cr by difference. The oxides formed by the ignition of the precipitate formed with NH$_4$OH were weighed, heated in a current of H, HCl gas passed over at red heat to remove the Fe, cooled in H, and weighed. The U was dissolved by HNO$_3$, leaving the Cr which was weighed, the loss in weight being considered U.

**VOLUMETRIC DETERMINATION.**

Nearly all of the methods given for the volumetric determination of U depend on its reduction and subsequent oxidation with a standard KMnO$_4$ solution. Belhoubek (5) first proposed this method in 1867, and since that time numerous variations have been used and criticized. Each investigator can secure good results by his own method, but not by that of another. This points to the fact that considerable experience with any volumetric method for the determination of U is necessary before the analyst can be sure of his results.

Guyard (31) found that the U was reduced below the tetravalent state when reduced with Zn, his results being too high. This has been confirmed by Goettsch (30) and others.

Zimmermann (82) reduced uranyl sulphate by means of Zn in a closed flask, then poured the solution into a dish before titration. His results under the conditions showed that tetravalent U, in a fairly stable state, had been titrated. Kern (40) found no over-reduction when the uranyl sulphate was reduced by a Jones reductor containing an 18-inch column of 20-mesh amalgamated Zn. His results agreed closely. He found that the reduction was satisfactory when either Zn, Al, or Mg were used, but that stannous chloride gave unreliable results. The presence of HCl always caused a reduction lower than UCl$_4$. This evil effect of chloride solutions, first noticed by Follenius (20), was said to be overcome by the presence of manganese sulphate (83).

Fritschle (27) used the volumetric method for the estimation of U in ores. The solution, freed from interfering elements, was fumed
with $\text{H}_2\text{SO}_4$, diluted and heated with strip Zn until a sea-green color formed, and then titrated with $\text{KMnO}_4$. Pulman (64) found that overreduction took place when the solution from a Jones reductor was collected in a receiver containing dry $\text{Na}_2\text{CO}_3$, but that pouring the solution through the air before titrating removed that difficulty.

Finn (19) uses the volumetric method for the determination of uranium in ores. McCoy and Bunzel (51) give a method with which they checked up gravimetric methods almost exactly. They found that when the $\text{H}_2\text{SO}_4$ acidity was about 4N, the reoxidation of the overreduced U was effected by the air, but that the rate of oxidation of the tetravalent U was quite slow. They boiled 125 c. c. solutions containing about 0.3 gram of U and 20 c. c. $\text{H}_2\text{SO}_4$ with strip Zn which had been activated with a preliminary treatment with acid containing a little $\text{CuSO}_4$. The heating was continued for about 15 minutes and the solution filtered into a large porcelain dish, the Zn being washed with cold $\text{H}_2\text{SO}_4$ (1:10). The final volume was made up to 300° C. and titrated with 1/10N $\text{KMnO}_4$. The brown color which resulted on reduction had changed to sea green during the filtration and washing.

Campbell and Griffin (14) determined U in the presence of V by first reducing with $\text{SO}_2$ and then titrating with $\text{KMnO}_4$ (the U not being reduced). The solution was then reduced with an Al spiral, reducing both the V and U, and titrated with $\text{KMnO}_4$, the difference in the amount of $\text{KMnO}_4$ being used to compute the quantity of U. The Al spiral was washed with ferric alum to prevent oxidation of the V. Hillebrand (32), however, questions the advisability of the use of ferric alum as a wash, due to the possibility of reduction of the Fe by this treatment. Johnson (36) finds this method satisfactory in pure U solutions or in the presence of small amounts of V, but large quantities of V give uncertain results.

Ibbotson and Clark (35) poured a solution of uranyl sulphate, with 2 to 5 per cent $\text{H}_2\text{SO}_4$ (by volume), into a flask containing 50 grams of 20-mesh Zn, heated until dark brown, cooled rapidly, and filtered cold, washing the Zn with cold water. Air was then passed through for one minute and the solution titrated with $\text{KMnO}_4$.

Pierle (62) found that overreduction always took place when reducing with Zn or Mg and that sodium amalgam, organic reducing agents, photographic developers, or hydroxylamine gave varying results; none, however, were good. He found the overreduction, when using Zn in a Jones reductor, never went to a valence of three or to any other definite value, the results being variable. He failed to get conditions such that the proper state of reduction was reached before titrating.
Newton and Hughes (57) in the absence of Fe reduced U with Ti₅(SO₄)₉, oxidized the excess Ti salt with bismuth trioxide, filtered off the remaining bismuth salt, and titrated the U with KMnO₄.

Auger (2) in the presence of Fe reduced the U with amalgamated Zn and titrated with a ferric salt, using KCNS as an indicator. In the presence of Fe and Ti a large excess of sodium tartrate was added and the mixture reduced with a titanic salt, using nitroinduline as an indicator.

Leduc & Co. (46) experienced no difficulty in the volumetric determination of U. They reduced it by amalgamated Zn in the Jones reductor, shook vigorously for a minute with free excess of air, and titrated with 1/20N KMnO₄. However, they suggested that 0.5 c. c. be subtracted from the KMnO₄ used to correct for endpoint and reductor errors.

Mohr (54) determined U volumetrically by titrating the acetate solution with NaHNNH₂PO₄, adding it drop by drop until brought in contact with a drop of freshly prepared K₄Fe(CN)₆; it failed to give a brown coloration.

Treadwell and Hall (78) give a method which was used by Belhoubék (4), Zimmerman (82), and Hillebrand (32) for testing the purity of a U₃O₈ precipitate. The U₃O₈ is placed in a tube with 10 to 15 c. c. of 1:6 H₂SO₄, the tube drawn out, the air replaced by CO₂, and the tube sealed. The tube is heated at 150 to 175°C until all the residue has dissolved, then cooled and the contents transferred to a porcelain dish, diluted, and titrated with 1/10N KMnO₄ solution. The reactions involved follow:

\[ \text{U}_3\text{O}_8 + 4\text{H}_2\text{SO}_4 = 2\text{UO}_2\text{SO}_4 + \text{U(SO}_4)_2 + 4\text{H}_2\text{O}. \]
\[ 2\text{KMnO}_4 + 5\text{U(O}_2\text{SO}_4) + 2\text{H}_2\text{O} = 2\text{KHSO}_4 + 2\text{MnSO}_4 + \text{H}_2\text{SO}_4 + 5\text{UO}_2\text{SO}_4. \]

Johnson (37) suggests a method for the determination of U in the presence of V and Fe. The U, Fe, V, etc., are precipitated with NH₄OH, filtered, washed, ignited, and weighed. The oxides are dissolved in HCl, taken to fumes with H₂SO₄, diluted to 150 c. c., reduced by H₂S, and the H₂S then removed with CO₂. The solution is then titrated to pink with KMnO₄, ferricyanide indicator added, and a standard ferrous ammonium sulphate solution added until the light blue solution darkens. The first titration less the second gives the Fe, and the second gives the V. The Fe and V, calculated to their oxides, are deducted from the total weight of the oxides to get the U₃O₈. If Al be present, it is determined in one-half of the solution and a correction made for it.

McCoy and Ross (52), Johnson (37), and others have used volumetric methods for the determination of U in different classes of material.
COLORIMETRIC DETERMINATION.

Bruttini (11) suggested that the depth of color produced by mixing K₄Fe(CN)₆ and a standard solution of U might be compared with that obtained from mixing an unknown solution with K₄Fe(CN)₆ under like conditions, and the U in the unknown solution be computed.

ORES.

GRAVIMETRIC DETERMINATION.

Fresenius and Hintz (25) digested the ore with acid, evaporated to dryness, dehydrated the SiO₂, and extracted with dilute HCl. K₄Fe(CN)₆ was added and the solution saturated with NaCl. After the precipitate had settled, it was filtered, washed with a solution of NaCl, and then decomposed in the cold with dilute KOH solution. The precipitate in which the U was then present as potassium uranate was washed free from ferrocyanide, with a solution containing NH₄Cl and NH₄OH. The residue, free from P and As, was dissolved in HCl, nearly neutralized with NH₃OH, and digested some time in the cold with an excess of (NH₄)₂CO₃. The Fe and Al were filtered off and the filtrate was acidified, heated, and H₂S introduced to remove the sulphide metals. The filtrate was boiled to remove H₂S and NH₄OH added to precipitate ammonium uranate, which was ignited to U₃O₈ or reduced by heating with H₂.

Bornträger's method (8) was to digest the ore with HNO₃, dilute, and filter. Excess Na₂CO₃ was added and the U with traces of other metals was dissolved, when the solution was boiled, and filtered off. NaOH was added to the filtrate to precipitate sodium uranate, which was filtered off, ignited, and dissolved in HCl. The U was then precipitated with NH₄OH and, after washing, was ignited to the oxide.

Kern (40) tried out methods of separation and analysis and gives methods for the estimation of U in pitchblende. By the first method 1.3 grams of ore were treated with 5 c. c. of water and 10 c. c. of HNO₃ (sp. gr. 1.42) and heated in a covered dish nearly at boiling until the residue was almost white, then the cover was removed and the substance evaporated to pastiness. The cooled residue was extracted with 50 c. c. of water and 3 c. c. of HNO₃, then boiled, filtered, and washed. The filtrate was diluted to 200 c. c., H₂S passed through the cold solution for an hour, and the precipitate filtered and washed with H₂S water. The filtrate was heated to remove the H₂S evaporated to 125 c. c., and the S filtered off. The solution was then boiled and 150 c. c. of a saturated Na₂CO₃ solution added, the boiling being continued for at least 15 minutes. The precipitate was washed with hot water and the filtrate evaporated to 150 c. c. HCl was then added so that the solution had 3 c. c. of free acid and the CO₂ removed by boiling for 30 minutes. NaOH
was then added in slight excess to the hot solution, and the covered beaker was boiled for 10 minutes, filtered, and washed with hot water. The determination from this point was carried on by several methods. The sodium uranate was ignited, washed, ignited, and weighed as NaO(U₂O₇); it was dissolved in HCl and the U precipitated with NH₄OH was ignited and weighed as U₂O₅; it was dissolved in HCl, diluted, made slightly alkaline and acidified with acetic acid and the uranium precipitated with (NH₄)₂HPO₄, ignited, and weighed as (UO₂)₂P₂O₇; it was evaporated to fumes with H₂SO₄ and determined volumetrically, reducing with zinc and titrating with KMnO₄; and, as a final check, a HNO₃ solution was evaporated to dryness and taken up with acetic acid, the uranium being removed electrolytically, ignited, and weighed as U₃O₈.

Kern's second method was to use an ether extraction for separating the U from Fe. The ore was decomposed with HNO₃ as before, then the pasty residue was taken to dryness twice with HCl, diluted, and the H₂S precipitation carried out. The U and Fe were precipitated from the H₂S filtrate by NH₄OH, after it had been boiled, to remove H₂S. This precipitate was dissolved in HCl and evaporated to dryness with it twice, finally being taken up with 15 c. c. HCl (sp. gr. 1:10). The Fe was then extracted by treating in a separatory funnel with ether, previously saturated with HCl; this required three extractions with ether, each ether extract being washed twice with HCl (sp. gr. 1:10). The water solution was allowed to stand until the ether had evaporated and was then evaporated to 40 c. c., diluted to 100 c. c., nearly neutralized with NH₄OH, and 100 c. c. of a saturated solution of (NH₄)₂CO₃ added, the solution boiled five minutes, and filtered. The filtrate was boiled to remove CO₂ and the U determined in this solution by the various methods outlined in the previous method. The results by this method were more uniform than by the previous one, the limit of error being about 0.6 per cent on an ore running 20 per cent U₃O₈.

Blair (7) determined U in carnitite as ammonium uranyl vanadate. Two grams of ore were boiled with 25 c. c. of HNO₃ and 25 c. c. of water for one-half hour, then diluted and filtered. NH₄OH was added until a precipitate formed, and (NH₄)₂CO₃ in a saturated solution was added in moderate excess. The volume was about 250 c. c. and was heated at 40 to 50° C. for 20 minutes. The precipitate settled out, was filtered and washed with 2 per cent (NH₄)₂CO₃ solution, then dissolved in hot dilute HNO₃ and reprecipitated. The combined filtrates and washings were boiled to remove CO₂, a few drops of HNO₃ being added and the solution evaporated to 200 c. c. NH₄OH was then added until a precipitate formed and enough HNO₃ just to clear the solution, after which 10 to 15 c. c. of ammonium acetate solution was added (30 per cent acetic acid added to strong NH₄OH
until it was acid to litmus. The precipitate, \( V_2O_5 \cdot 2UO_3 \cdot (NH_4)_2O \cdot H_2O \), settled after boiling a few minutes. (If the ore was deficient in \( V \), it was added before this precipitation.) The precipitate was filtered, washed with ammonium acetate solution, dissolved in \( HNO_3 \), and evaporated to dryness on a water bath. The residue was extracted with a little dilute \( HNO_3 \) and \( NH_4OH \) and \((NH_4)_2CO_3\) added to dissolve the U and precipitate Si and Al. The ammonium uranyl vanadate was precipitated in the filtrate (as above), filtered, ignited at a low red heat, and weighed as \( V_2O_5 \cdot 2UO_3 \).

Scott (74), Low (49), and Ledoux and Co. (46) give methods very much alike.

They treated the ore with aqua regia, evaporated to dryness, dehydrated the SiO₂, and took up with HCl. If the residue was considerable it was treated with HF in a platinum dish, ignited, and extracted with HCl. The solution was diluted, saturated with \( H_2S \), and the sulphides filtered off and washed. Fe and insoluble carbonates were removed from the filtrate by boiling with \( Na_2CO_3 \) and \( H_2O_2 \), a second precipitation being required for a good separation.

The solution acidified with \( HNO_3 \) was freed from CO₂ by boiling and the acid neutralized with \( NH_4OH \); then 10 c. c. of \( HNO_3 \) was added and the V precipitated as lead vanadate with a 25 per cent solution of lead acetate, followed by ammonium acetate solution to neutralize the free acid. The vanadate was allowed to settle, then filtered. Any occluded U was removed by a second precipitation. Most of the Pb was removed from the solution by the addition of \( H_2SO_4 \). The remainder of the Pb and all of the U were then precipitated with \( (NH_4)_2HS \) in the neutralized solution. The precipitate was dissolved in hot 1:2 \( HNO_3 \), then taken to fumes with \( H_2SO_4 \). The cooled residue was extracted with water, boiled, cooled, and filtered.

Al was removed from the filtrate with \((NH_4)_2CO_3\) in the cold and the U recovered from the filtrate, which had been acidified and boiled to remove CO₂, by precipitation with \( NH_4OH \). The ammonium uranate was ignited and weighed as \( U_2O_5 \).

Johnstone (38) gives a method for the determination of U when it occurs with the rare earths, as in thorite. In the absence of V and P, he adds an excess of \((NH_4)_2CO_3\) to the acid solution obtained from extracting an ore; the precipitate is filtered off and reprecipitated as before. Rare earths are removed from the filtrate by ammonium oxalate and the filtrate evaporated to dryness and ignited to remove the oxalates, dissolved in \( HNO_3 \), and the latter removed by repeated evaporation with \( H_2SO_4 \). The sulphates are dissolved in a little water and three times their bulk of alcohol added, and after 12 hours the solution is filtered off, evaporated to dryness,
and ignited. The residue is dissolved in HNO₃ and the U precipitated by NH₄OH and ignited to U₃O₈, as usual.

When phosphates are present, the phosphorus is removed by the addition of ferric sulphate and ammonium acetate to the solution, which is kept slightly acid. A second precipitation is used to recover occluded U. The filtrates are evaporated to dryness and treated as in the previous method.

Hillebrand (32) gives two methods for the determination of U and V. In the first, the ore is treated with acid, evaporated to dryness, taken up with cold water, and filtered, and practically all of the V is in the residue. To get the rest of the V in the residue, the filtrate is evaporated to dryness and again leached with water; this solution contains most of the U. The residues are dissolved in a little HNO₃, transferred to a porcelain boat, and evaporated to dryness. The V is removed as oxychloride when the boat, placed in a glass tube, is heated in a stream of HCl gas, and can be collected in U tubes filled with water and then determined. The treatment with HNO₃ and HCl gas should be repeated until the V is all removed. The contents of the boat are treated with HNO₃ and the solution added to the main U solution. H₂S is added to remove Cu or Pb and a drop of H₂SO₄ to separate Ba. The U can then be precipitated with NH₄OH and ignited to the oxide after first separating Fe, Al, lime, and the alkalies. Any P can be determined and deducted from the weight of U₃O₈ found.

A second method is given which is not applicable to pitchblende but can be used for carnitite. The ore is treated with cold 1:1 HCl, filtered, and H₂S added (if As is present heating for some time is necessary); the filtrate is heated to expel H₂S, and evaporated to dryness with HNO₃. The residue is extracted with cold water, filtered, and washed with cold water. The residue is treated with HNO₃ and again evaporated to dryness and most of the V is extracted with NH₄OH. The residue dissolved in HNO₃ is again evaporated to dryness and extracted with NH₄OH. The final residue is dissolved in HNO₃ and added to the U solution, which is then neutralized with NH₄OH and (NH₄)₂CO₃ and NH₄HS added. After it has stood 24 hours in a stoppered flask, the U solution is filtered off, evaporated to dryness, ignited gently, and dissolved in HNO₃. The U is precipitated from this solution with NH₄OH, filtered, washed, dissolved, then reprecipitated, filtered, washed, and ignited to U₃O₈ and weighed as crude U₃O₈. It is extracted with a little warm HNO₃ and the insoluble residue, whose weight is deducted from that previously found, is filtered off. One-half of the filtrate is tested for P₂O₅ and, if present, its weight deducted from that of the impure U₃O₈. The other half of the filtrate is evaporated with H₂SO₄, taken up with water and any BaSO₄ filtered off, weighed,
and its equivalent of BaO deducted from the crude U₃O₈. The V in the filtrate is determined volumetrically and the V₂O₅ deducted also from the crude U₃O₈.

Johnson (37) gives a method for the determination of U in carnitite or in Fe-U. He extracts or dissolves 2 grams of ore or 1 gram of the Fe-U for an hour with 100 c. c. of HCl, evaporates to 20 c. c., dilutes to 50 c. c., and filters, washing with dilute HCl. The residue is evaporated with HF and H₂SO₄, the residue from this treatment being fused with Na₂CO₃ and extracted with HCl. The solutions, diluted to 300 c. c., are nearly neutralized with NH₄OH, heated, saturated with H₂S, and filtered. The filtrate and washings from this precipitation are evaporated to 20 c. c., and 1 gram of KClO₃ and 50 c. c. of HCl are added to remove H₂S, the solution being again evaporated to 20 c. c., then diluted to 300 c.c. and an excess of Na₂O₂ added; next in order, 10 grams of (NH₄)₂CO₃, 10 grams of Na₂CO₃, and last of all 10 grams more of Na₂O₂ are added. The solution is brought to boiling, cooled, filtered, and washed. The solution, not less than 400 c. c., is neutralized with 1:1 HCl until it no longer turns turmeric the faintest brown. After one hour, the Al is filtered off. The filtrate is acidified, the CO₂ boiled off, and the uranium precipitated with NH₄OH, filtered, washed, ignited, and weighed as U₃O₈ and V₂O₅. The oxides are then taken to fumes with H₂SO₄, diluted, filtered, and the residue of SiO₂ weighed and deducted from the weight of the mixed oxides. The V is then determined volumetrically by reduction with HCl and the weight of its oxide deducted from that of the U₃O₈ plus V₂O₅.

Scholl (73) developed a rapid method for the determination of U in carnitite, which will be given in the following section, "Selected methods." (See p. 230.)

VOLUMETRIC DETERMINATION.

Fritchle (27), in his method for the estimation of U in carnitite, moistened 0.5 gram of the ore with water, added 10 c. c. of HNO₃, and digested in a covered beaker for about an hour just below boiling, to dissolve the U. The solution was diluted with 10 c. c. of water and, after neutralizing with a saturated Na₂CO₃ solution, 5 c. c. were added in excess, with 20 c. c. of a 20 per cent NaOH solution. After this was boiled for an hour, the Fe and U were filtered, washed with a hot NaOH solution, and dissolved in 20 c. c. of hot 1:1 HNO₃. After the addition of 40 c. c. of water and sufficient NH₄OH to just neutralize the solution, 40 c. c. of a saturated (NH₄)₂CO₃ solution was added, and the solution heated to boiling, filtered, and washed with a 2 per cent (NH₄)₂CO₃ solution. The filtrate was evaporated to fumes with 20 c. c. of H₂SO₄ (1:1), cooled, diluted to 100 c. c., reduced by boiling with Zn strips to a sea-green color, and then titrated with a standard solution of KMnO₄.
Kern (40) after treating the ore as given in his gravimetric method to obtain pure sodium uranate, dissolved the uranate in HNO₃, added 30 c. c. of H₂SO₄, and evaporated to fumes, then diluted to 150 c. c. and reduced by boiling with 50 grams of Zn for one-and-one-half hours. The reduced solution was quickly filtered into a flask containing about 1 gram of Na₂CO₃ to prevent oxidation of the reduced U salt, and after diluting to 400 c. c. was titrated with 0.01N KMnO₄.

Finn (19) fumed a quantity of ore containing about 0.25 gram of U₃O₈ with H₂SO₄, diluted it, and added an excess of Na₂CO₃, boiling to dissolve the U. The precipitate was freed from U by solution in H₂SO₄ and reprecipitated with Na₂CO₃. The combined filtrates were heated to boiling and 0.5 gram of ammonium phosphate and a slight excess of NH₄OH added. After this was boiled a few minutes, the precipitate was filtered off and washed with a weak solution of (NH₄)₂SO₄. The precipitate was dissolved in dilute H₂SO₄, reduced with Zn, and titrated with standard KMnO₄. V was determined in the filtrate from the phosphate precipitation.

By Campbell and Griffin's method (14) for the determination of U and V in an ore, 0.3 to 0.5 gram of the ore is dissolved in 40 c. c. of 1:5 H₂SO₄, with or without the addition of HNO₃, and the solution evaporated to fumes. The diluted solution is treated with an excess of Na₂CO₃, boiled and, after the addition of H₂O₂ to oxidize the Fe, etc., the solution is filtered. The precipitate is dissolved in 1:1 H₂SO₄, diluted, boiled, and again precipitated with Na₂CO₃, filtered, and washed. The combined filtrates and washings having from 2 to 5 c. c. of free H₂SO₄ are saturated with SO₂ and then boiled while passing in CO₂ to remove the excess. The hot solution is titrated with KMnO₄. The U is not reduced by SO₂, so that this titration estimates the V only. The solution is then reduced at 80° C. with an Al wire formed into a spiral. The wire is removed and washed with a ferric alum solution, which flows into the reduced solution, preventing the immediate oxidation of the V. The U and V are titrated with standard KMnO₄ and the amount of U computed from the difference in KMnO₄ used. Johnson (36) found this method accurate in the presence of small amounts of V, but useless when V was present in considerable quantity. Hillebrand thinks that the ferric iron might be reduced by the Al and thus introduce an error.

McCoy and Bunzel (51) separated U from the other elements found with it in an ore by precipitation as the phosphate. An aliquot from a H₂SO₄ solution of the phosphate was diluted to 100 c. c. and 20 c. c. of concentrated H₂SO₄ was added, the solution being poured upon 100 grams of pure Zn sticks, previously activated by treating with a little CuSO₄ in H₂SO₄. The solution was heated almost to boiling for 15 minutes and filtered, the Zn being washed
with cold 1:10 $\text{H}_2\text{SO}_4$. The volume was then made to 300 c. c. and the solution, which was brown after reduction, changing to sea green on filtration and washing, was titrated with 0.1 N $\text{KMnO}_4$. The results checked those obtained gravimetrically.

Low (49) digested the ore with aqua regia, evaporated to dryness, extracted with $\text{HCl}$ (dilute), and precipitated metals of the second group with $\text{H}_2\text{S}$. The $\text{H}_2\text{S}$ was boiled off from the filtrate, 10 c. c. of $\text{H}_2\text{O}_2$ and $\text{Na}_2\text{CO}_3$ added, and the solution boiled for some time. The precipitate was filtered off and dissolved in $\text{HNO}_3$ and the precipitate repeated in this solution as before. The combined filtrates and washings, boiled to 100 c. c., were acidified with $\text{HNO}_3$ and the $\text{CO}_2$ boiled off. The hot U solution was poured slowly into a boiling solution containing 15 grams of ammonium acetate, 5 grams of microcosmic salt, 50 to 75 c. c. of water, and 5 c. c. of glacial acetic acid, and boiled a few minutes. The settled precipitate was filtered, dissolved in hot 1:1 $\text{HNO}_3$, diluted, and the phosphate precipitation repeated, washing with $(\text{NH}_4)_2\text{SO}_4$. The precipitate was dissolved in hot 1:3 $\text{H}_2\text{SO}_4$ and diluted to 50 to 75 c. c., heated to boiling, and organic matter oxidized with $\text{KMnO}_4$. Ten grams of c. p. Zn were then added and the reaction allowed to proceed until it became very slow; then 25 c. c. of water and 10 c. c. of $\text{H}_2\text{SO}_4$ were added, and when the Zn was nearly dissolved the solution was filtered and cooled to room temperature, after which it was titrated with $\text{KMnO}_4$ solution. A blank was run to correct for Fe, etc., in the Zn. To prove the absence of V, the solution was reduced with $\text{SO}_2$ and titrated again with $\text{KMnO}_4$, after boiling off the excess $\text{SO}_2$.

Ledoux & Co. (46) and Scott (74) use similar methods. The U is extracted from the ore and separated from the other elements as by gravimetric methods, except that the U is finally precipitated as the phosphate.

The precipitate is dissolved with $\text{H}_2\text{SO}_4$, the organic matter oxidized with $\text{KMnO}_4$, and the solution passed through a Jones reductor, then shaken in contact with the air and titrated with standard $\text{KMnO}_4$.

**COLORIMETRIC DETERMINATION.**

Bruttini (11) extracted the ore with $\text{HNO}_3$, evaporating to dryness to remove the $\text{SiO}_2$, and separated the U as ammonium uranate after first treating with $(\text{NH}_4)_2\text{HS}$ and $(\text{NH}_4)_2\text{CO}_3$. The ammonium uranate was dissolved in hot dilute $\text{HNO}_3$ and aliquot parts taken for a colorimetric comparison with standard U solution, using $\text{K}_4\text{Fe(CN)}_6$ to produce the color in each solution.

**RADIOACTIVE METHOD FOR ORES.**

The ratio of Ra to U occurring in a given ore is usually constant. This makes possible the unusual case where the quantity of one element may be found through the determination of another. The
ionizing effect of the radiations from a radioactive ore has been used as an approximate measure of its U content. This ionizing effect of a radioactive ore causes the charged leaf of an electroscope to discharge more rapidly than its natural rate.

Moore and Kithil (55) give a method, based on this principle, for the approximate estimation of U in a carnottite ore. In order to make the method applicable to other ores, the analyzed sample used as a standard should be, as nearly as possible, identical with the unknown sample. The time required for the charged leaf of an electroscope to pass a certain number of divisions on a graduated scale is first noted. A sample of uniformly ground ore of a definite surface area and weight is placed at a fixed distance from a conductor fastened to the leaf section of the electroscope, and the time required for the charged leaf to pass the same divisions as before noted. Finally, an analyzed sample with weight, surface area, and physical properties similar to those of the unknown ore is placed at the same distance from the conductor, and the rate of fall of the charged leaf over the same divisions of the scale observed. After the rate of fall of the leaf, in divisions per second, found in the first test and known as the "natural leak," is deducted from the rate of fall of the leaf in the other tests (in the same units), the rates of fall of the leaf are proportional to the U in the samples. It is important that the same divisions be used in measuring the rate of fall of the leaf, and that the illumination be constant during the determinations.

METALS.

Trautmann (77), in his method for the estimation of U in Fe-U, dissolved 0.4 to 0.6 gram of the metal in diluted aqua regia, neutralized it with (NH₄)₂CO₃, and after 24 hours filtered off Al, Fe, and SiO₂. The CO₂ was boiled from the acidified solution and the U precipitated with NH₄OH, filtered, and washed with a dilute solution of NH₄OH and NH₄NO₃. The precipitate was ignited to U₃O₈ in a porcelain crucible. He found that a better separation of U from Fe and Al was obtained by using (NH₄)₂S and (NH₄)₂CO₃ than with the straight (NH₄)₂CO₃ treatment.

Johnson (37) found that Fe-U always contained considerable V and Al, and used the same method of analysis that he did for carnottite. This was given in the gravimetric section for ores.

König (43) gave a method for the determination of U in steel in the presence of V, Mn, Fe, Al, W, Ni, and Cu. A 2-gram sample of the metal was treated with aqua regia, evaporated, diluted, and the WO₃ filtered off. The HCl was removed by fuming with H₂SO₄, and the Fe, Ni, and Co removed from this diluted solution by electrolysis in the presence of ammonium oxalate, the process being continued
until the oxalate was all changed to carbonate. The filtrate was evaporated from 300 c. c. to 100 c. c. to remove CO₂ and the U precipitated with a trace of Co, V, Mn, Fe, and Al. The precipitate was dissolved in HCl, diluted, and (NH₄)₂CO₃ and (NH₄)₂S added, the whole being corked in a flask and allowed to stand 12 hours. The U and V were in solution and filtered off. Acetic acid was added, the solution boiled, and the V precipitated and filtered off. HNO₃ was added to the filtrate and the U precipitated from the boiling solution with NH₄OH, was filtered, washed, ignited to U₃O₈, and weighed or reduced to UO₂ in hydrogen and then weighed.

Johnson (37) suggested a method for the estimation of U in steel in the presence or absence of W, Cr, Al, Co, Ni, and V. A 1-gram sample was heated with 40 c. c. of 1:3 H₂SO₄, then 15 c. c. of HNO₃ was added and the material heated until red fumes were gone; 100 c. c. of water was added and, after warming, W and SiO₂ were filtered off. The filtrate and washings were diluted to 200 c. c., a slight excess of Na₂O₂ added, and then 10 grams of (NH₄)₂CO₃, followed by 10 grams of Na₂CO₃ and then 10 grams more of Na₂O₂ introduced. The solution was heated to boiling, cooled, filtered, and washed with a carbonate solution. The precipitate was dissolved and given the peroxide treatment as long as any U was occluded. The filtrate and washings were just neutralized with 1:3 H₂SO₄, using turmeric paper as the indicator. After several hours the U and some V were filtered off and their solution, acidified with H₂SO₄, boiled to remove CO₂, and a slight excess of NH₄OH added to the hot solution. After about one-half hour of boiling, the U-V precipitate was filtered off, washed with (NH₄)NO₃ dissolved, and reprecipitated. The precipitate was ignited, weighed, and treated with H₂SO₄, taken to fumes, diluted, SiO₂ filtered off, ignited, and weighed. The V was determined volumetrically in the solution and the SiO₂ and V₂O₅ deducted from the weight of the mixed oxides to get the weight of U₃O₈.

Johnson (36) also gives other methods for the determination of U in steel. For plain steel he dissolves the sample in H₂SO₄ (1:3), filters, and washes with 1 per cent H₂SO₄. The residue is ashed and treated with HF and H₂SO₄ to drive off the SiO₂. The residue is leached with water and the solution added to the main filtrate, which is then diluted to 250 c. c. NH₄OH (1:1) is added with constant stirring until a slight precipitation takes place, then drop by drop until it just begins to take on a blackish tint. The U is filtered off at once and redissolved in HCl (1:1). Na₂O₂ is then added to oxidize the Fe, then 5 grams of Na₂CO₃ and 5 grams of (NH₄)₂CO₃ added and the U dissolved by boiling. The U solution is filtered off and HCl (1:1) added until it no longer turns turmeric paper brown but is still alkaline to litmus. After boiling off CO₂, 5 grams of (NH₄)₂HPO₄ is added to the cooled solution; then the solution is made alkaline
with NH₄OH (1:1) and acidified with acetic acid (1:1), 5 c. c. being added in excess. The U is filtered and, after washing, is dissolved in 50 c. c. of hot H₂SO₄ (1:3). For high V steels a second phosphate precipitation is necessary. KMnO₄ is then added and the solution boiled, cooled, and reduced with Zn in a Jones reductor followed by titration with standard KMnO₄ solution.

In chrome-tungsten steel the procedure is the same except that the decomposition of the steel is accomplished by first treating with H₂SO₄, then boiling the residue with HNO₃, and filtering off the W.

Kelley, Myers, and Illingsworth (39) give a method for the determination of U in steels, which will be described in the following section.

NEW METHODS.

The following new methods have not been tried out in the Bureau of Mines laboratories.

Scott (73a) uses a mixture of glacial CH₃COOH and dilute HNO₃ to extract the residue obtained by heating carnotite ore with 1:1 HNO₃, evaporating to dryness, and baking. The mixture is boiled and, after filtering, the solution is evaporated to dryness, ignited, and extracted with a fresh acetic acid mixture. This extract is filtered, evaporated to dryness and taken up with dilute HNO₃ and the uranium is determined gravimetrically by precipitation with NH₄OH, after first removing Fe and Al with NH₄OH and (NH₄)₂CO₃. The ignited U₅O₈ is weighed and dissolved with HNO₃, the weight of the residue being deducted.

Treadwell, Lüthy, and Rheiner (73a) use Cd in a Jones reductor to reduce UO₂SO₄ in solution to the uranous condition previous to titration with KMnO₄.

Treadwell and Weiss (78b) give a volumetric method in which the KMnO₄ titration is carried out electrometrically, using insoluble electrodes. (See also Ewing and Eldridge (17a).)

Müller (56a) bases a colorimetric method on the colors produced when aliphatic alpha-hydroxy and keto acids, as well as aromatic hydroxy carboxylic acids and higher phenol, are added to a uranyl salt solution.

SELECTED METHODS.

GENERAL.

In the past, considerable difficulty has been experienced in the determination of uranium in complex ores. The Bureau of Mines, in connection with its work on the extraction of radium, uranium, and vanadium from carnotite ores, had an opportunity to study the various proposed methods of analysis.
BUREAU OF MINES METHOD.

Loudoux & Co. (46) give a method which, although long and tedious, has been used by the Bureau of Mines and found satisfactory for the determination of U in complex carnitite ores.

RESUME OF METHOD.

The ore is treated with HCl and HNO₃ and, after evaporating to dryness, extracted with dilute HCl, filtered, and washed. If the ore is not completely decomposed, the residue is ignited, treated with HF, and taken to dryness twice with HCl to expel all of the HF. The residue is extracted with dilute HCl and the filtrates and washings saturated with H₂S, filtered, and boiled free from H₂S. The solution, oxidized with H₂O₂, is neutralized with Na₂CO₃ and 2 to 3 grams in excess added, then boiled 15 minutes, filtered, and washed. The Fe precipitate is dissolved in 1:1 HNO₃ and reprecipitated as before. The filtrates are evaporated somewhat, HNO₃ added, and the solution boiled to expel CO₂. The solution is neutralized with NH₄OH, acidified with HNO₃, and lead acetate solution added, the HNO₃ being neutralized with a strong ammonium acetate solution. After the solution has heated for an hour, the lead vanadate is filtered off, dissolved, and reprecipitated as before. The filtrates are evaporated and H₂SO₄ added to precipitate most of the Pb. The U and the rest of the Pb are precipitated by the addition of (NH₄)₂HS to the solution, which has been neutralized with NH₄OH. The precipitate is dissolved with 1:2 HNO₃ and fumed with H₂SO₄, then diluted and the lead sulphate filtered off.

To remove the Al, the solution is nearly neutralized with NH₄OH and (NH₄)₂CO₃ added in excess to the cold solution. After standing, the Al is filtered off. A second precipitation is necessary in the presence of much Al. The filtrate is acidified with H₂SO₄, boiled to expel CO₂, and the U precipitated in the hot solution with NH₄OH. The precipitate is filtered, ignited, and weighed as U₂O₅ and tested for the presence of V.

REACTIONS INVOLVED.

The U is dissolved by HNO₃ and remains in solution when the elements of the second group are precipitated by H₂S in the slightly acid solution; it is not precipitated when Na₂CO₃ and H₂O₂ are added to remove insoluble carbonates, or when the lead acetate is added to the acetate solution. It is first precipitated by (NH₄)₂HS as UO₂S:

\[ UO₂(NO₃)₂ + NH₄OH + NH₄HS = 2 NH₄NO₃ + UO₂S + H₂O. \]

This sulphide is dissolved in HNO₃ and remains in solution when the Pb is thrown out as sulphate, and when Al is removed with (NH₄)₂CO₃.
and NH₄OH. After the removal of CO₂, the U is precipitated as ammonium uranate, the hydroxide being formed first.

$$2\text{UO}_2\text{(NO}_3\text{)}_3 + 6\text{NH}_4\text{OH} \rightarrow (\text{NH}_4)_2\text{U}_3\text{O}_7 + 4\text{NH}_4\text{NO}_3 + 3\text{H}_2\text{O}.$$ 

On ignition, the ammonium uranate goes to U₃O₈.

**METHOD OF PROCEDURE.**

Treat from 2 to 5 grams of ore, according to the proportion of vanadium, iron, and uranium present, in a covered beaker, with 10 c. c. of HCl and let it stand 15 minutes, shaking it occasionally. Add 5 c. c. of HNO₃ and heat on a steam bath. When the solution is quiet, remove the cover and evaporate to dryness. Add 3 c. c. of HCl and 5 c. c. of water to the residue and let it stand on the steam bath for a few minutes, stirring occasionally. Dilute with 25 c. c. of hot water, filter into a small beaker, and wash the residue with warm water.

Some ores do not yield all the vanadium to this treatment, a little remaining with the insoluble residue. To make sure that all vanadium is in solution, ignite the residue in a platinum dish, treat it with 5 c. c. of HF, and evaporate to dryness on a steam bath. Do not bake the residue, for it is not necessary to expel all SiO₂. Add 3 c. c. of HCl to the residue from the HF treatment and evaporate to dryness. Repeat this treatment to insure expulsion of HF. Treat the residue with 2 c. c. of HCl and 2 c. c. of water and stir with a glass rod until any red crust is dissolved, then dilute the solution with water and filter it into the main liquid.

Pass H₂S into the liquid to separate copper, lead, and other metals of this group, filter, and boil the liquid to expel the H₂S. Concentrate the liquid to 100 c. c. If necessary, oxidize it with an excess of H₂O₂, and then neutralize with dry Na₂C₂O₄, adding 2 or 3 grams in excess. Boil the liquid for about 15 minutes until the yellowish uranium precipitate dissolves, leaving a brown precipitate which is principally iron. Filter and wash the iron precipitate with water, reserving the filtrate. Dissolve the iron precipitate in the least possible amount of HNO₃ (1:1), and add 10 c. c. of H₂O₂, neutralize with Na₂C₂O₄, add an excess of 2 grams of Na₂C₂O₄, and boil as before. Filter into the beaker containing the first filtrate. The iron precipitate may contain a little vanadium; reserve it for further treatment.

Evaporate the united filtrates from the iron precipitation to a volume of about 200 c. c., add 10 c. c. of strong HNO₃, and boil until all CO₂ is expelled. Neutralize the free acid with ammonia (until a slight permanent precipitate appears), then add 4 c. c. of HNO₃ for each 100 c. c. of liquid. Now add 10 c. c. of a 20 per cent lead acetate solution, and enough of a strong solution of ammonium acetate to neutralize the nitric acid present and substitute acetic acid for it. The object is to precipitate the vanadium as lead vanadate in an acetic acid solution. The ammonium acetate solution may be made by mixing 80 c. c. of strong ammonia, 100 c. c. of water, and 70 c. c. of acetic acid 99 per cent pure.

Heat the liquid containing the lead vanadate precipitate on the steam bath for one hour or more, filter on a tight filter, and wash with warm water. Dissolve the precipitate in the least possible quantity of hot dilute nitric acid, neutralize as before, add 3 c. c. of nitric acid in excess, add 2 c. c. of lead acetate solution, and repeat the precipitation of lead vanadate by adding ammonium acetate in excess, filter and add the filtrate to the one from the first precipitation of lead vanadate. Reserve the precipitate of lead vanadate for treatment as described below. Evaporate the united filtrates from the lead vanadate to about 400 c. c. Add 10 c. c. of strong H₂SO₄ to separate the bulk of the lead (derived from the excess of lead acetate) as PbSO₄, filter, and wash the precipitate with cold water. Neutralize the filtrate from the PbSO₄ with ammonia and add freshly prepared (NH₄)₂HS until the solution is yellow,
and the uranium and what little lead is present are precipitated as sulphides. Warm the mixture on a steam bath until the sulphides settle well. Filter and wash slightly with warm water.

Dissolve the precipitate in a No. 2 beaker with hot dilute 1:2 HNO₃, add 5 c. c. of H₂SO₄, and evaporate till fumes of H₂SO₄ appear, cool and take up with water, boil, and let the small precipitate of PbSO₄ settle until the solution is cold, filter the precipitate, and wash it with very dilute H₂SO₄.

Nearly neutralize the filtrate with ammonia, have the solutions cool (not warmer than 30° C.), and add powdered carbonate of ammonia in about 2 grams excess to precipitate the aluminum. Let the precipitate settle, filter, and wash it with warm water. If the precipitate is bulky or is at all yellow, dissolve it in a little dilute H₂SO₄ and reprecipitate with carbonate of ammonia as described. Acidulate the filtrate from the alumina with H₂SO₄, and boil thoroughly to expel CO₂. Make the liquid slightly alkaline with NH₄OH while it is hot, and heat on the water bath until the ammonium uranate collects and settles. Filter and wash with a very dilute (2 per cent) solution of (NH₄)NO₃. Do not allow the precipitate to run dry on the filter after the first washing. Dry the precipitate, ignite it in a porcelain crucible, and weigh as U₃O₈. Dissolve the precipitate in HNO₃ and test it with H₂O₂ for vanadium and with (NH₄)₃CO₃ for aluminum.

**Notes on Ledoux's Method.**

1. The U in some forms of thorite may best be recovered from the residue of the acid treatment by fusing with Na₂CO₃ and extracting with HCl.
2. It has been found that the lead vanadate is much more easily handled if NaOH instead of NH₄OH is used to neutralize the acid, if 2 c. c. instead of 4 c. c. of HNO₃ is added, and if the precipitate is allowed to settle for some time in the cold, instead of boiling. The precipitate should be washed with water, acidulated with acetic acid, otherwise the precipitate tends to run through the filter.
3. It is very important that all the CO₂ be removed. To do this, the boiling must be continued at least 30 minutes.
4. HCl may be used instead of HNO₃ in neutralizing solutions.
5. The volume, when the (NH₄)HS precipitation takes place, should not be over 800 c. c. If the washings have not been carried out using the minimum quantity of solutions, much time is lost in evaporating to the required volume.
6. The Al precipitate should stand overnight before filtering; if not, the final U₃O₈ residue will be contaminated. However, if the quantity of precipitate at this point be large, it will settle and may be filtered in two hours.
7. If the final precipitate is small in amount, it is well to test it qualitatively to confirm U.
8. When filtering the ammonium uranate, it should not be allowed to dry on the sides of the beaker, for its removal, can then be accomplished only by dissolving in acid and reprecipitating with NH₄OH.
9. The greatest care should be used in the addition of carbonates near the neutral point, for determinations are often lost through the foaming over of solutions.
10. A more delicate reaction for V will be obtained if HCl is added to the HNO₃ solution of U₃O₈ before adding the H₂O₂.
11. U₃O₈ times 0.8483 = U.

REMARKS.

The process is slow, three days being required to finish a batch of analyses. If six determinations are started each day, after the second day there will be 18 determinations on the way. This is as many as one man can conveniently handle.

An analyst who has had a little experience with this method, will obtain satisfactory results.

VOLUMETRIC METHOD FOR CARNOTITE AND VANADIFEROUS URANIUM ORES.

A convenient method for the commercial analysis of ores has been developed by Finn (19), Engle (17), and Ledoux & Co. (46), and was published by the Bureau of Mines (55).

RÉSUMÉ OF PROCESS.

The ore is treated with HNO₃, fumed with H₂SO₄ to remove the HNO₃, then diluted and treated with H₂S to remove the second group elements. To the boiled solution is added H₂O₂ and Na₂CO₃ and the mixture is boiled and filtered to remove Fe and Al. The Fe-Al precipitate is dissolved in acid and again precipitated to remove occluded U. To the filtrates (NH₄)₂HPO₄ and H₂SO₄ are added and, after boiling off all CO₂, the solution is first made alkaline with NH₄OH and then slightly acid with CH₃COOH. The uranium phosphate precipitate is filtered off, dissolved in H₂SO₄, and again precipitated to remove occluded V. The final phosphate precipitate is dissolved in H₂SO₄, tested for V with H₂O₂, oxidized with K₂MnO₄, then reduced in a Jones reductor, shaken to oxidize any over reduction, and titrated with standard KMnO₄ solution.

REACTIONS INVOLVED.

The U is dissolved in HNO₃ and H₂SO₄ and stays in solution while the elements of the second group, iron and aluminum, are removed. The U is first precipitated as UO₂(NH₄)₂PO₄ in CH₃COOH solution by the addition of (NH₄)₂HPO₄.

\[ 2 \text{(NH₄)}₂\text{HPO₄} + 2 \text{UO₂SO₄} = 2 \text{UO₂NH₄PO₄} + (\text{NH₄})₂\text{SO₄} + \text{H₂SO₄} \]

The UO₂NH₄PO₄ is dissolved in H₂SO₄ and reduced by amalgamated Zn to U(SO₄)₂.

\[ 2 \text{H₂SO₄} + \text{UO₂SO₄} + \text{Zn} = \text{U(SO₄)}₂ + 2 \text{H₂O} + \text{ZnSO₄} \]

The U(SO₄)₂ is then oxidized to UO₂SO₄ by KMnO₄.

\[ 5 \text{U(SO₄)}₂ + 2 \text{KMnO₄} + 3 \text{H₂SO₄} + 2 \text{H₂O} = 5 \text{UO₂SO₄} + \text{K₂SO₄} + 2 \text{MnSO₄} + 5 \text{H₂SO₄} \]
Treat 5 grams of the ore, or a quantity containing not over 0.3 gram of metallic uranium, in a No. 3 beaker with 10 c.c. of HNO₃ (1.42) and 20 c.c. of H₂SO₄ (1.84). Cover with a watch glass supported above the beaker with glass hooks and evaporate till white fumes of H₂SO₄ begin to come off. Wash the cover with a little water, remove it, add a little more water to the beaker, mix the contents well, and evaporate them almost to dryness, leaving a slightly moist residue containing about 2 c.c. of free H₂SO₄. This operation is easily conducted on a good hot plate; it does not require much time if the temperature is sufficient and the draft is good.

The object of using a large excess of nitric and sulphuric acids is to destroy organic matter, which is present in many samples. The purpose of adding water after the first evaporation to fumes is to break up nitrosousulphuric compounds and to completely eliminate nitric acid.

Add 75 to 80 c.c. of water to the residue and heat until all soluble matters are dissolved; then, without filtering, pass H₂S gas into the warm solution until all members of the H₂S group are precipitated. Filter and wash with warm water, collecting the filtrate and washings which may measure 150 c.c., in a No. 3 beaker. Boil until all excess of H₂S is expelled and add H₂O₂ until all iron is oxidized. Neutralize the liquid with Na₂CO₃ and add about 2 grams in excess; then add 10 c.c. more of H₂O₂ and boil for 15 minutes. Filter through a 12.5-cm. S. and S. No. 489 paper, and wash the precipitate four or five times with hot water, stirring it well with the jet of the wash bottle.

Collect the filtrate and washings in a No. 5 beaker. Wash the precipitate from the filter into the No. 3 beaker with a fine stream of water, neglecting the small part that may adhere pertinaciously to the paper. Dissolve the precipitate in a little dilute H₂SO₄, neutralize as before with Na₂CO₃, adding about 2 grams in excess, add 10 c.c. of H₂O₂, and boil again as before. Filter through the same paper into the No. 5 beaker and wash the precipitate three times with hot water.

The combined filtrates and washings from the two Na₂CO₃ precipitations will contain all of the uranium and most of the vanadium. Add 5 grams of ammonium phosphate and 10 c.c. of H₂SO₄ to the liquid, boil it well until all CO₂ is expelled, make it slightly alkaline with ammonia and then slightly acid with acetic acid. Uranium is precipitated as ammonium-uranium phosphate and vanadium is retained in solution. Cool the beaker for three-quarters of an hour in ice water or let it stand overnight. This precaution is necessary for the complete separation of the uranium precipitate. The precipitation appears to be more complete in faintly acid solutions than it is in ammoniacal liquids; hence the addition of acetic acid.

The precipitate is slimy and difficult to wash. Filter through a 12.5-cm. No. 589 S. and S. paper which has been treated with an emulsion of paper pulp. The paper pulp aids filtration and prevents the precipitate from passing through the paper.

Let the precipitate drain on the filter, and then from a wash bottle direct a stream of a dilute solution of ammonium sulphate (2 per cent) toward the inside seam of the filter paper at the top of the precipitate. The precipitate can thus be made to open, affording a better drainage. Rinse the beaker with ammonium-sulphate solution and wash down the filter from the top until the paper is full. The precipitate is rather impervious and the object of this washing is to remove the vanadium-bearing solution from the beaker and the filter paper rather than actually to wash the precipitate. After the filter has drained, remove as much as possible of the precipitate from it with a glass rod, transferring it to the beaker. Wash the filter well from the top to remove vanadium from it. While the filter is draining, add a little ammonium-sulphate solution to the beaker and beat the precipitate to a thin paste with it, breaking up all aggregations; then add about 100 c.c. of ammonium sulphate wash-solution, stir well, and filter as before. This method of washing is fairly rapid, and is more
effective for large precipitates than washing on the filter would be; small precipitates may be washed on the filter.

Transfer the precipitate with a glass rod as completely as possible to the beaker and dissolve what remains on the paper in a little hot dilute (1:4) H₂SO₄, letting the acid run through the paper into the beaker containing the precipitate. Wash the paper well with hot water so that it may be used for filtering the second precipitation. See that all of the uranium phosphate in the beaker is dissolved in the acid. A little pulp will, of course, remain. Add 2 grams of ammonium phosphate, dilute to 250 c. c. with warm water, make slightly alkaline with ammonia, boil cautiously for several minutes, and then make slightly acid with acetic acid. Cool the liquid as before and filter through the same filter, washing the beaker and the filter paper several times with ammonium sulphate solution. This procedure removes all, or all but a small trace, of vanadium in the case of the usual grade of uranium-vanadium ores, such as contain not over 4 per cent U₃O₈ and less than 6 per cent V₂O₅. In the analysis of richer ores a third precipitation as phosphate may be required to remove every trace of vanadium.

Dissolve the uranium phosphate through the filter paper in hot H₂SO₄, using in all not over 40 c. c. of dilute (1:4) acid. Wash the filter well with water, let the solution cool, and test it with a few drops of H₂O₂ to make sure that no vanadium is present. Since the solution is dissolved through the filter, the liquid should be free from any suspended paper pulp. Add an excess of a strong solution of K₂MnO₄ and heat the solution to boiling. The object of adding K₂MnO₄ is to destroy sugars and other organic compounds formed by the action of the solution on cellulose and traces of starch from the filter papers. Omission of this precaution will often cause variations in the titration of solutions that have been passed repeatedly through filter paper.

Cool the liquid, dilute it to a volume of 150 c.c., and pass it through a reductor in the same way as in determining iron. The reductor we employ is simple. The zinc column is 19 cm. long and 2 cm. in diameter, of 30-mesh granulated zinc that has been amalgamated by treatment with a dilute solution of mercuric chloride. The reductor is worked by suction from a filter pump, and the precautions usual in making iron determinations are observed. The time required to pass the solution through the reductor is about two minutes, exclusive of washings.

After reduction, shake the solution vigorously for one minute with free access of air and titrate with a standard solution of K₂MnO₄.

A blank determination should be run through the reductor using distilled water and H₂SO₄ in amounts similar to those used in the regular determination to correct for end point and reductor errors.

NOTES ON VOLUMETRIC METHOD.

1. Descriptions of reductors are given by Scott (74) and Treadwell and Hall (78).

2. For some ores the separation with H₂S may be omitted, thus shortening the time required for an analysis.

3. The agitation with air oxidizes any overreduction that may have occurred.

REMARKS.

Many chemists who have experimented with the zinc-reduction method have laid stress on the difficulty of completely reducing uranium solutions and the danger of reoxidation by atmospheric oxygen during titration. It is our experience that reduction from UO₂ to UO₄ is easily attained, and further, that very prolonged re-
duction is apt to lead to formation of a lower oxide. This lower oxide is oxidized with great rapidity by atmospheric oxygen to the uranous condition, but solutions of uranous sulphate are stable in the presence of air and may be exposed to it with impunity. In fact, they may be agitated with air for several minutes without altering the state of oxidation in a measureable degree.

**Scholl's Rapid Method.**

Scholl (73) has devised a method for the determination of U in carnotite, which is not only rapid, but (by using certain precautions) is also fairly accurate, checking the previous method closely.

**Résumé of Process.**

The U is extracted from the ore with 1:1 HNO₃, diluted, filtered, and ferric chloride and Na₂CO₃ added to precipitate V, Fe, and most of the Al. The U is precipitated from the filtrate by boiling with NaOH and purified by dissolving in HNO₃ and precipitating with NH₄OH, the ammonium uranate being ignited to U₃O₈.

**Reactions Involved.**

The V is precipitated as iron vanadate along with insoluble carbonates by the addition of ferric chloride and Na₂CO₃, the U remaining in solution. The U is precipitated as Na₂U₂O₇, then dissolved and precipitated as (NH₄)₂U₂O₇ and finally ignited to U₃O₈.

**Method of Procedure (73).**

To a sample of the material containing about 0.2 gram uranium oxide, add 25 to 50 c. c. 1:1 nitric acid and heat until all the uranium is in solution. Keep warm over night if necessary. Dilute with warm water to about 250 c. c. and filter. Add ferric chloride equivalent to about three times the weight of the vanadium present. Add slowly to the cold or slightly warm solution solid sodium carbonate until all the acid is neutralized, and then about 1 gram in excess, keeping the beaker covered with a watch glass. Place on a hot plate and heat to about 90° C., but do not boil. Keep it warm for at least 15 minutes. Filter. The precipitate contains all the iron and vanadium and most of the aluminum. Neutralize the filtrate slowly with nitric acid until uranium begins to precipitate, and boil to eliminate most of the carbon dioxide. Add sodium hydroxide in excess and boil 15 minutes. Filter. The filtrate contains the remainder of the aluminum and any vanadium not previously precipitated. Dissolve the precipitate in dilute nitric acid and heat to about 90° C. Add an excess of ammonia and boil. Filter, ignite, and weigh as uranium oxide (U₃O₈). In case of doubt as to the purity treat the precipitate with dilute warm nitric acid. Filter, ignite, and weigh the insoluble matter. Subtract this from the previous weight and report the result as U₃O₈. Some iron is usually found in the precipitate because the chemicals, especially nitric acid, usually carry iron as an impurity.

**Notes on the Scholl Method.**

1. To remove U, which may be held by the iron vanadate precipitate, a repetition of the Na₂CO₃ treatment should be performed on an HNO₃ solution of the precipitate.
2. The final precipitate of U is usually free from V, but it is well
to test the $\text{U}_3\text{O}_8$ for it by dissolving in $\text{HNO}_3$, adding $\text{HCl}$ and then
$\text{H}_2\text{O}_2$. The addition of $\text{HCl}$ makes the test more delicate.

3. The tendency of dry ammonium uranate to stick to glass, the
care necessary in adding $\text{Na}_2\text{CO}_3$, the necessity of complete removal
of $\text{CO}_2$ before precipitating $\text{U}$, and the advisability of a qualitative
test of the final precipitate, if it is small, have been discussed in the
notes of the previous method.

4. The decomposition of the ore may be carried out as given in
the previous method and shorten the time required for an analysis;
however, if the sample is left overnight, no time is lost.

REMARKS.

An analysis can be completed in one day by this method, and the
results check closely those obtained by the longer method.

FERROURANIUM AND ALLOY STEELS.

The comparatively recent use of U in steels has led to the develop-
ment of methods suited to the estimation of U in the presence of those
elements associated with it in Fe-U and alloy steels.

METHOD OF KELLEY, MYERS, AND ILLINGSWORTH.

Kelley, Myers, and Illingsworth (39) give a method for the deter-
mination of U in steels and Fe-U, applicable in the presence of Fe, Cr,
Mo, V, W, Co, Ni, Mn, P, Cu, Al, Ti, Si, S, and C.

RESUME OF PROCESS.

A sample of steel is dissolved in $\text{HCl}$ and oxidized with $\text{HNO}_3$.$\text{W}$ is filtered off, after diluting and boiling, and the filtrate is evapo-
rated to dryness, baked, and extracted with dilute $\text{HCl}$, leaving
most of the $\text{SiO}_2$ and the rest of the W as a residue. The filtrates
are evaporated to a sirupy consistency and extracted with ether,
removing most of the Fe. The water layer is evaporated to a small
volume, diluted, and an excess of $\text{Na}_2\text{CO}_3$ added. The solution is
boiled, allowed to settle, and filtered and the precipitate containing
Fe, Cr, Mn, Co, Ni, Cu, Al, Si, Ti, P, and V is reprecipitated to remove
occluded U. The filtrates are acidified with $\text{H}_2\text{SO}_4$ and boiled to
remove $\text{CO}_2$. $\text{NH}_4\text{OH}$ is then added and U, V, and traces of impuri-
ties are precipitated from the solution on boiling. If P is present
in large quantities the precipitate is dissolved in $\text{HNO}_3$ and the
$\text{P}_2\text{O}_5$ removed with ammonium molybdate. The U is precipitated
from the filtrate with $\text{NH}_4\text{OH}$, filtered, and dissolved with ($\text{NH}_4$)$_2\text{CO}_3$,
leaving Mn, Fe, Al, etc., undissolved. U is precipitated, with some V,
after the removal of $\text{CO}_2$, by means of $\text{NH}_4\text{OH}$. The precipitates
are ignited to the oxides, the V determined, and the U found by
difference.
For the determination of U in FeU, the metal is dissolved in HNO₃ with the addition of HCl and then evaporated to dryness. After the removal of SiO₂, the method is the same as that for steel.

**REATIONS INVOLVED.**

The U reactions involved in this method have been given in the selected method for ores.

**METHOD OF PROCEDURE.**

This method is quoted from Kelley, Myers, and Illingsworth (39).

A 2-gram sample is dissolved in 75 c. c. of 1:1 hydrochloric acid. After solution is complete the solution is oxidized by the dropwise addition of nitric acid. In the case of samples where tungsten is present an easily filterable product is obtained by diluting to 300 c. c. and boiling for 15 minutes. The tungstic oxide is then filtered out and washed, the filtrate and wash waters being returned to the original beaker for evaporation to dryness, followed by baking at a moderate temperature. On dissolving the residue with 50 c. c. of 1:1 hydrochloric acid and diluting with hot water, a solution is obtained from which the balance of the silica and the last traces of tungsten can be separated by filtering. The two precipitates after washing are available for the determination of tungsten and silicon by the usual methods. Filtrates and wash waters from these precipitates are combined and evaporated to a sirupy consistency in preparation for the extraction of most of the iron with ether. In the absence of tungsten the original solution is evaporated to dryness and baked with the object of removing silica. After the extraction of the iron, the aqueous layer is evaporated to a small volume to free it from the excess of acid. It is then diluted to a volume of 150 c. c. with hot water, and an excess of sodium carbonate in the form of a saturated solution is added. This solution is boiled and, after settling, filtered, the precipitate being washed with hot water. The precipitate consists of the hydroxides of chromium, iron, manganese, cobalt, nickel, copper, and aluminum, if all of these elements are present, together with traces of silica, titanic oxide, phosphorus, and vanadium compounds. The filtrate contains uranium, molybdenum, vanadium, and traces of the elements which occur chiefly in the precipitates.

Bulk precipitates should be dissolved in hydrochloric acid and reprecipitated one or more times with sodium carbonate solution to insure a complete separation of the uranium. The difficulties from this source are not as great as might be expected.

All filtrates from the precipitate are cautiously acidified with sulphuric acid and boiled long enough to insure the complete removal of all carbon dioxide. Ammonia free from carbonate is then added in slight excess. Boiling precipitates the uranium, much of the vanadium, and traces of impurities. The molybdenum is left in the filtrate. Steels contain only small amounts of phosphorus and the contamination of the uranium from this source is usually negligible. When, however, as may occur, the amount of phosphorus is large, it may be necessary to dissolve the precipitate in nitric acid, and after suitable oxidation, precipitate the phosphoric acid with ammonium molybdate. The phosphorus can then be removed as ammonium phosphomolybdate. The uranium and vanadium may be reprecipitated from this filtrate along with the manganese, if permanganate is used to oxidize the phosphorus, by adding a few drops of sulphuric acid, a small amount of ammonium persulphate, and enough carbonate-free ammonium hydroxide to give an excess. The precipitate obtained by boiling the solution is in the condition corresponding to the first uranium precipitate mentioned above.

The impure uranium precipitate containing phosphorus in negligible amounts, or free from it, is transferred to a beaker with a little water and solid ammonium
carbonate added. On heating this solution under conditions and for a time calculated to result in only a partial decomposition of the ammonium carbonate, the uranium and vanadium go into solution leaving the manganese, iron, and other impurities undissolved. The filtrate is acidified with sulphuric acid and boiled until it is free from carbon dioxide, when a slight excess of carbonate-free ammonium hydroxide is added. This precipitates only the uranium, and vanadium. In common with other investigators we have not been successful in finding convenient and satisfactory procedures for separating these elements.

The combined precipitates of uranium and vanadium are ignited at dull redness in a platinum crucible, allowing free access of air to reoxidize any reduced material. The ignited residue is weighed as $U_3O_8 + V_2O_5$. In general, only a small part of the vanadium is present in this precipitate, thus making it unavailable for the vanadium determination. It is necessary, however, to determine the vanadium to correct the weight of uranium oxide. For this purpose the precipitate is dissolved in 50 c. c. of concentrated hydrochloric acid and evaporated with 30 c. c. of sulphuric acid (sp. gr. 1.58) until fumes appear. The sulphuric acid solution is diluted to 250 c. c. with hot water and titrated at 80° C. to the first pink color. At the same time like quantities of sulphuric and hydrochloric acids are evaporated, diluted, and titrated in similar fashion to obtain a blank correction for the vanadium. (See Part VII on "Vanadium").

The determination of uranium in ferrousuranium is similar to the analysis of steel for this element. A 1-gram sample was dissolved in a small amount of concentrated nitric acid, and when solution was completed, hydrochloric acid was added cautiously to the amount of 30 c. c. The solution was then evaporated to dryness with the object of separating silica. After the removal of silica, the procedure was identical with that in the case of steel.

NOTES ON THE METHOD OF KELLEY, MYERS, AND ILLINGSWORTH.

1. The best procedure in extracting Fe from U by means of ether is to place the sirupy solution in a separatory funnel with 50 c. c. of alcohol-free ether, which has previously been shaken with HCl. After shaking about seven minutes, opening frequently to relieve the pressure, the funnel is allowed to rest. The water layer is drawn off and extracted twice more with ether, first with 50 c. c. and then with 30 c. c. The ether layer is extracted with 5 c. c. of HCl (sp. gr. 1.10). The water portions are then treated as shown above.

2. As already stated, in methods for ores, dry ammonium uranate tends to stick to glass and the CO$_2$ must be completely removed before the precipitation of U with (NH$_4$)$_2$OH.

3. A good plan, after carrying out the (NH$_4$)$_2$CO$_3$ treatment, is to cool, add more (NH$_4$)$_2$CO$_3$, and let the precipitate settle overnight before filtering.

REMARKS.

The method has given satisfactory results in the analysis of a Ni-Cr steel containing Mn, and in the analysis of a high-speed steel containing Mn, Cr, W, V, Co, etc.
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URANIUM.


PART VII.—VANADIUM.

By J. E. Conley.

INTRODUCTION.

Vanadium is one of the most useful of the rare metals. The chief deposits, by far the most important in the world, are at Minasragra, Peru, 20 miles from Cerro de Pasco. The main ore body is a lens-shaped mass about 30 feet wide by 300 to 400 feet long; it contains several minerals, that constituting the larger part of the deposit being called "quisquite." This mineral is a black carbonaceous substance containing sulphur, but no vanadium. The vanadium lies mostly at the southern end of the ore body, and to a depth of 20 feet is present as red calcium vanadate; this vanadate is brighter than that in Colorado and Utah, and it may carry as much as 50 per cent V₂O₅. It occurs in small pockets and fills the cracks and fissures in the fine shale. Below is the mother lode, which carries as high as 10 per cent vanadium oxide, and nearly as much sulphur. On the east and south sides of the mother lode is a hard blue-black vanadium shale carrying as much as 13 per cent vanadium oxide and 4 to 5 per cent sulphur. The main mineral is patronite, which is greenish black and contains 19° to 24.8 per cent vanadium oxide.

In the United States the largest deposits are in San Miguel County, southwestern Colorado. The mineral at that place is roscoelite, which is a vanadium mica. The vanadium mineral, which is light to dull green and fine-grained, is found in a sandstone that occasionally carries splotches of carnolite, but the amount of uranium present is extremely small. The average ore mined has a content of from 1 to 2 per cent V₂O₅.

Vanadium ore has also been discovered in Huerfano County, Colo., near the Sangre de Cristo Range. The ore is heavy, black, and banded, and contains small quantities of uranium oxide. It shows 2 to 7 per cent V₂O₅.

In Eagle County, 7 miles southeast of the town of Eagle, a silver ore has been found carryng vanadium, but it is more or less local in character. Zinc desclizite has been found in limited quantities in Nevada, and cuprodesclizite exists in reasonable quantities in the Shattuck mine, at Bisbee, Ariz. Vanadanite, or lead vanadate, occurs in several places in the West, particularly in Arizona, New
Mexico, Nevada, and California. This mineral is almost invariably found as a low-grade ore carrying from 0.1 to 0.6 per cent $V_2O_5$, seldom in high-grade pockets.

The principal use of carnotite during the last few years has been in the production of radium. Ordinary carnotite ores carry from 3 to 6 per cent $V_2O_5$, and the vanadium in the ore is recovered during extraction of radium. Some ores high in vanadium but low in uranium and radium have been treated primarily for vanadium, but this procedure is not usual. From 200,000 to 300,000 pounds of vanadic oxide is probably produced annually as a by-product in the extraction of radium.

Vanadium is used chiefly in steel for purposes requiring great toughness and torsional strength, such as automobile parts, gears, piston rods, tubes, boiler plates, transmission shafts, bolts, gun barrels, gun shields, and forgings that have to withstand heavy wear and tear. The vanadium content of such steels ranges from 0.1 to 0.4 per cent. Vanadium is also used occasionally in certain tungsten alloys for making high-speed tool steel, as the introduction of a small proportion of vanadium reduces the proportion of tungsten required to give the alloys the desired hardness and toughness.

Vanadium differs from tungsten in having a beneficial effect not only on tool steel, but also on structural steel. Arnold has shown that vanadium does not form a double carbide with iron, but gradually takes the carbon from the carbide of iron until Fe$_3$C can not exist, if 5 per cent of vanadium is present, and only a vanadium carbide, V$_4$C$_2$, containing 15 per cent of carbon, is present; this constituent is constant, at least in tool steels containing 5 to 14 per cent of vanadium.

Chrome-vanadium steels and chrome-vanadium-molybdenum steels are the latest development in structural alloy steels that have gained an extensive market. Almost all these steels are made in the open-hearth furnace, chromium and vanadium alloys being added shortly before casting. In their physical properties these steels are much like chrome-nickel steels, but they have a greater construction of area for a given limit. Most of the chromium-vanadium steels made go into automobiles. Some manufacturers prefer them because of their greater freedom from the surface imperfections, notably seams, which the steels that contain nickel are likely to have. Some chromium-vanadium steel, which is not face-hardened but has high resistance imparted by heat treatment, is used in armor plate of medium thickness.

Vanadium is used to some extent in making bronzes, in medicines, and in dyeing. Methods of analysis that are applicable to vanadium ores and their products are described in the following pages.
METHODS OF SOLUTION OF ORES AND ALLOYS.

The following facts are given to assist the reader in selecting a method for the decomposition of vanadium compounds likely to be encountered in analysis.

Metallie vanadium is insoluble in dilute HCl or H₂SO₄; it is soluble in HF, HNO₃, and in concentrated HCl or H₂SO₄. It is insoluble in aqueous alkalies, but is readily decomposed by fused alkalies.

No salts of the brown suboxide, V₂O₅, have been prepared, hence its compounds are not encountered in analysis.

V₂O₃ is readily soluble in acids and yields a lavender or violet solution.

V₂O₅ is insoluble in most acids but is soluble in HF, yielding a green solution.

V₂O₄ is readily soluble in acids, forming vanadyl compounds which have a beautiful blue color.

V₂O₅ is the most important of the oxides and is soluble in mineral acids as well as in aqueous and fused alkalies. Fused V₂O₅, however, dissolves less readily in acids, but is easily dissolved in hot solutions of either sodium or potassium hydroxides to which a little H₂O₂ has been added.

The alkali vanadates are soluble in water. All vanadates of the heavy metals are nearly insoluble in water or dilute acetic acid, but are readily soluble in strong acids. Ammonium vanadate is nearly insoluble in cold water and in a concentrated ammonium chloride solution, but is soluble in hot water.

DECOMPOSITION OF ORES.

TREATMENT WITH MINERAL ACIDS.

Most vanadium ores readily yield their vanadium to acids. An initial treatment with HCl, followed by the addition of HNO₃, then of H₂SO₄ to fumes, usually extracts all the vanadium. The common minerals—vanadinite, carnotite, deschoizite, cuprodeschoizite, eusynchite, and other natural vanadates—readily yield their vanadium to this treatment, and patronite may also be dissolved thus if most of the sulphur is first removed by ignition.

The vanadium in roscocelite does not respond readily to acid treatment, doubtless because of its occurrence in complex silicate. Hence, it is recommended that roscocelite be decomposed by alkaline fusion, preferably after the elimination of most of the silica with HF; it may be decomposed, however, as are other ores of high silica content by treating the insoluble material with HF in the usual manner to eliminate the silica, and then by giving the residue a second treatment with mineral acids.
Traces of occluded vanadium remaining in the residue from an alkaline fusion may be recovered by dissolving in HNO₃ and then pouring the solution into a 10 per cent solution of caustic soda. The vanadium passes into the filtrate.

HCl alone usually dissolves most of the vanadium minerals, but it does not decompose other minerals present; aqua regia is more effective.

H₂SO₄, although very effective with many ores, is seldom used alone. Obviously, it should not be used when the procedure of analysis includes the precipitation of the vanadium as lead vanadate.

For specific information on the decomposition of ores, the following methods are given:

1. Dissolve 1 gram of ore in 25 c. c. of concentrated HCl and 20 c. c. of 1:1 HNO₃, evaporate to small volume, dilute, and filter.
2. Dissolve 1 gram of ore in 30 c. c. of aqua regia, heat to small volume, cool, add 15 c. c. of 1:1 H₂SO₄, evaporate to SO₃ fumes, cool again, dilute, warm to dissolve ferric sulphate, and filter.
3. For high siliceous ores, decompose as in 2, then treat the residue in a platinum dish with 25 c. c. of HF and 1 c. c. of H₂SO₄; evaporate the mixture to dryness and treat the residue with aqua regia, or fuse with 3 grams of sodium or potassium bisulphate, dissolve the melt in water, filter, and add the solution to the original filtrate.

**TREATMENT BY FUSION.**

Fusion methods are also satisfactory for decomposing vanadium ores. Vanadium forms soluble vanadates in alkaline fusions, especially when an oxidizing agent is present.

Vanadium minerals respond readily to fusions with sodium or potassium carbonates, or with mixtures of them and an oxidizing agent, such as niter. An oxidizing fusion is always recommended for the decomposition of a vanadium ore.

Sodium peroxide, either alone or with sodium hydroxide, is very effective for extracting vanadium from its minerals.

Fusion with pyrosulphate or bisulphate is not used except in a few cases to remove the final traces of vanadium from the insoluble material after an acid decomposition.

1. For high siliceous ores, remove the bulk of silica with HF and H₂SO₄, then fuse the ignited residue with five times its weight of niter mixture—10 parts Na₂CO₃ to 1 part KNO₃—or with 53 parts Na₂CO₃, 69 parts K₂CO₃, and 15 parts KNO₃. The latter mixture is very satisfactory and fuses more readily than the former. Low siliceous ores are fused directly.
2. For low siliceous ores, mix 1 gram of ore with from 3 to 4 grams of Na₂O₂ and heat in a nickel crucible until the mixture darkens;
fusion is unnecessary and should be avoided. Then remove the crucible, cool, and place it in a beaker of water carefully to avoid spattering.

3. Treat as in 2, except that as much as one-half of the peroxide may be replaced by sodium hydroxide. Heating is continued until a quiet fusion is obtained.

4. Fuse 1 gram of ore with three times its weight of potassium pyrosulphate, and dissolve the cooled melt in warm water. Heat to effect solution and filter. Any undecomposed residue is fused a second time and the resulting solution is added to the first filtrate. This method of decomposition may also be used as a final treatment after an acid solution.

DECOMPOSITION OF ALLOYS.

IRON AND STEEL.

Vanadium steels are decomposed by the same general methods as other steels, and many methods for decomposing ores may be applied to iron and steel. The following suggestions may prove useful:

1. Two to five grams of the drillings are treated with from 30 to 50 c. c. of 1:3 H₂SO₄. After the first action has ceased, 25 to 30 c. c. of 1:1 HNO₃ is added, or, if preferred, the carbides insoluble in the H₂SO₄ may be filtered off, ignited, and treated with from 3 to 5 c. c. of concentrated HNO₃, then added to the original filtrate. HF also assists the solution of refractory samples.

2. Two to five grams of steel are dissolved in 50 to 60 c. c. of aqua regia and evaporated to dryness. The residue may be either dissolved in dilute HCl or transferred to a platinum crucible and fused with Na₂CO₃ plus KNO₃ as in (1) for ores (p. 242). The addition of HF to the original sample usually assists in decomposing a refractory steel.

3. Another useful method is to treat a sample of the desired size with H₂SO₄ as in (1), and then to filter off any undecomposed material, ignite, and fuse with acid sulphate as under (4) for ores.

FERROVANADIUM.

In general, ferrovanadium may be decomposed by the same methods as are used for iron and steel. The use of HF is very effective for decomposing obstinate samples. High-silica ferrovanadiums are best decomposed by HF and H₂SO₄, or by fusion with Na₂CO₃ as under (1) for ores (p. 242).

The use of large quantities of aqua regia for effecting solution of ferrovanadium can not be recommended, as vanadium tends to separate out as the oxide, especially from high-vanadium ferros.

VANADIUM BRONZES.

Vanadium bronzes, or brasses, dissolve readily in aqua regia
QUALITATIVE ANALYSIS.

DETECTION OF VANADIUM.

Vanadium yields either colorless or slightly yellow solutions in alkaline solutions. Acid solutions may vary from colorless to yellow or deep orange, depending on the acidity and the amount of vanadium. In reduced conditions, acid solutions are blue or green, shading in the lowest stages of oxidation into lavender and violet.

Alkaline vanadates near the neutral point, or in solutions slightly acid with acetic acid, yield vanadates with the heavy metals. Lead acetate forms a yellow basic vanadate which turns white on standing. Mercurous nitrate precipitates yellow mercurous vanadate.

Distinction is made between pyrovanadates and metavanadates by the color of their respective copper salts. Copper pyrovanadate is a yellow crystalline precipitate, whereas copper metavanadate is an apple green.

An acid solution of vanadium yields a blue or green color, due to the formation of vanadyl salts when reduced with SO₂, H₂S, HI, HCl, HBr, Na₂S₂O₃, oxalic acid, or tartaric acid. Al and Zn produce a blue, green, and finally a violet color when all of the vanadium has been reduced to V₂O₇.

HYDROGEN PEROXIDE.

By far the most important test for vanadium is made by adding H₂O₂ to a strongly acid vanadium solution. Low concentrations of vanadium produce a light yellow to orange color; higher concentrations yield the deep brownish-red color of pervanadic acid, HVO₄. Small quantities of vanadium may be confused with chromium, iron, or titanium, and possibly with large quantities of molybdenum. Vanadium may be distinguished from chromium by adding ether to the solution after the H₂O₂. Chromium colors the ether solution blue, whereas vanadium yields the same yellow as to the aqueous solution. The yellow color due to iron may be destroyed by H₃PO₄; the titanium compound is easily destroyed by adding NH₄F or HF to the test solution. Any yellow or brownish-red coloration persisting after the addition of these reagents is due to the vanadium.

DETECTION IN ROCKS AND MINERALS.

Vanadium may be detected in high-grade minerals by moistening the specimen with a drop of concentrated HCl. A deep red, which changes rapidly to green, indicates vanadium. The same test may be applied by placing a few pieces of the mineral in a small beaker and adding concentrated HCl. The deep-red color forms at once with most minerals, but soon disappears and changes to a deep-green color, especially on heating. H₂O₂, however, immediately restores the color.
For the detection of very small quantities of vanadium in rocks and slags, a method outlined by Hillebrand is very satisfactory. Fuse 5 grams of the pulverized sample with 20 grams of Na₂CO₃ and 3 grams of NaNO₃. Cool the fusion, extract with cold water, and precipitate the manganese by the addition of alcohol. Filter the solution, which will contain the vanadium as well as any arsenic, phosphorus, molybdenum, chromium, and tungsten in the original ore. The solution is nearly neutralized with HNO₃, is evaporated to small volume, diluted again, and filtered. Mercurous nitrate is added to the alkaline solution to precipitate the mercurous vanadate. Any or all of the elements enumerated above are similarly precipitated. The precipitate is filtered off, after boiling a short time, dried on the filter paper, and separated as completely as possible. The dried precipitate is then ignited to volatilize the mercury. The residue is fused with a very little Na₂CO₃, extracted with water, and slightly acidified with dilute H₂SO₄. Platinum, molybdenum, and arsenic are removed by a stream of H₂S and filtered off. The filtrate is evaporated to dryness and excess H₂SO₄ is expelled. The residue is taken up in a few cubic centimeters of water, and a small quantity of H₂O₂ is added. Any blue color due to chromium is removed by adding a small quantity of ether. A yellow or brownish red color remaining in the aqueous solution shows the presence of vanadium.

Detection of vanadium in minerals by means of the borax bead is not very satisfactory and is seldom used. The borax bead of vanadium minerals is yellow in the oxidizing flame and light green in the reducing flame.

**DETECTION IN IRON AND STEEL.**

A 0.5-gram sample is dissolved in a 10-inch test tube in 10 c. c. of 1:3 H₂SO₄, and 5 c. c. of concentrated HNO₃ is added after the cessation of the first action. The contents of the test tube are then heated until the evolution of nitrous fumes has ceased. Any deposited WO₃ is filtered off, and a few cubic centimeters of H₂O₂ is added. A reddish-brown solution shows vanadium. If ferric iron makes the presence of vanadium uncertain, a little sirupy H₃PO₄ is added. Any color due to titanium is destroyed by adding ammonium fluoride or HF.

Gregory (29) detects vanadium in iron or steel by the following procedure: The sample is dissolved in acid and the iron is removed by Na₂CO₃ and H₂O₂. The filtrate is acidified with H₂SO₄ and then treated with a few cubic centimeters of H₂SO₄ solution of strychnine (4 grams of strychnine in 1 liter of concentrated H₂SO₄). A violet coloration forms immediately, and gradually changes to orange. Titanium, molybdenum, tungsten, or aluminum do not interfere.
SEPARATION OF VANADIUM FROM THE COMMON ELEMENTS

GENERAL COMMENT.

By the passing of H₂S through the acid solution, vanadium is separated very readily from all members of the hydrogen sulphide group and remains in solution as the vanadyl compound. Ammonium sulphide does not precipitate vanadium from solution, but yields a brownish-red solution on account of the formation of a thio-salt. This reaction may be used for the qualitative detection of vanadium. Ammonium sulphide can not be used, however, to separate vanadium quantitatively from members of the ammonium sulphide group, as precipitates of iron, manganese, zinc, and other vanadates are thrown out when the solution is made alkaline. Moreover, when a vanadium solution has been treated with ammonium sulphide and then acidified, part of the vanadium is precipitated as the brown oxy-sulphide.

Fusion of a vanadium mineral or compound with sodium carbonate and potassium nitrate, followed by solution in hot water, separates vanadium from a large number of elements. Silica, chromium, tungsten, molybdenum, arsenic, phosphorus, and uranium pass into solution.

According to Fisher (25), vanadium may be separated quantitatively from these elements by precipitating them all together as their respective lead salts and digesting the precipitate with potassium carbonate. All of the lead salts are decomposed with the exception of lead vanadate.

SEPARATION FROM IRON.

Iron in large quantities may be separated from vanadium by means of a large excess of Na₂CO₃ and Na₂O₂. The acid solution containing the iron is diluted to about 200 c. c., and Na₂CO₃ is added until a slight precipitate of ferrous carbonate begins to form. The balance of the acid is neutralized with Na₂O₂ and then 10 grams excess of each is added. The iron is obtained in the precipitate, the vanadium in the filtrate. Traces of occluded vanadium are removed by dissolving the iron precipitate in the least possible quantity of HNO₃ and peroxidizing again. Except in unusual cases, this step effects complete separation.

Large quantities of iron may be removed from large quantities of vanadium by precipitation with ammonia after the addition of 10 to 15 c. c. of 3 per cent H₂O₂. In the presence of a large amount of vanadium, as many as three precipitations followed by solution in HNO₃ and reprecipitation are sometimes required.

Iron may also be separated effectively from vanadium by the method of Rothe. If iron is present in HCl in the ferric state, ether
will extract it, together with molybdenum, whereas the vanadium will remain in the aqueous solution. Best results are obtained if the strength of the acid is such that it has a specific gravity of 1.13. The separation is easily accomplished in a separatory funnel. Details of the separation are given by Blair (4).

Vanadium present in solution with a large amount of iron may be precipitated with but a little iron by the following methods:

1. Add 2 c. c. of ammonia in excess of that quantity required to form the first permanent black precipitate. The black precipitate will contain all of the vanadium.

2. Zinc oxide or hydroxide solution added to an iron solution containing vanadium will precipitate the vanadium with but little iron.

3. According to Cain (8), vanadium and chromium in an acid solution are separated from iron by neutralizing most of the acid with sodium carbonate and then adding cadmium carbonate.

**SEPARATION FROM IRON AND ALUMINUM.**

Iron and aluminum may be precipitated from an acid solution by the addition of NH₄OH, or NH₄OH and H₂O₂. In the presence of a large amount of V, as many as three precipitations followed by solution in HNO₃ and reprecipitation are sometimes required. If NH₄OH alone is used, the precipitate will contain V. If the precipitate is digested with ammonium phosphinate, the V is extracted, whereas the Fe and Al remain in the residue.

Hillebrand separates Al from V when present in a strongly alkaline solution by incomplete neutralization of the alkalinity with HNO₃. Johnson (34) uses 1:1 HCl, and gives the precautions. He says the best condition of alkalinity is that which does not turn turmeric paper quickly even to a faint brown. Al and P are precipitated together under these conditions practically free from vanadium. In the presence of large quantities of V, it is necessary to redissolve the Al precipitate in HNO₃, to make strongly alkaline with NaOH, and reprecipitate. Two precipitations usually effect a clean separation.

**SEPARATION OF VANADIUM FROM CHROMIUM.**

When vanadium and chromium are present in solution as sodium vanadate and chromate, they are separated as follows:

1. The chromate, after acidifying, is first reduced by means of SO₂ and the solution is then poured into a warm 10 per cent solution of NaOH. The chromium is precipitated, and the vanadium goes into the filtrate.

Vanadium may also be separated from chromium by precipitation with lead acetate. This separation is accomplished by adding glacial acetic acid to the neutral solution containing vanadium and chro-
mum, and reducing the chromium by the addition of $\text{H}_2\text{O}_2$. The vanadium is precipitated as lead vanadate, the chromium remaining in solution.

Cain (8) separates chromium from vanadium by electrolysis of a sulphuric acid solution, using 5 to 6 amperes at 6 to 7 volts and a mercury cathode. The vanadium remains in solution.

**SEPARATION FROM ARSENIC AND ANTIMONY.**

Arsenic and antimony are readily separated from vanadium by precipitation with $\text{H}_2\text{S}$ from a solution made slightly acid with $\text{H}_2\text{SO}_4$. The arsenic should first be reduced with a current of $\text{SO}_2$ gas and the excess removed. Vanadium remains in solution as the vanadyl salt.

According to Turner (60), vanadium may be quantitatively separated from arsenic as well as phosphorus by precipitation in acid solution with a 6 per cent cupferron solution. Arsenic and phosphorus remain in solution.

Magnesia mixture will also precipitate arsenic or phosphorus from an alkaline vanadium solution.

Arsenic may be removed from vanadium by distilling their combined sulphides in a current of $\text{HCl}$ gas at $150^\circ \text{C}$. The arsenic is volatilized (22).

**SEPARATION FROM $\text{P}_2\text{O}_5$.**

Vanadium and phosphorus present in solution as vanadate and phosphate may be separated as follows:

If the solution is alkaline, it is first acidulated with a slight excess of $\text{H}_2\text{SO}_4$. The vanadium is then reduced by means of sulphurous acid. To 100 c. c. of the cold solution, 20 c. c. of a 75 per cent $\text{NH}_4\text{NO}_3$ solution and 50 c. c. of ammonium molybdate—75 grams ammonium molybdate in 500 c. c. $\text{H}_2\text{O}$—are added. The solution is then allowed to stand at $60^\circ \text{C}$ for one hour, and the phosphorus filtered off. The vanadium, if present in the solution in the vanadic state, is precipitated with the phosphorus, hence the necessity for reducing to the tetravalent state. Krophi (38) shows that vanadium may also be reduced with ammonium citrate before precipitation of the phosphorus.

According to Rodeja (49), cupferron will precipitate vanadium away from phosphorus.

Phosphorus may also be separated from vanadium by precipitation as cerium phosphate. A $\text{HCl}$ solution of the vanadium and phosphorus is treated with a solution of sulphurous acid or a stream of $\text{SO}_2$ gas to reduce the vanadium to the tetravalent form. Five cubic centimeters of acetic acid, 90 per cent, and 10 c. c. of a cerium chloride solution are then added, followed by enough dilute ammonia to cause slight turbidity. The solution is then heated to boiling and the precipitated $\text{CePO}_4$ filtered off.
Vanadium may be separated from silica by the following means:

1. When present in solution as sodium silicate and vanadate, the solution may be made acid with HCl and then evaporated to dryness and dehydrated, as is ordinarily done with silica. However, there is a tendency for the dehydrated silica to retain part of the vanadium so that it is necessary to wash repeatedly with a dilute solution of HCl to insure a complete extraction of the vanadium.

2. Vanadium may be separated from SiO₂ (see Friedheim (26)) as well as from many other compounds or elements by passing a dry current of HCl gas or chlorine over the substance. The vanadium is volatilized as the oxytrichloride and recovered by collecting the distillate in water. The method is particularly useful when the composition of the mineral is sought, and is much used in this capacity by Hillebrand. However, for ordinary separation the method is far too tedious.

3. Mennicke (42) claims that Fischer and Manchot have shown that the use of HF for the volatilization of silicon in the presence of V₂O₅ is not permissible, owing to the volatilization of part of the vanadium. Unquestionably ignition of a residue containing vanadium and fluorides is to be avoided.

SEPARATION OF V₂O₅ FROM BARIUM, CALCIUM, ZINC, AND LEAD.

Vanadium may be separated from Ba, Ca, Zn, and Pb by evaporating the HCl solution to dryness and by extracting the residue with saturated ammonium oxalate, to which a few drops of acetic acid have been added. The solution is then mixed with acetic acid as long as any oxalates are precipitated. V₂O₅ remains in solution.

Barium and lead are also separated effectively from vanadium by evaporation with H₂SO₄ to convert them to their respective sulphates. The lead sulphate should be kept as insoluble as possible by diluting the solution, cooling, and adding alcohol. Filtration is then made in the cold.

Calcium is precipitated easily from vanadium as calcium oxalate in the usual manner. The vanadium should be in the reduced form and other elements which precipitate the vanadium as vanadates in alkaline solution should of course be absent.

Zinc is best separated from vanadium by precipitation as zinc sulphide in a slightly acid solution. H₂SO₄ is recommended as the most satisfactory acid, and should not be present at a concentration greater than 1/20 N. A strong current of H₂S should be passed through the solution for at least 30 minutes. The precipitate of zinc sulphide is filtered much more readily if precipitation is made in the cold.
ANALYTICAL METHODS FOR CERTAIN METALS.

SEPARATION OF VANADIUM FROM THE ALKALIES.

Vanadium may be separated from the alkalies and alkaline earths by precipitation as NH₂VO₃ from a concentrated NH₄Cl solution by evaporation. Geerland (27) claims that the precipitate retains small quantities of potassium.

The volatilization of the vanadium as the oxytrichloride by HCl gas or chlorine, as outlined under separation from silica (p. 249), can also be used to separate vanadium from the alkalies and the alkaline earths.

SEPARATION OF VANADIUM FROM THE RARE METALS FOUND OR ASSOCIATED WITH IT IN ORES OR COMMERCIAL ALLOYS.

SEPARATION OF VANADIUM FROM URANIUM.

Vanadium and uranium present together in a sodium carbonate solution may be separated by the following method:

1. By precipitating the vanadium as lead or mercurous vanadate after decomposing the carbonate with a slight excess of HNO₃, followed by the addition of the lead or mercury salt and ammonium acetate to replace the free HNO₃.

2. By acidifying the carbonate solution with H₂SO₄ and boiling off the excess CO₂, adding NH₄HPO₄, and then ammonia and ammonium acetate, which precipitate the uranium as UO₂NH₄PO₄. (See Finn (23).) The vanadium remains in solution.

SEPARATION OF VANADIUM FROM MOLYBDENUM.

1. The most commonly used method for separating molybdenum from vanadium is to precipitate the molybdenum in an acid solution as MoS₂ by means of H₂S. Complete precipitation of the molybdenum is best obtained by heating on a water bath in a pressure flask. The solution containing the vanadium and molybdenum should be slightly acid with H₂SO₄. The solution is then saturated with a rapid stream of H₂S and the bottle corked and placed in a water bath. After the expiration of several hours, the bottle is removed and the solution again saturated with H₂S and then filtered.

2. Molybdenum may also be separated from vanadium by means of ether. HCl (1.1 sp. gr.) is recommended as the most desirable solution for the extraction of molybdenum. The vanadium remains in the aqueous solution while the molybdenum is extracted in the ether. (See Bleecker (6).)

3. Molybdenum may be precipitated away from vanadium as ammonium phosphomolybdate. (See under "Separation from P₂O₅" (p. 248).)

4. See method given by Fischer (25) for the separation of vanadium from the common elements.
5. Vanadium may also be precipitated in the presence of molybdenum without precipitation of the latter by the method of Carnot (12). The solution should be alkaline with ammonia and should contain a small amount of ammonium chloride. Manganese chloride added to this ammoniacal solution precipitates the vanadium as manganese vanadate, $2\text{MnO} \cdot \text{V}_2\text{O}_5$, on boiling.

**SEPARATION OF VANADIUM FROM TUNGSTEN.**

1. Tungsten may be removed from a vanadium solution by evaporating in nitric acid solution to throw out the tungsten as $\text{WO}_3$, or by precipitation in an HCl solution by means of cinchonine solution.

2. Vanadium is separated from tungsten as $\text{NH}_4\text{VO}_3$ by evaporating a strongly ammoniacal solution that has been saturated with NH$_4$Cl and extracting the residue with cold water. The vanadium is found in the precipitate and the tungsten in the solution. Details are given by Brauner. (See Mennicke (42), p. 125.)

3. Tungsten and vanadium may be separated by the same method that Fischer (25) used for separating Mo, P, As, etc., from vanadium, namely, the decomposition of the mixed lead salts by boiling with potassium carbonate solution.

**SEPARATION OF VANADIUM FROM ZIRCONIUM AND TITANIUM.**

The separation of vanadium from zirconium and titanium very rarely presents any difficulty. If present together in solution, however, their separation is usually necessary.

1. Sodium carbonate or hydroxide added to a solution containing vanadium, titanium, and zirconium will precipitate all of the titanium and zirconium as hydroxides.

2. After alkaline fusions of an ore or other material, the zirconium and titanium remain behind in the residue if the melt is extracted with water. Dilute acids, however, particularly HCl, carry into solution with the vanadium a large part of those elements.

3. Ammonia added to the solution will precipitate the zirconium and titanium, but its use is not recommended, as part of the vanadium is usually precipitated either by the ammonia itself or by other elements present.

**QUANTITATIVE ANALYSIS.**

**METHODS FOR THE GRAVIMETRIC DETERMINATION OF VANADIUM.**

**DETERMINATION BY MERCURIOUS NITRATE METHOD.**

The alkaline solution from a fusion of the ore with sodium carbonate and potassium nitrate is nearly neutralized by the careful addition of HNO$_3$. A solution of mercurous nitrate is then added drop by drop
until no further precipitate of mercurous vanadate forms. The solution is then heated to boiling and the yellow precipitate allowed to settle. The precipitate is filtered off, washed with a dilute mercurous nitrate solution, ignited, and the residue weighed as $V_2O_5$.

It is self-evident that no elements precipitated from alkaline solution by mercurous nitrate, particularly chromium, arsenic, phosphorus, molybdenum, or tungsten, should be present. The method gives good results if the interfering elements are first removed.

**DETERMINATION OF VANADIUM AS AMMONIUM VANADATE.**

The Berzelius-Hauer method (3) is particularly adapted to the determination of vanadium in alkaline vanadate solutions. The procedure consists of treating the alkaline solution with enough ammonium chloride to produce a saturated solution. The vanadium separates out as ammonium metavanadate which on ignition yields pure vanadium pentoxide. Roscoe (51) and Holverscheit (32) claim that this method gives low results, on account of the solubility of the metavanadate, as well as from loss by volatilization during ignition. Gooch and Gilbert (28) as well as Campagne obtained satisfactory results, and Beard (2) found that the addition of alcohol improved the method and insured complete precipitation of the vanadium.

**LEAD ACETATE METHOD.**

The lead acetate method originally proposed by Roscoe (50) is one of the most satisfactory methods for the determination of vanadium.

When lead acetate is added to a weakly acetic acid solution of a vanadate, the vanadium is quantitatively precipitated as basic lead vanadate. Roscoe's original method proposed the direct weighing of this precipitate after drying at 100° C. Owing to the doubtful composition of the lead vanadate precipitate, Cormimboeuf (14) suggested dissolving in $HNO_3$, eliminating the lead by fuming with $H_2SO_4$, and evaporating the filtrate, then weighing as $V_2O_5$.

With this modification the method is essentially as follows: The solution from the sodium carbonate-potassium nitrate fusion is nearly neutralized with $HNO_3$, and enough lead acetate is added to precipitate the vanadium completely. The precipitate is filtered off and washed with dilute acetic acid solution. The precipitate is then dissolved in the minimum amount of hot dilute $HNO_3$, and the lead removed by fuming with $H_2SO_4$ and filtering. The filtrate is evaporated to small volume in a porcelain dish, then transferred to a weighed platinum crucible, taken to dryness, and finally ignited. The residue is weighed as $V_2O_5$.

Several other methods have been proposed for separating the lead from the vanadium. Holverscheit first proposed the use of
H₂S in acid solution. The lead sulphide with deposited sulphur is filtered off and the filtrate evaporated as above. The lead may likewise be removed as the chloride from the solution after adding two volumes of alcohol.

This method has also been made the basis of large numbers of volumetric methods in which the separation is accomplished by the use of lead acetate, followed by the separation of the lead and titration of the vanadium in the filtrate with KMnO₄ after suitable reduction to the vanadyl salt.

**Miscellaneous Gravimetric Methods.**

In addition to those better-known methods already given, other direct and indirect gravimetric methods for the determination of vanadium have been proposed.

**Estimation as Barium Pyrovanadate.**

The gravimetric estimation of vanadium as barium pyrovanadate has been proposed by Carnot (12). The vanadium is precipitated from neutral or slightly alkaline solution by the addition of barium chloride. The precipitate settles readily so that the solution may be decanted off. The precipitate upon ignition is light yellow in color and is weighed as Ba₃V₂O₇. According to Beard results are satisfactory if care enough is used to obtain the proper conditions.

**Estimation as Manganese Vanadate.**

The estimation of vanadium as the manganese salt has similarly been used by Carnot (12). The vanadium solution is treated with ammonium chloride and ammonia, and boiled. The vanadium is then precipitated with a solution of manganese chloride or sulphate containing ammonium chloride. The precipitate is recovered, ignited, and weighed as 2MnO.V₂O₅, which is slightly reddish in color. Hensen claims that the method does not yield very satisfactory results.

The method of Perkins (47) is an example of an indirect gravimetric method. It is based on the reduction of vanadium pentoxide by means of KI in HCl solution, which results in the liberation of free iodine. The iodine is then determined gravimetrically as silver iodide. The reactions involved are as follows:

\[
V₂O₅ + 2KI + 2HCl = V₂O₇ + 2KCl + H₂O + I₂
\]

\[
I₂ + 2Ag = 2AgI.
\]

Browning and Palmer (7) determine vanadium directly as AgVO₄, obtained by the addition of AgNO₃ to a NH₃·VO₃ solution, from which the excess ammonia has been removed. They gently ignite the precipitate before weighing.

The determination of vanadium by precipitation with cupferron, C₆H₅N(ONH₂)NO₃, has been worked out by Turner (61), in which the
metavanadate is precipitated by a 6 per cent solution of cupferon with subsequent ignition and recovery of vanadium as \( V_2O_5 \). This method apparently requires very careful manipulation to yield satisfactory results.

**VOLUMETRIC METHODS FOR THE QUANTITATIVE DETERMINATION OF VANADIUM.**

Volumetric methods are used for the estimation of vanadium much more extensively than are gravimetric methods, probably on account of their shortness as well as the generally accepted belief in their accuracy.

\( \text{KMnO}_4 \) is by far the most important chemical used for titrating the vanadium. Innumerable methods have been developed for reducing the vanadium salts before titration, but the reoxidation is usually made by adding a standard permanganate solution. Ferrous sulphate or ferrous ammonium sulphate is now being used extensively as the titrating agent, especially in the analysis of iron and steel. It is used either alone or with potassium permanganate or bichromate.

Volumetric methods that are based on the estimation of the quantity of halogen liberated in the reduction of vanadium compounds—the so-called iodometric methods—have also been developed and are being used increasingly.

Colorimetric methods, particularly valuable for the estimation of small quantities of vanadium, have also been receiving attention.

**TITRATION BY MEANS OF POTASSIUM PERMANGANATE.**

The titration of vanadium by \( \text{KMnO}_4 \) is based on the oxidation of the lower oxides, usually the tetroxide, to the pentoxide. It is applicable to the estimation of vanadium in ores and minerals, iron and steels, ferrous and nonferrous alloys; also in slags, as well as in all vanadium compounds.

Titration of vanadium with standard permanganate is best accomplished at an acidity of approximately 5 per cent free \( \text{H}_2\text{SO}_4 \) and at a temperature of 60 to 70° C. Titration in the cold in the presence of chromium does not yield as sharp an end point. The end point even in the hot solution is rather fleeting. A definite pink, persisting for one minute, is a satisfactory end point. The reaction of titration with \( \text{KMnO}_4 \) is given as follows:

\[
5\text{V}_2\text{O}_5 + 2\text{KMnO}_4 + 3\text{H}_2\text{SO}_4 = 5\text{V}_2\text{O}_8 + \text{K}_2\text{SO}_4 + 2\text{MnSO}_4 + 3\text{H}_2\text{O}.
\]

\( 1/10N \) \( \text{KMnO}_4 \) is a suitable strength solution for general use, but for the determination of small quantities, \( 1/100N \) \( \text{KMnO}_4 \) is used.

1 c. c. \( N/10 \) \( \text{KMnO}_4 \) = 0.0091 gram \( \text{V}_2\text{O}_5 \), or 0.0051 gram \( \text{V} \).
METHODS OF REDUCING VANADIUM SOLUTION.

Many methods are in use for the reduction of vanadium to the vanadyl compounds preparatory to titration with KMnO₄. Reduction may be accomplished by evaporating a solution of vanadium with concentrated hydrochloric acid as originally suggested by Campagne (10). Wilms and Fischback (65) decrease the volatilization losses by the addition of H₂SO₄, thus improving the results. Other chemists using this reduction have found that the presence of iron insured complete reduction in one evaporation. In the presence of iron the method of reduction is as follows: About a 25 c. c. H₂SO₄ solution of the vanadium, containing 10 c. c. concentrated H₂SO₄, to which 0.25 gram of FeSO₄—if no iron is present—has been added, is treated with powdered KMnO₄ to a strong pink. Then 40 to 50 c. c. of concentrated HCl is added and the solution evaporated to heavy SO₃ fumes. The cool solution, after dilution and warming, is ready for titration.

Similarly, vanadium in an acid solution may be reduced to the vanadyl state by a rapid current of SO₂ gas, or by the addition of a sulphite or acid sulphite. Of course, the excess SO₂ must be removed before titration. This removal is accomplished efficiently either by taking to fumes or by active ebullition, while a rapid stream of CO₂ is passed through the solution.

Reduction by a stream of H₂S gas is also a satisfactory method of reducing vanadic acid to the tetroxide, and it is much used by Hillebrand. The excess may be removed by the same means as the SO₂ and the deposited sulphur is removed by filtration. Koenig (37) claims that both the HCl and the SO₂ reduction of vanadium yield low results and hence recommends the use of H₂S. It has been the experience of the author that reduction by H₂S does give a trifle higher result, but he has had no reason for questioning the completeness of reduction with SO₂ or HCl.

Alcohol may also be used for the reduction if added to the acid vanadium solution just before the solution begins to yield SO₃ fumes. (See Wegelin (64).) Ferrous salts also quantitatively reduce the pentoxide to the tetroxide.

Bleecker (6) reduces vanadic sulphate to the tetravalent state by simple electrolysis. He uses the same apparatus as for electrolytic copper determinations and electrolyzes the sulphuric acid solution for 10 minutes after adding 50 gms. of CuSO₄.

H₂O₂, according to Cain and Hostetter (9), quantitatively reduces V₂O₅ to V₂O₃ if added in small portions to a concentrated H₂SO₄ solution of the vanadium. After the excess H₂O₂ has been removed, the vanadium is found to be completely reduced.

According to Glasmann, metallic magnesium reduces vanadic solutions to V₂O₅, but Cain and Hostetter claim only incomplete
reduction. The vanadium is reduced to $\text{V}_2\text{O}_3$ and reoxidized to $\text{V}_2\text{O}_5$ when an acid solution of the metal is passed through the Jones reductor. Since $\text{V}_2\text{O}_5$ is extremely unstable, Gooch and Gilbert used silver sulphate to oxidize the compound to the stable tetroxide preparatory to subsequent titration with permanganate.

USE OF THE JONES REDUCTOR IN THE ESTIMATION OF VANADIUM.

The Jones reductor of the usual form used for iron and molybdenum determinations may also be used for the reduction of vanadium solutions. Satisfactory types of reductors are described by Scott (52), page 281, and by Treadwell and Hall (57), page 637.

The vanadium should be in a warm $\text{H}_2\text{SO}_4$ solution of a volume from 25 to 50 c.c. containing about 2.5 per cent of free $\text{H}_2\text{SO}_4$. Immediately preceding the vanadium solution, 100 c.c. of warm water and 100 c.c. of a warm 2.5 per cent $\text{H}_2\text{SO}_4$ solution should always be passed through the reductor. The last traces of vanadium solution should be removed by at least 100 c.c. of warm water. All of the precautions necessary with the use of the reductor should be carefully observed in the reduction.

The so-called "titrating mixture" should also be used in the receiver of the reductor. An excess of a 10 per cent solution of ferric alum with from 5 to 6 c.c. of sirupy phosphoric acid is very satisfactory. In adding the ferric alum, it should be remembered that the vanadium is reduced to $\text{V}_2\text{O}_3$ by the zinc and reoxidized to $\text{V}_2\text{O}_5$ by the ferric salt. Blank determinations should always be made with the same quantity of reagents used in an actual determination.

$$5\text{V}_2\text{O}_3 + 6\text{KMnO}_4 + 9\text{H}_2\text{SO}_4 = 5\text{V}_2\text{O}_5 + 3\text{K}_2\text{SO}_4 + 6\text{MnSO}_4 + 9\text{H}_2\text{O}.$$  

1 c. c. N/10 KMnO$_4$ = 0.003033 gram $\text{V}_2\text{O}_5$ = 0.0017 gram V.

TITRATION OF VANADIUM BY MEANS OF FERROUS SULPHATE.

The estimation of vanadium by titration with a standard solution of ferrous ammonium sulphate, whereby the vanadium is reduced from the pentavalent state to the tetravalent state, has met with much approval, particularly in the analysis of iron and steel. Johnson (34) has developed the method as first proposed by J. Kent Smith, and estimates the vanadium by titration with a standard solution of double sulphate of iron and ammonia. He uses potassium ferrocyanide as the internal indicator. He also extends the method to cover the simultaneous determination of chromium, by titrating with an excess of ferrous sulphate before adding the indicator, and then titrating back with KMnO$_4$. The difference between the amount of ferrous sulphate and the amount of permanganate represents the equivalent of chromium present.
Clark (13) also determines vanadium by the ferrous sulphate method but uses an excess of sulphate, then titrates back with standard potassium bichromate. The actual procedure in the titration is essentially as follows:

The solution containing the vanadium is diluted to about 450 c. c. and should contain about 50 c. c. of concentrated H$_2$SO$_4$. Titration is made at about 65° C. with 1/10 N solutions. First, sufficient KMnO$_4$ is added to produce a pink, then an excess of 1/10 N ferrous sulphate solution is added to reduce all the vanadium and chromium; then an excess of KMnO$_4$ is added as before. The pink of the KMnO$_4$ is first discharged and the actual titration is begun. If K$_3$Fe(CN)$_6$—0.6 c. c. of a solution of 5 grams in 130 c. c. water—is used as internal indicator, the blue ferroferricyanide gives the end point. If an excess of double sulphate is added and determined by titration with K$_2$Cr$_2$O$_7$, the end point is found by K$_3$Fe(CN)$_6$ as an external indicator.

**ELECTROMETRIC DETERMINATION.**

The electrometric titration used by Hillebrand for the estimation of chromates has been applied by Kelley and Conant (35) to the determination of vanadium. The vanadium is oxidized in solution, then titrated by means of ferrous sulphate, and the change in electromotive force of a suitable cell is used as the end point of titration.

Oxidation of the vanadium was accomplished in the original method by titration with permanganate, but in the later methods (35) has been extended to use ammonium persulphate and HNO$_3$. (See "Methods for steel analysis," p. 266.)

**IODOMETRIC TITRATION OF VANADIUM.**

The iodometric determination of vanadium is based on the estimation of the quantity of iodine liberated during the reduction of the pentoxide to lower oxides. Holverscheidt (32) gives the reduction of vanadium to V$_2$O$_5$ by the use of HBr. HI may be used similarly, the vanadium being reduced to the trivalent state.

Scott outlines a method and describes the apparatus used by Edgar (18) for the iodometric determination of vanadium. This method depends on the reduction of vanadic oxide by means of HBr.

Ditz and Bardach (16) use the method much as does Edgar; they make the reduction by means of HBr, catch the liberated bromine in an absorption tube attached to the same flask, and finally wash back the iodine solution and titrate in the original flask, with subsequent liberation of Br. The amount of bromine liberated is estimated by collecting it in an alkaline KI solution, which is finally acidified and the liberated iodine titrated in the usual manner with standard thiosulphate.
The procedure consists of placing an alkaline solution of the vanadium in a Voit flask. About 2 grams of KBr and 15 to 20 c. c. of concentrated HCl are added. The liberated Br is collected in an absorption bottle containing an alkaline solution of KI in either Na₂CO₃ or NaOH. The Voit flask containing the vanadium solution is heated for 10 minutes while a slow stream of hydrogen is being passed through the entire apparatus. The absorption bottle and contents are then cooled with running water, enough HCl to make slightly acid is added, and the liberated iodine titrated with 1/10 N sodium thiosulphate.

Chromium interferes with the determination of vanadium by this method, and Edgar has developed the method for the simultaneous estimation of both elements. Chromium is determined by taking the solution in the distilling flask after its initial reduction with HBr and running through the same procedure, except that KI is used in the distilling flask instead of KBr. Three cubic centimeters of sirupy phosphoric acid is also added, and the boiling is continued until a volume of 10 or 12 c. c. remains. This manipulation insures complete reduction of the vanadium from V₂O₅ to V₂O₃. The iodine liberated in the first reduction corresponds to that of the following reaction:

\[
V₂O₅ + 2CrO₃ + 8HBr = V₂O₃ + Cr₂O₃ + 4Br₂ + 4H₂O,
\]

whereas the second reduction is as follows:

\[
V₂O₅ + 2HI = V₂O₃ + I₂ + H₂O.
\]

The reduction and titration are carried out in a 1.5-liter flask fitted with a ground stopper carrying a separatory funnel and an absorption tube. The solution containing the vanadium is placed in the flask together with 10 c. c. of a 10 per cent KBr solution. By means of the separatory funnel, 75 c. c. of concentrated HCl is run into the flask. After 15 minutes the solution is diluted to 1 liter. The liberated bromine is caught in the alkaline KI solution in the absorption tube. Twenty c. c. of a 5 per cent KI solution is added to the contents of the flask, and the solution from the absorption is washed back into the flask. The free iodine is titrated with Na₂S₂O₅. The reactions are as follows:

\[
V₂O₅ + 2KBr + 2HCl = V₂O₃ + 2KCl + H₂O + Br₂,
\]

\[
Br₂ + 2KI = 2KBr + I₂,
\]

\[
I₂ + 2Na₂S₂O₅ = 2NaI + Na₂S₄O₆.
\]

Oberhelman (45) uses Na₂S₂O₅ for reducing the vanadium in the presence of a copper salt, then titrates the excess of Na₂S₂O₅ by standard iodine. The conditions are, briefly, as follows: Five grams of CuSO₄·5H₂O, 15 c. c. of 32 per cent HCl, and an excess of 0.1N Na₂S₂O₅ are added to the vanadium solution diluted to 400 c. c. After the reduction is complete, as shown by the clear sky-blue color
of the vanadyl salt, 0.4 gram of KI is added and the excess Na₂S₂O₃ titrated with standard iodine.

1 c. c. 1/10 N Na₂S₂O₃ = 0.0091 gram V₂O₅ = 0.0051 gram V

TITRATION OF VANADIUM BY MEANS OF POTASSIUM FERRICYANIDE.

H. E. Palmer (46) oxidizes vanadium tetroxide in alkaline solution by means of a large excess of potassium ferricyanide, then titrates with KMnO₄ the amount of ferrocyanide formed in acid solution. The procedure is essentially as follows: A vanadate solution is acidified with HCl and the vanadium reduced to V₂O₅ by means of SO₂. Excess SO₂ is removed by a current of CO₂. Ten times the theoretical quantity of potassium ferricyanide necessary to reoxidize the vanadium and a solution containing 6 grams of KOH are then added to the reduced vanadium solution. Ba(OH)₂ is added to precipitate the vanadium which is filtered off on an asbestos filter. The filtrate is acidified and titrated with KMnO₄.

\[ V₂O₅ + 2K₄Fe(CN)₆ + 2KOH = V₂O₅ + 2K₂Fe(CN)₆ + H₂O. \]
\[ 5K₄Fe(CN)₆ + KMnO₄ + 4H₂SO₄ = 5K₃Fe(CN)₆ + 3K₂SO₄ + MnSO₄ + 4H₂O. \]

Chromium reacts in the same manner and must therefore be removed.

Müller and Diefenthaler (44) have applied their original experiments upon the determination of hydroferricyanic acid to the estimation of vanadium. The vanadium is reduced by means of potassium ferrocyanide. The resulting ferricyanide thereby obtained is then reduced by means of potassium iodide, and the liberated iodine is titrated with standard thiosulphate.

The method, briefly stated, is as follows:

To a solution of NH₄VO₃ containing somewhat less than 0.1 gram in 20 c. c., 60 c. c. of molar K₄Fe(CN)₆, 10 c. c. of molar H₂SO₄, 3 grams of KI, and 15 c. c. of ZnSO₄ solution—15 grams ZnSO₄. 7H₂O in 100 c. c. of H₂O—are then added. After diluting to a volume of 200 c. c., starch solution is added and the I titrated by means of .05 N Na₂S₂O₃.

\[ V₂O₅ + 2K₄Fe(CN)₆ + H₂O = V₂O₅ + 2K₂Fe(CN)₆ + 2KOH. \]
\[ 2K₃Fe(CN)₆ + 2KI = 2K₂Fe(CN)₆ + I₂. \]

1 c. c. .05 N Na₂S₂O₃ = 0.01646 K₄Fe(CN)₆ = 0.00255 gram V₂O₅.

TITRATION OF VANADIUM BY MEANS OF TITANIUM CHLORIDE

Several methods have been developed for the titration of vanadium, either alone or in the presence of molybdenum, chromium, and iron, by means of titanium chloride.

Attack (1) has developed a method whereby he reduces the vanadium with methylene white and titrates the amount of methylene blue formed with standard TiCl₃.
The HCl solution of vanadium is oxidized by means of Na₂O₂ and diluted to a known volume. An excess of methylene white—prepared by treating a 0.02 N solution of methylene blue with TiCl₃ solution immediately before titrating—is then added to the solution. The methylene blue formed is in turn titrated with TiCl₃ in an atmosphere of CO₂.

This method is applicable to the simultaneous estimation of chromium and iron. Iron is titrated in another aliquot just as is vanadium after the vanadium and chromium have been reduced with HCl. The vanadium and iron are determined in another aliquot after reducing the solution with SO₂ and reoxidizing all except the chromium by means of KMnO₄. Titration with methylene white followed by titration with TiCl₃ is then carried out.

Travers (55) uses a similar method, except that he reduces the vanadium directly with an excess of TiCl₃ and titrates the excess by means of ferric chloride under conditions such that the vanadium is not reoxidized. He gives the conditions as follows: 0.05 gram of V₂O₅ per liter with an acidity of 1 c. c. concentrated HCl in 100 c. c. water. The indicator used is potassium thiocyanate. Molybdenum responds to the same reaction and is estimated by the same method.

Travers also modifies his original method to make it especially applicable for the estimation of vanadium in the presence of molybdenum. A HCl solution from which the Fe has been removed is titrated with TiCl₃ after the addition of KCNS for indicator. A vermillion tint appears immediately, but disappears on shaking until all the vanadium is reduced, when it becomes permanent and is regarded as the end point. If the molybdenum content is also desired he titrates the vanadium and molybdenum with an excess TiCl₃, then brings back with FeCl₃ as in the original method.

MISCELLANEOUS VOLUMETRIC METHODS.

Edgar (19) has developed a volumetric method for indirect volumetric determination of vanadium in an alkaline solution containing an excess of carbonate, but containing no other elements precipitated by AgNO₃. The alkaline solution is acidified with HNO₃ and the excess of CO₂ boiled off. The solution is then made slightly alkaline with NaOH and a known quantity of standard AgNO₃ solution is added to precipitate the vanadium as Ag₃VO₄.

1 c. c. 0.1N AgNO₃ = 0.00304 gram V₂O₅

The precipitated Ag₃VO₄ is filtered off and the filtrate acidified with HNO₃, and the excess of AgNO₃ titrated with standard NH₄SCN.

This method is applicable also to the simultaneous estimation of phosphorus. The phosphorus and vanadium are precipitated as
their respective silver salts, and the vanadium is determined in the precipitate by dissolving in H₂SO₄, reducing with SO₂, and titrating with KMnO₄.

Warinski and Mdivani (63) developed a stannometric method for the estimation of vanadium. They titrated the vanadium in either an HCl or an H₂SO₄ solution with a standard stannous chloride solution (2 per cent). They used ammonium molybdate on a porcelain spot plate for the indicator. The stannous chloride solution reduces the vanadium from the pentavalent to the tetravalent state.

COLORIMETRIC METHODS.

Colorimetric methods have been developed for the estimation of very small quantities of vanadium, but have not met with general approval. Nearly all the proposed methods are based on the intensity of color produced by the addition of either H₂O₂ or strychnine sulphate to acid vanadium solutions. The principal use of such methods has been limited mostly to estimation of the small percentages of vanadium found in iron and steel.

In a method developed by Slavik (53), H₂O₂ is used to produce the reddish-brown color of pervannic acid, the intensity of which determines the quantity of vanadium present in steels. Slavik emphasizes the necessity of running a nonvanadium steel in precisely the same manner as the unknown sample. One-fourth gram samples are dissolved in 4 c. c. of dilute 1:1 HNO₃, 0.3 gram of ammonium persulphate is added to destroy the color due to carbon present, and the solution is fumed, then 0.1 c. c. of a standard vanadium solution (0.0001 gram V) is added to the blank. H₃PO₄ is used to decolorize the ferric iron, H₂O₂ is added, and the intensity of the color produced compared with the known standard.

Pickard (48) uses a very similar method, and Fenner (21) applies the same scheme for determination of vanadium in the presence of iron and titanium. He destroys the color of the ferric iron by the addition of H₃PO₄ and decomposes the titanium compound by means of ammonium fluoride or hydrofluoric acid.

Mellor (41) determines vanadium colorimetrically by the use of a chart of curves of equations resulting from plotting the concentrations of TiO₂ or V₂O₃ against the intensity of the red rays in solutions colored with H₂O₂ and Fenton's acid, C₆H₄O₆·2H₂O, as measured by Lovibond's tintometer.

Gregory (29) uses the color produced by adding strychnine to a vanadic acid solution as the basis of a colorimetric method. The vanadium solution is oxidized with KClO₃ and the chlorine removed by taking to H₂SO₄ fumes. A standard solution—0.1778 gram V, 10 c. c. concentrated H₂SO₄ diluted to 1 liter—is treated in the same manner. Strychnine—4 grams per liter H₂SO₄—is added in the
cold and the solution is allowed to stand until the violet color first formed is replaced by the orange tint. The orange color of the unknown is now compared with that of the standard, and the quantity of vanadium in the unknown can then be calculated.

**ELECTROLYTIC DETERMINATION OF VANADIUM.**

Truchot (59) has worked out the following electrolytic process for the determination of vanadium. The solution of sodium vanadate in the presence of excess of sodium carbonate is made very slightly acid with $\text{H}_2\text{SO}_4$ and boiled to remove the liberated $\text{CO}_2$. The solution is then made barely alkaline by the addition of an excess of from 20 to 30 drops of ammonia ($22^\circ$ B), heated from 80 to $85^\circ$ C., and electrolyzed with a current of 2 to 2.5 volts of 0.3 ampere for 8 to 10 hours. The solution is maintained at a constant level of about 200 c. c. volume by adding warm dilute ammonia. The vanadium is precipitated on the platinum cone as a lower oxide, which is washed with water, then with alcohol, and is heated for a short time to convert the deposit to the brown pentoxide free from any blue or green colors, cooled, and weighed. Truchot applies this method for estimating quantities of vanadium from 0.012 to 0.500 gram calculated as the pentoxide, and claims to have obtained satisfactory results.

**SPECIAL METHODS OF ANALYSIS FOR ORES, SLAGS, AND OTHER PRODUCTS.**

**METHODS FOR THE ANALYSIS OF CARNOTITE ORES FOR ESTIMATION OF URANIUM AND VANADIUM.**

**VOLUMETRIC METHOD OF LEDOUX.**

A volumetric method used by Ledoux, which is based on the procedure outlined by Engle (20), is essentially as follows: Five grams of ore are dissolved in 10 c. c. $\text{HNO}_3$ (1.42) and 20 c. c. $\text{H}_2\text{SO}_4$ (1.84), and the solution is heated to fumes, cooled, and diluted to 70 to 80 c. c. The heavy metals are removed by a current of $\text{H}_2\text{S}$, and the excess $\text{H}_2\text{S}$ is boiled off. After oxidizing with hydrogen peroxide, the iron is precipitated with $\text{Na}_2\text{CO}_3$. The filtrate is treated with 5 grams of ammonium phosphate and 10 c. c. $\text{H}_2\text{SO}_4$, and the $\text{CO}_2$ is expelled by boiling. The solution is then made alkaline with ammonia and just acid with acetic acid, whereupon the uranium is precipitated as ammonium uranyl phosphate and the vanadium remains in solution. The uranium is determined by dissolving the precipitate in $\text{H}_2\text{SO}_4$, reducing with zinc, and titrating with permanganate. The vanadium is recovered from the filtrate by the addition of lead acetate. The resulting precipitate of lead vanadate is dissolved in 1:1 $\text{HNO}_3$, fumed with $\text{H}_2\text{SO}_4$, and the lead is removed by filtration. The vanadium is then reduced with $\text{SO}_2$ and titrated with $\text{KMnO}_4$. 

Much the same procedure is outlined by Finn (24) except that after the precipitation of the uranium he determined the vanadium directly in the filtrate.

**METHOD OF LEDOUX AND LOW.**

The method of Ledoux, which is also given by Low (40) is volumetric for vanadium but gravimetric for uranium. The procedure is as follows: Two to five grams of ore are dissolved in 10 c. c. HCl and 15 c. c. HNO₃. The solution is evaporated to dryness, the residue dissolved in dilute HCl, and filtered. The insoluble residue is treated with HF, then the solution is evaporated to dryness, and again dissolved in dilute HCl. This solution is added to the original filtrate. The heavy metals are removed by a stream of H₂S, and the filtrate—which should have a volume of about 100 c. c.—is oxidized with H₂O₂, and the iron is removed with Na₂CO₃. The vanadium is precipitated by the addition of lead acetate after acidifying with HNO₃ and replacing the free nitric with ammonium acetate—80 c. c. strong ammonia, 100 c. c. H₂O, and 70 c. c. 99 per cent acetic acid. The vanadium is then determined as outlined above. The uranium is recovered from the filtrate as ammonium uranate, ignited, and subsequently weighed as U₃O₈.

**METHOD OF BLAIR.**

A method developed by Blair (5) for the determination of uranium and vanadium in carnotite is given as follows: Two grams of ore are dissolved in 50 c. c. of 1:1 HNO₃ and the solution is diluted. NH₄OH and (NH₄)₂CO₃ are added to precipitate iron, aluminum, etc. The filtrate, after being made slightly acid with HNO₃, is treated with 10 to 15 c. c. of ammonium acetate solution—30 per cent acetic acid added to strong ammonia until it is just slightly acid to litmus—added to replace the free HNO₃. The uranium is precipitated as ammonium uranyl vanadate, which is carefully washed, ignited, and weighed as V₂O₅.2UO₃. If an excess of vanadium is not originally present in the ore, a small quantity is added. The vanadium is determined in a separate sample of the ore by a process essentially the same as Campagne’s (10) original HCl reduction method.

**VANADIUM ORES CONTAINING CHROMIUM.**

Owing to the similar chemical behavior of vanadium and chromium, many methods used for the determination of vanadium are affected by the presence of chromium; hence several methods originally intended for the estimation of vanadium have been extended to cover the simultaneous determination of chromium.

Campagne (11) modified his original method for the estimation of vanadium to include the estimation of chromium, according to the following procedure:
The sample is decomposed by HCl if possible, but if necessary HNO₃ is also used. If HNO₃ is used, it must be expelled by evaporating to dryness and by redissolving the residue in dilute HCl. The solution containing the vanadium and chromium is evaporated to small volume and 50 c. c. of concentrated HCl added. Three evaporation are required, followed in turn by the addition of 50 c. c. of HCl. H₂SO₄ is added only after the third evaporation, and the solution then heated to fumes. The solution is cooled and diluted, and is titrated in the cold by means of KMnO₄. This titration gives the quantity of vanadium present. The chromium is then oxidized by boiling with an excess of KMnO₄. The excess of KMnO₄ is then destroyed by adding filter paper. The vanadium and chromium are again reduced with a known excess of standard ferrous sulphate and retitrated with KMnO₄. The difference between the equivalent amount of ferrous sulphate and KMnO₄ represents the amount of chromium present.

Palmer (46) determines the chromium and vanadium present in an ore by the following procedure: The ore is decomposed by fusing with Na₂CO₃ and KNO₃. The filtrate is acidified with HCl, and the chromium and vanadium are reduced by a current of SO₂, the excess being removed by CO₂. The V and Cr are oxidized by a large excess of potassium ferrocyanide, and after the removal of the vanadium and chromium with barium hydroxide the resulting ferrocyanide is titrated with KMnO₄. The vanadium is determined in a separate aliquot by separating from the chromium as lead vanadate after reducing the chromium to Cr₂O₃ with H₂O₂ in glacial acetic acid. The lead vanadate is dissolved in H₂SO₄, reduced with SO₂, and titrated with KMnO₄.

VANADIFEROUS SANDSTONES.

A method used by Hillebrand for the analysis of vanadiferous sandstones, but also applicable to carnitite and other vanadium ores, is as follows: One gram of the finely pulverized ore is treated with 3 c. c. of H₂SO₄ and 20 c. c. of HF. The solution is evaporated to dryness and the H₂SO₄ expelled over a free flame. The residue is extracted with hot water and acidified with H₂SO₄. Any arsenic or molybdenum present is precipitated with H₂S and filtered off. The vanadium now present in the vanadyl state is titrated with KMnO₄, and checked by a second reduction with SO₂ and with KMnO₄.

For the estimation of vanadium in sandstone containing small amounts of uranium and iron with traces of arsenic or molybdenum, Wilson (66) uses a method which is, briefly, as follows: Finely ground ore is digested with HNO₃ and H₂SO₄ and the SiO₂ filtered off. The iron is oxidized with H₂O₂ and precipitated with NaOH. The vanadium is determined in the filtrate by reduction with SO₂ and subsequent titration with KMnO₄. Uranium does not interfere.
VANADIUM IN IRON ORES, ROCKS, AND SLAGS.

Hillebrand (31) describes as follows a method applicable to the determination of vanadium in iron ores and rocks: A 5-gram sample is fused with 20 grams of Na₂CO₃ and 3 grams of niter. The melt is extracted with water, and the elements present in solution with the vanadium are removed as directed under "The detection of vanadium in rocks" (p. 244). The vanadium after being freed from other elements is reduced by H₂S, titrated with KMnO₄, then again reduced by SO₂, and titrated as before with KMnO₄. Campagne's original method as described below is also applicable for this determination.

H. F. Watts (62) describes a method for the estimation of vanadium in ores and various products as follows:

**MATERIALS LOW IN SILICA.**

A 1-gram sample is decomposed by heating in a nickel crucible with 3 to 4 grams of Na₂O₂. The resulting mass is carefully dissolved in water and the solution filtered. The filtrate is made slightly acid with HNO₃ and the vanadium is precipitated as lead vanadate by the addition of lead acetate and ammonium acetate. The precipitate is dissolved in HNO₃ and fumed with H₂SO₄. Reduction is made with SO₂ and titration with KMnO₄.

In treating ores, Campagne dissolves in aqua regia, filters off the insoluble, removes the iron by pouring into NaOH solution, and then

continues. see above.

**MATERIALS HIGH IN SILICA.**

For materials high in silica, the water leach from the Na₂O₂ fusion will contain a large amount of silica. Campagne removes the bulk of this silica by acidifying with HNO₃, making just alkaline with NH₄OH, then adding (NH₄)₂CO₃, and filtering. He then precipitates the vanadium as lead vanadate and proceeds as for materials of low silica content.

Bleecker (6) decomposes rich vanadium ores, slags, iron, and steel, also ferrovanadium, by heating from 0.2 to 2 grams, depending on the vanadium content, with from 1 to 5 grams of Na₂O₂. He recommends heating only long enough to darken the entire mass without actual fusion. The mass is carefully dissolved in water, acidified with 10 c. c. of H₂SO₄, and electrolyzed for 10 minutes after the addition of 50 mg. of copper sulphate, as in a copper determination. The reduced vanadium is titrated in the ordinary way with KMnO₄. The solution should be free from uranium before electrolysis.

Jannasch and Harwood (33) have developed a method for the determination of vanadium in vanadinite, endlichite, carnotite, and sodium or ammonium vanadate, by volatilization in a current of
CCl₄ vapor. The material for analysis is placed in a porcelain or silica boat in a combustion tube, and a stream of CCl₄ vapor passed over it. The vanadium is volatilized as the chloride, and is recovered by collecting in a receiver containing HNO₃. The solution is evaporated to dryness, dissolved in dilute H₂SO₄, reduced with SO₂, and titrated with KMnO₄.

**ANALYSIS OF VANADIUM METAL AND ALLOYS.**

**VANADIUM METAL.**

Pure vanadium metal is rarely analyzed. Most methods used for vanadium steel or for ferrovanadium are applicable with but slight modifications to the analysis of vanadium metal.

Trautman (54) decomposes vanadium metal by heating the finely pulverized sample on a sand bath with concentrated HCl, then diluting, and heating on a water bath. The SiO₂ is filtered off, and the residue is washed carefully with 10 per cent HCl until free from vanadium.

For the analysis of the metal, Ruff and Martin merely dissolve it in HNO₃ with the addition of HCl and filter off the insoluble. They then add H₂SO₄ to the filtrate and heat to fumes, dilute, reduce, and titrate with KMnO₄.

**VANADIUM STEEL AND IRON.**

Many of the methods described above for determination of vanadium in ores are applicable also to the estimation of vanadium in iron, steel, and ferro-alloys. In the analysis of iron and steel, it is always advisable to run blank determinations with regular analyses. For this purpose, a steel or iron containing no vanadium, but otherwise having as nearly as possible the same composition, should be used when available. The use of a blank on a nonvanadium steel is very important, especially in the analysis of low-percentage vanadium steels. When the results obtained on a sample show an exceedingly small amount of vanadium, the actual presence of the vanadium should be confirmed by one of the methods given on page 245 for the detection of vanadium in iron and steel.

**FERROUS SULPHATE METHOD FOR STEEL.**

Johnson (34) gives the following method for the determination of vanadium in steels: Two grams of steel are dissolved in 30 c. c. of 1.3 H₂SO₄ and 20 c. c. of water. After the first action ceases, 60 c. c. of 1.20 HNO₃ is added and the solution boiled, then diluted with warm water, and oxidized with KMnO₄. The titration is carried out as outlined on page 275. Blank is from 0.4 to 0.9 c. c.

Clark (13) makes a slight modification of the method and proceeds as follows: 0.501 gram of the alloy is dissolved in 25 c. c. of 1:2 H₂SO₄,
and 10 c. c. of HNO₃. Evaporation is continued to white fumes, and HF is added to the sample in a platinum dish if the alloy is refractory. Finally 75 c. c. of 1:2 H₂SO₄ is added and heated until everything is in solution. The solution is placed in a casserole and 75 c. c. more of 1:2 acid is added, then diluted to 400 to 500 c. c. with hot water. The rest of the procedure is outlined on page 275. The actual titration is made with an excess of double sulphate, the excess being determined with K₂Cr₂O₇ with K₃Fe(CN)₆ as external indicator.

Dougherty (17) uses the same method as Johnson, but shortens the procedure.

Demorest (15) uses a method based on the selective oxidation of ferrous sulphate in the presence of vanadyl sulphate by means of MnO₂, for destroying the excess of ferrous sulphate used in reducing the vanadium. The vanadium is then reoxidized with a measured amount of standard KMnO₄, the excess of which is titrated with standard Na₂AsO₃. A 2-gram sample of steel is dissolved in 12 c. c. of concentrated H₂SO₄ and 50 c. c. of water; 1 c. c. of 1.42 HNO₃ is finally added, and the solution is heated to fumes, cooled, and diluted to 30 c. c. Five cubic centimeters of phosphoric acid and an excess of KMnO₄ are added. Excess of ferrous sulphate is added to reduce the vanadium, then the solution is diluted to 250 c. c., and is reoxidized with 1/10N KMnO₄ to deep pink. Excess FeSO₄ (1 c. c. = 0.001 gram of Fe) is again added, then 1 gram of c. p. MnO₂, followed by vigorous shaking of the solution until all the iron is oxidized. Excess MnO₂ is removed by filtering through asbestos. After one minute, the excess KMnO₄ is titrated with standard Na₂AsO₃ solution. This method is also applicable to the analysis of ferrovanadium.

Cain and Hostetter (9) have developed a method for the estimation of vanadium in which the vanadium is precipitated from the solution by occlusion in ammonium phosphomolybdate. They precipitate the vanadium under conditions exactly similar to those required for the precipitation of phosphorus, dissolving the precipitate in H₂SO₄ and reducing with H₂O₂. Then they titrate in the usual manner with KMnO₄. The method was originally devised for analyzing iron and steel, but they consider it applicable to the estimation of vanadium in low-grade ores, as it is possible to use as much as a 50-gram sample for the analysis. The procedure is essentially as follows: Dissolve a quantity of steel containing from 2 to 10 milligrams of vanadium in 1.135 HNO₃. Boil off free fumes, add KMnO₄, and finally dissolve any precipitated MnO₂ with KNO₃ solution. Nearly neutralize with ammonia (0.96) and add sodium phosphate in sufficient quantity to make the ratio of P:V at least 10:1. Precipitate the phosphorus with molybdate solution in the usual
manner. Filter through a Gooch crucible and dissolve the precipitate in hot concentrated H$_2$SO$_4$. Add a few drops of HNO$_3$ and fume, cool, and reduce the vanadium with repeated additions of small quantities of H$_2$O$_2$. Remove excess H$_2$O$_2$ by heating to fumes, cool, dilute, and titrate with 1/10N KMnO$_4$. The vanadium is reduced to V$_2$O$_4$ by the peroxide and reoxidized to V$_2$O$_4$ by the permanganate.

**HCl Method for Iron and Steel.**

The determination of vanadium in iron and steel, based on Campagne's original method in which the vanadium is reduced by means of HCl, is as follows: A 5.1-gram sample of steel is dissolved in dilute 1:2 HCl, to which HNO$_3$ is added for complete oxidation. The solution is placed in a separatory funnel, and the bulk of the iron is removed with 100 c. c. of ether. The aqueous solution is then boiled and a crystal of sodium chlorate is added to remove the ether; 20 c. c. of 1:1 H$_2$SO$_4$ is added to the solution, and enough KMnO$_4$ to give a distinct pink; 40 to 50 c. c. of concentrated HCl is added and the solution evaporated to fumes, cooled, diluted, and titrated with 1/50N KMnO$_4$.

**Colorimetric Method for Steel.**

Most of the colorimetric methods in use have been devised for the estimation of small amounts of vanadium in iron and steel. Practically all are based on the formation of brownish-red pervanadic acid when H$_2$O$_2$ is added to an acid solution. Methods of Slavik, Pickard, Gregory, and Fenner, as outlined under "Colorimetric methods," page 261, may be used for the estimation of vanadium in iron and steel.

**Method for Cr-V Steel.**

The similarity of the chemical properties of chromium and vanadium makes the presence of chromium interfere with the estimation of vanadium in iron and steel. Many of the methods for the estimation of vanadium are easily modified, however, to include the simultaneous estimation of chromium.

Both the methods of Johnson and Clark, as outlined on page 266, provide for the estimation of chromium. The vanadium and chromium are obtained in solution, and after being thoroughly oxidized, are titrated with ferrous ammonium sulphate which reduces both the vanadium and chromium, and reoxidized with KMnO$_4$, which oxidizes only the vanadium. The difference between the equivalent amounts of ferrous sulphate and permanganate represents the amount of chromium.

The method of Demorest given on page 267 is also extended to cover the estimation of chromium. (See Lord and Demorest (39).) The reactions involved are practically the same as in the methods
of Johnson and Clark. The end point, however, is not given by the
permanganate pink but by the disappearance of the pink by back
titration with Na$_2$AsO$_3$.

Campagne's method for iron and steels is used for the estimation
of vanadium in chrome-vanadium steels, but the chromium is
removed. After separation of the iron by ether, the solution is
poured into a 10 per cent NaOH solution. The vanadium is recov-
ered from the filtrate by precipitation as lead vanadate, is then
dissolved in HCl and fumed with H$_2$SO$_4$, reduced by again evapo-
rating with 40 to 50 c. c. of concentrated HCl, cooled, diluted, and
titrated.

J. R. Cain (8) determines V in Cr–V steels as follows: 2 to 4 grams
of steel are dissolved in 40 to 60 c. c. 10 per cent H$_2$SO$_4$. The
insoluble material is decomposed by fusing with KHSO$_4$ and the
water leach is added to the main filtrate. The bulk of the acidity
is neutralized with Na$_2$CO$_3$, and the vanadium and chromium are
precipitated by the addition of a solution of cadmium carbonate.
The cadmium precipitate is dissolved in H$_2$SO$_4$ and the resulting
solution is treated with H$_2$S to precipitate the cadmium. Chromium
is removed from the filtrate by electrolyzing with 5 to 6 amperes at
6 to 7 volts. The vanadium remains in solution and is first oxidized
with KMnO$_4$, then reduced with SO$_2$, and titrated with standard
KMnO$_4$.

**ELECTROMETRIC DETERMINATION OF VANADIUM IN IRON AND STEEL.**

The electrometric method of Kelley (35), outlined on page 257,
was originally devised for the estimation of vanadium in steels, and
is applicable in the presence of chromium. This method is based on
the change in the electromotive force of a suitable cell by titration
of the oxidized vanadium with standard ferrous sulphate; KMnO$_4$,
ammonium persulphate, or HNO$_3$ may be used for oxidizing the
vanadium. The method using HNO$_3$ is essentially as follows:
A 2-gram sample of the steel up to 0.5 per cent vanadium, or a 1-gram
sample of higher percentages, is dissolved in from 80 to 100 c. c. of
1.20 H$_2$SO$_4$. After solution, 2 c. c. of HNO$_3$ is added, drop by drop,
and the solution boiled, finally diluted to 100 to 175 c. c., and treated
with 40 c. c. of concentrated HNO$_3$. Boiling is then continued for
one hour, during which the volume of solution must not be less than
100 c. c. Finally, cool, dilute to 300 c. c., and titrate with ferrous
sulphate and potassium dichromate at a temperature of 20° C. or
lower.

The oxidation of the vanadium by the HNO$_3$ is selective, so that
chromium does not interfere in the titration. Ninety-nine per cent
of the vanadium is obtained by this method so that a correction is
necessary. The method is recommended especially for small percentages of vanadium usually found in steels; it might be used satisfactorily on low-grade ores.

**GRAVIMETRIC METHODS FOR ESTIMATION OF VANADIUM IN IRON AND STEEL.**

Purely gravimetric methods have not been used very extensively for the estimation of vanadium in iron, steel, or ferrovanadium. Any of the gravimetric methods outlined from pages 251 to 254 may be used if desired for estimating the vanadium. The usual practice is to decompose by solution in acids, evaporation to dryness, then fusion with alkalies, in order to eliminate most of the iron. Some chemists prefer to take the acid solution of steel or alloy, and to remove the iron with Na$_2$CO$_3$ and peroxide, or by NaOH, rather than to precipitate the vanadium from the alkaline solution.

Pickard (48) gives a gravimetric method used by him in which he dissolves the steel in HNO$_3$ and evaporates to dryness. The oxide residue is then fused with Na$_2$CO$_3$ and Na$_2$O$_2$, and the melt extracted with water. He then precipitates the vanadium as mercurous vanadate and proceeds as outlined on page 252.

**ESTIMATION OF VANADIUM IN FERROVANADIUM.**

The methods for the estimation of vanadium in ferrovanadium vary but slightly from those devised for iron and steel. The same methods are used excepting that a much smaller sample is used. For iron or steel a 2 to 5 gram sample is usually taken, whereas with ferrovanadium a larger sample than 0.5 gram is seldom used.

**SELECTED METHODS FOR THE ANALYSIS OF MATERIALS CONTAINING VANADIUM.**

Several methods for the analysis of vanadium products that have given more or less satisfactory results are described in the following pages. The selection of a single method of analysis that will give absolutely reliable results, on any type of product, will not be attempted, as the most suitable method usually depends on the nature of the product to be analyzed, the accuracy necessary, and the time allowed for analysis.

**METHODS FOR THE DETERMINATION OF VANADIUM IN ORES.**

Under this section is given a number of analytical methods that have proved very satisfactory for the estimation of vanadium in a large variety of ores. A rather long method, much used by Ledoux & Co., is accurate and applicable to almost any type of ore. Similarly, a much shorter method that is applicable to most ores and that gives reliable results for technical analysis is also given. The long method is recommended if accuracy is of primary importance and
VANADIUM.

speed of secondary importance, whereas the short method is recom-
mended if speed is necessary and only a fair degree of accuracy is
required.

METHOD OF LEDOUX.

RESUME OF METHOD.

The ore to be analyzed, having been carefully sampled and suitably
pulverized, is decomposed by treatment with mineral acids. The
heavy metals are removed by a current of H₂S in acid solution. The
iron is removed by sodium carbonate after oxidation with hydrogen
peroxide. The vanadium is then recovered from solution by pre-
cipitation as lead vanadate, dissolved in HNO₃, fumed with H₂SO₄,
reduced with SO₂ gas, and titrated with standard KMnO₄.

PROCEDURE IN ANALYSIS.

From 2 to 5 grams, depending on the grade of the ore, or a sample
of finely pulverized ore containing at least 50 milligrams of V₂O₅, is
treated with 15 to 25 c. c. of concentrated HCl (1.20) and 5 to 10
c. c. of concentrated HNO₃. After the first violent action ceases,
the beaker is uncovered and evaporated to dryness on the water
bath. The residue is then moistened first with 3 to 4 c. c. of con-
centrated HCl and finally diluted to 25 to 30 c. c. with hot water
and filtered.

Nearly all vanadium ores yield their vanadium to this treatment,
but occasionally part of the vanadium is still retained by the residue.
To insure complete extraction, the residue obtained on the filter is
ignited in a platinum dish and treated with 5 c. c. of HF to expel the
SiO₂, and is then evaporated to dryness on the steam bath. The
residue is moistened with 2 to 3 c. c. of concentrated HCl and stirred
until the red crust is dissolved and then diluted with warm water.
After filtering, the solution is added to the main filtrate.

Now pass a rapid current of H₂S through the solution to precipitate
lead, copper, and other heavy metals of the H₂S group, then filter,
and remove the excess H₂S by boiling. Concentrate the solution to
100 c. c. and thoroughly oxidize the iron with an excess of H₂O₂, then
neutralize the solution by the addition of dry Na₂CO₃, and add at least
5 grams in excess. Boil only long enough, usually about 15 minutes,
to redisolve any yellowish precipitate, if uranium is present, then
filter off the iron, and reserve the filtrate. Invariably the iron
precipitate will contain vanadium. To recover the vanadium it is
necessary to redisolve the iron precipitate in the least possible
amount of 1:1 HNO₃ and reprecipitate the iron. This purpose is
accomplished by placing the filter in a beaker and adding the acid.
The filter paper is disintegrated with a stirring rod and furnishes paper
pulp to facilitate the next filtration. The solution is oxidized with 10
c. c. of $\text{H}_2\text{O}_2$ and the iron is precipitated with $\text{Na}_2\text{CO}_3$ as before, and filtered off. The filtrate is added to the main solution. Usually two precipitations insure a good separation of the iron and vanadium, but in ores containing much iron as many as three precipitations are sometimes required.

Evaporate the combined filtrates from the iron precipitation to a volume of 150 to 200 c. c., make acid with $\text{HNO}_3$, and boil to expel the $\text{CO}_2$. Nearly neutralize the excess $\text{HNO}_3$ with ammonia and add 2 c. c. of concentrated 1.2 $\text{HNO}_3$ for each 100 c. c. of solution and allow to cool to 50° C. or lower. The vanadium is then precipitated as basic lead vanadate by the addition of 10 c. c. of a 20 per cent lead acetate solution, and enough ammonium acetate solution—345 c. c. of 80 per cent acetic acid and 320 c. c. $\text{NH}_4\text{OH}$ diluted to 1 liter—to replace the free $\text{HNO}_3$. Usually about 15 c. c. of the ammonium acetate solution is required.

The precipitate of yellow basic lead vanadate settles rapidly and may be filtered almost immediately, but if possible it should be allowed to stand overnight. Wash the precipitate on the filter with dilute ammonium acetate—10 c. c. of ammonium acetate used above to 100 c. c. of $\text{H}_2\text{O}$.

Dissolve the lead vanadate in a few cubic centimeters of dilute $\text{HNO}_3$, add 10 c. c. of concentrated $\text{H}_2\text{SO}_4$, and evaporate to $\text{SO}_2$ fumes. Cool, dilute to 150 c. c., and reduce with a current of $\text{SO}_2$ gas. Remove the excess $\text{SO}_2$ by boiling, and titrate with 1/25 N $\text{KMnO}_4$ at 60 to 70° C. A pink that persists for one minute is a satisfactory end point. Blank determinations should be made and taken through the same operations as the original. With 1/25 N $\text{KMnO}_4$, the blank is usually from 0.2 to 0.3 cubic centimeters.

NOTES ON THE LEDOUX METHOD.

The procedure given above is essentially that used by Ledoux & Co. with a few modifications. The method is used for the estimation of uranium and vanadium so that if desired the uranium may be determined in the filtrate after removal of the lead vanadate.6

Special attention is called to the conditions as outlined in the procedure under which the vanadium is precipitated, as the yellow basic lead vanadate. The basic vanadate possesses less colloidal tendency than the white normal lead vanadate; hence it does not run through the filter paper and adhere to the beakers after boiling. Very little error is found by filtering the basic lead vanadate immediately after precipitation, but, if possible, the precipitate should stand over night; the supernatant liquid is then easily decanted through the filter.

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If the analysis is followed as outlined, practically no elements interfere, except chromium, which is seldom encountered in ores to be analyzed for vanadium. If chromium is encountered, it should be removed by one of the methods outlined on page 247 under "Separation of chromium from vanadium."

**Calculations and Factors.**

The following factors are used in the Ledoux method in analysis:

1 c. c. of normal KMnO₄ = 0.091 grams V₂O₅ = 0.051 grams of V.
1 c. c. of N/25 KMnO₄ = 0.00364 grams V₂O₅ = 0.00204 grams of V.
Fe factor of KMnO₄ × 1.6296 = V₂O₅.
Fe factor of KMnO₄ × 0.9133 = V.

The accuracy of this method of analysis depends primarily on the care taken to see that no vanadium remains insoluble in the residue from the ore, and also on the care used to recover all of the vanadium carried down with the iron during the separation of the latter. The actual reduction of the vanadium with SO₂ gas and the titration with permanganate give uniform results. As an example of the results to be expected with this method, the figures on the analysis of a low-grade carnottite ore are given as follows:

**Analysis of low-grade carnottite by SO₂ reduction.**

<table>
<thead>
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<th>No. of sample</th>
<th>Weight of sample</th>
<th>KMnO₄</th>
<th>V₂O₅</th>
<th>No. of sample</th>
<th>Weight of sample</th>
<th>KMnO₄</th>
<th>V₂O₅</th>
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<td>8</td>
<td>2.00</td>
<td>18.3</td>
<td>3.63</td>
</tr>
</tbody>
</table>

Average per cent. ........................................... 3.66
Blank c. c. of KMnO₄ ........................................ 0.40
Greatest deviation from mean, per cent. .................... 0.03
Highest percentage of error, per cent. .................... 0.82

**Rapid Method for Ores—Reduction with HCl.**

**Résumé of Method.**

The short method for ores is adapted from Campagne's original method for estimation of vanadium in iron and steels. It is based on the reduction of the vanadium to the tetravalent state by evaporation with concentrated HCl in the presence of iron. The reduced vanadium is then reoxidized in the usual manner by titration with standard permanganate.

**Procedure in Analysis.**

Place 2 to 5 grams of the finely pulverized ore, or a quantity containing from 150 to 175 milligrams of V₂O₅, in a 400 c. c. beaker,
treat with 25 to 30 c. c. of concentrated HCl, and warm for one-half hour. Then add from 8 to 10 c. c. of concentrated HNO₃ and evaporate to dryness on the steam bath. Moisten the residue with 5 c. c. of concentrated HCl and warm, until the red crust has dissolved, then add 20 c. c. of water and 20 c. c. of 1:1 H₂SO₄ and evaporate to white fumes of H₂SO₄. Remove from the hot plate and allow to cool, then add 10 to 15 c. c. of water and an excess of powdered KMnO₄ while the solution is still warm. If the ore contains little or no iron, about 250 mg. of ferrous sulphate should be added before the powdered KMnO₄. Now add 50 c. c. of concentrated HCl and evaporate to expel the HCl and to produce SO₃ fumes. Evaporation is best accomplished on a steam bath or hot plate and should require at least one hour to insure complete reduction. Cool, then dilute the solution to 150 to 200 c. c. with warm water and titrate at 60 to 70° C. with standard 1/25N KMnO₄.

The vanadium is reduced from V₂O₅ to V₂O₃ by the HCl and re-oxidized to V₂O₅ by the permanganate. The end point is rather fleeting, so that a pink which persists for one minute is satisfactory. A blank determination containing the same quantity of iron as the ore should be run with the sample. For 1/25N KMnO₄ and the quantity of reagents used, the usual blank runs about 0.4 to 0.5 c. c.

**FACTORS.**

1 c. c. N. KMnO₄ = 0.091 grams V₂O₅ = 0.051 gram V.
1 c. c. 1/25N KMnO₄ = 0.00364 gram V₂O₅ = 0.00204 gram V.
Fe factor of KMnO₄ × 1.6296 = V₂O₅.
Fe factor of KMnO₄ × 0.9133 = V.

**NOTES ON THE HCl REDUCTION METHOD.**

The advantages of this method are obvious. Large samples of ore may be used with very little trouble. Care should be taken, however, when large samples are used to see that the ore is completely decomposed, or at least that all of the vanadium is rendered soluble. Nearly all vanadium ores yield their vanadium to this treatment, but refractory samples should be treated with HF and the residue after volatilization of the silica should be treated again with acid. The insoluble material need not be filtered off unless "bumping" becomes objectionable. Iron does not interfere with the analysis; in fact, its presence is essential to complete reduction. In the absence of iron as many as three evaporations with 50 c. c. of HCl are required to insure complete reduction. Contrary to general belief, neither arsenic nor molybdenum interferes and need not be removed. The presence of even as much arsenic as vanadium does not seriously affect the results. Chromium, however, interferes, and when present the titration with KMnO₄ is made in the cold or, better yet, the chromium is removed.
Accuracy is obtained in this method by the use of a large sample of ore. A 5 or 10 gram sample can be used with very little difficulty, especially with an ore of high "insoluble" content. The soluble salts obtained in the analysis of ores containing but a small amount of "insoluble" material limits the size of the sample which should be used.

As an example of the results to be expected in the analysis of an ore by this method, the figures obtained on a carnitite ore containing 3.66 per cent V₂O₃ are given. A 5-gram sample of the ore was used for analysis.

**Analysis of carnitite ore by HCl reduction method.**

<table>
<thead>
<tr>
<th>Number of test</th>
<th>Weight of sample (Grams)</th>
<th>KMnO₄ (C. c.)</th>
<th>V₂O₃ (Per cent)</th>
<th>Number of test</th>
<th>Weight of sample (Grams)</th>
<th>KMnO₄ (C. c.)</th>
<th>V₂O₃ (Per cent)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5.00</td>
<td>46.5</td>
<td>3.69</td>
<td>6</td>
<td>5.00</td>
<td>47.0</td>
<td>3.73</td>
</tr>
<tr>
<td>2</td>
<td>5.00</td>
<td>46.4</td>
<td>3.68</td>
<td>7</td>
<td>5.00</td>
<td>46.5</td>
<td>3.59</td>
</tr>
<tr>
<td>3</td>
<td>5.00</td>
<td>46.3</td>
<td>3.67</td>
<td>8</td>
<td>5.00</td>
<td>46.2</td>
<td>3.67</td>
</tr>
<tr>
<td>4</td>
<td>5.00</td>
<td>46.7</td>
<td>3.70</td>
<td>9</td>
<td>5.00</td>
<td>46.6</td>
<td>3.70</td>
</tr>
<tr>
<td>5</td>
<td>5.00</td>
<td>46.7</td>
<td>3.70</td>
<td>10</td>
<td>5.00</td>
<td>46.6</td>
<td>3.70</td>
</tr>
</tbody>
</table>

Average, per cent: 3.69
Greatest deviation from mean, per cent: 0.036
Found in ore by SO₃ reduction, per cent: 3.66

**SELECTED METHODS FOR THE ESTIMATION OF VANADIUM IN IRON, STEEL, AND FERROVANADIUM.**

**METHOD OF JOHNSON.**

A method that has proved satisfactory for the estimation of vanadium in steels and ferrovanadium is the method developed by Johnson (34), which is also much used by others. The method is applicable either for the estimation of vanadium alone, or to the simultaneous estimation of chromium.

**RESUME OF METHOD.**

The method is based on the reduction of the vanadium in acid solution by means of an excess of ferrous ammonium sulphate and titration of the reduced vanadium by means of standard KMnO₄.

**PROCEDURE IN ANALYSIS.**

From 2 to 5 grams of the steel are dissolved in a mixture of 30 c. c. of 1:3 H₂SO₄ and 20 c. c. of water in a 600 c. c. beaker. After the first reaction is over, 60 c. c. of 1.20 HNO₃ is added to the sample and heating is continued for several minutes. Two hundred c. c. of water is added and enough dilute KMnO₄ solution to produce a slight precipitate of MnO₂ in 20 minutes. The precipitate is then removed by filtering through an asbestos filter or an alundum thimble and is carefully washed with dilute H₂SO₄ (20 c. c. of 1:3 H₂SO₄
in 500 c. c. of $H_2O$). Thirty c. c. of dilute $1:3 H_2SO_4$ is then added to the filtrate, the volume of which should be nearly 350 c. c. The solution is then ready for titration.

**PROCEDURE FOR VANADIUM ONLY.**

Ferrous ammonium sulphate solution is added to the solution until the solution is practically colorless; in treating a chrome steel, an excess is assured when the color of the chrome green does not deepen upon further addition of double sulphate.

Standard potassium permanganate is then added to a pink which persists after 30 seconds stirring. The actual titration for the vanadium is then made as follows: 0.5 c. c. of a 4 per cent solution of potassium ferrocyanide is added to the solution, and the ferrous ammonium sulphate is added carefully until a pure green solution is obtained with one drop of sulphate. The number of cubic centimeters then required to produce a blue coloration is equivalent to the amount of vanadium present.

**PROCEDURE FOR SIMULTANEOUS ESTIMATION OF CHROMIUM.**

If it is desired to determine the chromium in the steel, this step is accomplished before the addition of the indicator. The double sulphate reduces both vanadium and chromium, and the $KMnO_4$ oxidizes only the vanadium in the cold solutions, hence the quantity of chromium is determined by noting the difference between the quantity of double sulphate required to reduce the solution and the quantity of permanganate required to reoxidize it. All of the chromium is reduced when the solution shows a clear green color free from all yellow tints.

$1\text{ c. c. of } \frac{N}{20} \text{ ferrous ammonium sulphate} = 0.00255 \text{ gram vanadium.}$

The method is also applicable to the estimation of vanadium in ferro-vanadium, vanadium bronzes, and such substances, by decreasing the size of sample taken. From 0.2 to 0.5 gram of a ferro containing from 30 to 40 per cent of vanadium is usually taken. Blank determinations should be made upon a similar sample of a nonvanadium steel in exactly the same manner as in the actual determination. The usual blank varies from 0.4 c. c. to 1.0 c. c., depending on the amount of chromium present. This method requires some experience on the part of the analyst to obtain satisfactory end points, but it is rapid and accurate for iron and steel.

**HYDROCHLORIC ACID REDUCTION METHOD FOR THE DETERMINATION OF VANADIUM IN IRON AND STEEL.**

The rapid method outlined for ores on page 273, essentially the method of Campagne (10), may also be applied to the estimation of vanadium in alloys. Slight modifications are necessary. A satisfactory procedure is outlined by Scott (52).
PROCEDURE IN ANALYSIS.

Dissolve 5.1 grams of steel in 60 c. c. of concentrated 1.20 HCl. After solution is complete, add 25 to 30 c. c. of HNO₃ to oxidize the iron. Then evaporate to a sirupy consistency and add 40 c. c. of concentrated HCl and again evaporate to 20 to 25 c. c. Cool and separate the iron as follows: Place the solution in a separatory funnel and add 100 c. c. of ether. Cork and shake a short time and keep the solution cool under a tap of running water. Finally uncork and allow the mixture to stand until the two layers have separated; then draw off the lower aqueous solution into a beaker and continue the analysis.

Evaporate off the ether and add a few crystals of sodium chlorate. Then boil again to remove the free chlorine. Add 50 c. c. of 1:2 H₂SO₄ and take to fumes. Cool and add enough powdered K MnO₄ to give a decided pink, then 40 c. c. of concentrated HCl and evaporate to fumes.

Scott recommends two evaporations to insure complete reduction, but the same object can be obtained by a single evaporation if a little iron is present. The presence of the iron may be obtained by either making an incomplete separation with the ether or by adding a small amount of iron salt—250 mg. of ferrous sulphate being sufficient.

After reduction is complete, cool the solution and add 150 c. c. of warm water, then titrate in the usual manner with 1/50N KMnO₄.

1 c. c. N/50 KMnO₄ = 0.00102 gram of V, so that each cubic centimeter of permanganate used corresponds to 0.02 per cent of vanadium.

NOTES ON METHOD.

The presence of chromium necessitates a further modification. After the iron has been removed by the ether separation, the ether is evaporated from the aqueous solution; 5 c. c. of HNO₃ is added and then enough NaOH solution to make alkaline. Finally enough HNO₃ is added to make the solution slightly acid. This solution is then poured into a hot 10 per cent solution of NaOH, as outlined on page — The vanadium is then recovered from the filtrate by precipitating as lead vanadate, and dissolving in a few cubic centimeters of concentrated HNO₃. The lead is removed by adding H₂SO₄ and evaporating to fumes, then diluting and filtering. Iron sulphate is added, and 50 c. c. of concentrated HCl, and reduction is made by evaporation and titration in the usual manner.
BIBLIOGRAPHY ON VANADIUM.


34. JOHNSON, C. M., Chemical analysis of special steels, steel-making alloys, and graphite. 2d. ed., 1914.


PART VIII.—TITANIUM AND ZIRCONIUM.

By J. W. Marden.

INTRODUCTION.

Not many years ago there were few uses for titanium minerals and products, but since 1900 the use of ferro-alloys containing titanium has decidedly increased and a considerable number of patents relating to the production of such alloys have been issued. This increase has resulted from the general recognition of the efficiency of titanium as a purifying agent in the manufacture of steel. Metallic titanium has properties that restrict its use. It is white, but can not readily be forged; it burns in oxygen to the oxide, and reacts directly with nitrogen.

Zirconium is a metal whose commercial uses have been developed even more recently than those of titanium. During the World War there were many demands to make special steels containing zirconium. One company experimented with such steels and claimed to have gotten some remarkable results, but these results could not be duplicated. Another company has recently claimed that zirconium steels are successful for certain specific purposes, but the results have not yet been published.

The Bureau of Mines, cooperating with the United States Navy, did some experimental work on zirconium steels without obtaining any especially interesting results. Zirconium-aluminum alloys have been prepared, but up to the present time the largest commercial use has been of zirkite ore (a mixture of zircon and Baddeleyite) for furnace linings and other refractories. The purified oxide is claimed to be decidedly superior to tin oxide in opacifying properties.

Owing to the increased interest in these metals, the analytical methods for their determinations are of considerable use.

TITANIUM.

INTRODUCTION.

Titanium is commonly found as titanium dioxide in the following minerals:

<table>
<thead>
<tr>
<th>Mineral</th>
<th>TiO₂, per cent.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rutile (TiO₂)</td>
<td>90 to 100</td>
</tr>
<tr>
<td>Brookite (TiO₂)</td>
<td>90 to 100</td>
</tr>
<tr>
<td>Octahedrite (TiO₂)</td>
<td>90 to 100</td>
</tr>
<tr>
<td>Perovskite (CaTiO₃)</td>
<td>60</td>
</tr>
<tr>
<td>Ilmenite (Fe TiO₃)</td>
<td>3 to 59</td>
</tr>
<tr>
<td>Titanite (CaTiSiO₅)</td>
<td>34 to 42</td>
</tr>
</tbody>
</table>

281
Variable quantities of titanium occur in granite, gneiss, mica slate, syenite rocks, and sometimes in granular limestone and dolomite, as well as in magnetite, hematite, monazite, zirconium ores, and auriferous sands. (See Dana (5).) Ilmenite (FeTiO₃) is often present in deposits of magnetite.

In recent years the commercial importance of titanium has increased and methods for its detection and analysis have, therefore, been developed.

The most important use of titanium has been in making the ferro-alloy (Fe-Ti), which is employed chiefly as a deoxidizer of iron and steel. (See Ladoff (10).) Paints for protective coatings on iron and steel are made by mixing 10 to 15 per cent asphalt with rutile and thinning with turpentine. Titanium compounds are also of value in the dyeing industry; alkali titanium salts of organic acids, such as potassium titanium oxalate, are used as mordants and under some conditions give better results than aluminum salts. Titanous chloride or sulphate is used for bleaching silk and wool and TiO₂ has been used as a catalytic agent in the esterification of acetic acid. The use of TiO₂ as a pigment in ceramic glazes probably consumes much of the oxide.

Methods of analysis for Ti must be general enough to apply to the many sets of conditions that may be encountered in (1) ores such as magnetite, hematite, rutile, ilmenite, granitic rocks, auriferous sands, clays, etc.; (2) furnace slags; and (3) ferro-alloys which may contain many other elements than Fe and Ti. Most of these compounds are insoluble in acids, and there seems to be much divergence of opinion as to the best fusion mixture for getting the substance into solution. Technical journals have recently given new methods for analyzing Ti in the presence of other substances, such as the methylene-blue titration for Ti in the presence of Fe and fluorides, which does not seem to have found its way into many textbooks.

At present there are about 12 methods for the separation and estimation of Ti. The Bureau of Mines believed that it would render the industries a service by collecting, abstracting, and discussing these methods, and calling attention to those that give rapid, accurate results, thus aiding the analyst who does not have time to review current literature carefully or to test new methods for himself. At present, methods are in demand for the determination of titanium in the presence of other elements without long and tedious separations. The colorimetric method with H₂O₂, which has been of such great value to the analyst in the past, can not be used in the presence of fluorides, V, U, Mo, chromates, or large amounts of Fe, H₃PO₄, or K₂SO₄.
METHOD OF SOLUTION OF ORES AND ALLOYS.

TREATMENT WITH ACIDS.

In ferro-alloys containing small percentages of Si and Ti, hot $\text{H}_2\text{SO}_4$ or $\text{HNO}_3$ will dissolve the metals if heated, but in those containing a high percentage of Ti, solution in these acids is often difficult. It is claimed that Ti in alloys can exist in two forms, one soluble and the other insoluble in $\text{H}_2\text{SO}_4$.

Ti metal or its ferro-alloys can be dissolved fairly easily in aqua regia. When HNO₃ has been used in making the solution, however, it must usually be removed by volatilization (by heating to dryness with HCl) before analysis is undertaken.

$\text{H}_2\text{SO}_4$ dissolves the metal, its alloys, or the ores with difficulty. HF, however, rapidly dissolves practically any Ti compound. The fluorides introduced by this method must be removed by heating the solution, after treatment with HF, to fumes with $\text{H}_2\text{SO}_4$ if present methods of analysis are employed.

When the solution is to be made with acids, it has been found easier to use a mixture of HF, $\text{H}_2\text{SO}_4$, and HNO₃. For example, Scott (17) treats 5 grams of ore with 10 to 20 c. c. of a 1:5 $\text{H}_2\text{SO}_4$-HF mixture to which a few drops of HNO₃ have been added. The metal and slag can be treated in the same way, but the SiO₂ is either lost or must be determined by difference.

TREATMENT BY FUSION.

SODIUM CARBONATE AND POTASSIUM CARBONATE MIXTURE.

Browning (3) has suggested the fusion of rutile with three parts of a mixture of Na₂CO₃ and K₂CO₃. The Ti is converted in such a fusion to sodium or potassium titanate (Na₂TiO₃) which is insoluble in water. If this method gives a satisfactory fusion of the ore, it is acceptable for eliminating most of the SiO₂ and phosphates, which in the original ore are very troublesome. Satisfactory fusions are sometimes difficult to obtain by this method, although the addition of a small amount of KNO₃ may help.

SODIUM HYDROXIDE AND SODIUM CARBONATE.

The author has had good results from a mixture of NaOH and Na₂CO₃. The caustic soda lowers the melting point of the soda ash and gives a clear fusion, which is complete in a few minutes if the amount of SiO₂ is low. One part of ore and four to six parts of the mixture are fused in a nickel dish, the Ti being converted into sodium titanate.

SODIUM HYDROXIDE AND SODIUM PEROXIDE.

Mixtures of NaOH and Na₂O₂, one part of ore to three or four of fusion agent in a nickel dish, give excellent results. However, when
the melt is extracted with water much of the Ti goes into the filtrate as a pentitanate and the SiO₂ must be separated by bringing the entire solution to fumes of H₂SO₄ after the melt has been cooled and taken up with acid. Nevertheless, this is the most rapid method for fusing the ore.

SODIUM OR POTASSIUM BISULPHATE.

The fusion most frequently used is that with KHSO₄ or K₂S₂O₇, one part of ore to six or more of KHSO₄. The fusion must be made in a covered platinum dish, very carefully at first, to avoid spattering and loss by foaming, and must continue for about one hour after a dull-red heat is attained. With this fusion the SiO₂ is rendered insoluble, and the Ti goes into solution as the sulphate.

POTASSIUM BIFLUORIDE.

The mineral (TiO₂ or other Ti ore) is often fused with three parts of KHF₂. The fused mass is dissolved in hot water containing a little HF, and then filtered; the KTiF₅ + H₂O separates out on standing. This method of fusion can not ordinarily be recommended for analytical purposes.

SODIUM CARBONATE AND BORAX.

Occasionally it is recommended that Ti ores be fused with 25 parts of a 1:1 mixture of Na₂CO₃ and borax. This fusion, however, needs a high temperature for proper interaction and can not be recommended.

FUSIONS RECOMMENDED.

The fusions recommended are listed below:
1. KHSO₄ (1:10) in a platinum crucible for one hour at a dull-red heat.
2. NaOH (1:4) in a nickel crucible for one-half hour at a dull-red heat.
3. NaOH + Na₂O₂ (1:4) in a nickel crucible for 20 minutes to a clear fusion.

The procedure employed in making these fusions is described in the section on zirconium (pp. 301 to 320).

QUALITATIVE ANALYSIS.

DETECTION OF TITANIUM.

Ti shows the following qualitative reactions:
H₂O₂ added to Ti solutions gives a red-brown solution. The same color is given by V. HF destroys the color.
Na₂HPO₄ precipitates Ti(OH)PO₄ from faintly acid solution. This precipitate is insoluble in acetic acid but soluble in strong mineral
acids. The phosphate precipitation is prevented by the presence of $\text{H}_2\text{O}_2$.

A neutralized solution containing about 1 gram of TiO$_2$ to 300 to 400 c. c. of water, when boiled, precipitates white TiO(OH)$_2$.

$\text{Na}_2\text{S}_2\text{O}_3$ or SO$_2$ precipitates TiO(OH)$_2$ from slightly acid solutions on boiling.

NaC$_3$H$_{10}$O$_2$, when boiled with a slightly acid solution of Ti, deposits TiO(OH)$_2$.

Zn or Sn in HCl solution produces a violet solution containing Ti$_2$Cl$_6$.

Methylene-blue solution, 1/50 N, is decolorized by titanoctous chloride solution according to the following equation:

$$\text{TiCl}_3 + \text{C}_{16}\text{H}_{18}\text{N}_3\text{SCl} = \text{C}_{16}\text{H}_{18}\text{N}_3\text{S} + \text{TiCl}_4.$$  

This reaction is carried out in HCl solution. V and W give a similar reaction.

Thymol.—Ti salts dissolved in concentrated H$_2$SO$_4$ and treated with a little 1 per cent thymol solution yield a red solution. The thymol is first dissolved in glacial acetic acid and this solution diluted with 10 per cent alcohol to contain 1 per cent thymol. This test is said to be 25 times more delicate than the H$_2$O$_2$ test. The concentration of the H$_2$SO$_4$ should not fall below 80 per cent and any W in the original solution must first be removed.

Bead test.—When rutile is mixed with a little tin and microcosmic salt and fused on charcoal, violet color indicates Ti.

**Separation of Titanium from Other Elements.**

In making a qualitative analysis for Ti, the ore or metal is brought into solution by one of the methods suggested above. (If a metal, use aqua regia; if an ore, the Na$_2$CO$_3$-NaOH fusion.) The Ag and Cu groups of metals are separated with HCl and H$_2$S as usual, and the Fe, Al, Cr, with Zr, Th, and the rare earth metals are precipitated as hydroxides. It has been stated that Ti practically never exists in Cr minerals, but Ti and Cr are frequently found together in ferroalloys. If V is absent, the freshly precipitated hydroxides can be dissolved in dilute H$_2$SO$_4$ and this solution tested directly for Ti with H$_2$O$_2$, thymol, etc. V and W must be separated before either of the above tests is applied. If the presence of V and W is in doubt, the hydroxides precipitated above must be ignited, fused with Na$_2$CO$_3$, the fused mass extracted with hot water, filtered, and thoroughly washed with hot water. The V and W go into the filtrate, but the sodium titanate remains insoluble and is retained on the filter paper.

Browning, Simpson, and Porter (4) have recently suggested a method for the qualitative separation of Fe, Ti, Zr, and Ti. The
hydroxides of the elements are dissolved in $\text{H}_2\text{SO}_4$, made faintly alkaline with $\text{NaOH}$, and $\text{Na}_2\text{HPO}_4$ added. The solution containing the precipitate is acidified with $\text{H}_2\text{SO}_4$ containing $\text{H}_2\text{O}_2$. The precipitate remaining insoluble is $\text{ZrOHPO}_4$. In the filtrate, the Fe and Tl are precipitated with $\text{NaOH}$ and again filtered. The Ti is precipitated from the filtrate by acidifying with $\text{H}_2\text{SO}_4$ and boiling with $\text{Na}_2\text{SO}_3$ and $\text{Na}_2\text{HPO}_4$. The Ti precipitates as $\text{TiOHPO}_4$, a white voluminous gelatinous precipitate.

Brown and Madden (2a) describe a similar procedure in which the zirconium is separated as phosphate and the titanium precipitated as the phosphate from 2 per cent $\text{H}_2\text{SO}_4$ after the $\text{H}_2\text{O}_2$ has been removed by heating.

If phosphates are present in the original sample, it should first be fused with a mixture of $\text{Na}_2\text{CO}_3$ and $\text{NaOH}$ and the cooled, fused mass taken up with water and filtered. The titanium hydroxide or sodium titanate should be well washed on the filter paper, in which process the phosphates, $\text{Al}$ and $\text{SiO}_2$, may be removed. This fusion treatment also removes the V and W, which cause the difficulties in the color tests for Ti.

**QUANTITATIVE ANALYSIS FOR TITANIUM.**

**GRAVIMETRIC METHODS.**

**SEPARATION OF TITANIUM BY ALKALI ACETATES.**

See the method of Gooch (6) modified by Thornton (18), taken from Scott’s Methods of Chemical Analysis (17).

**PREPARATION OF THE SAMPLE.**

Ores high in $\text{SiO}_2$ may be decomposed by heating to $\text{SO}_3$ fumes with a mixture of 10 to 15 c. c. of 50 per cent $\text{HF}$ and 3 to 4 c. c. of concentrated $\text{H}_2\text{SO}_4$ per gram of sample.

**OXIDES.**

Oxides are decomposed by fusion with sodium or potassium bisulphate. The fusion is dissolved in 10 per cent $\text{H}_2\text{SO}_4$, keeping the volume as small as possible. The sample should contain not over 0.2 gram Ti.

**PRECIPITATION OF IRON.**

To the solution containing Ti, tartaric acid equal to three times the weight of the oxides to be held in solution is added. This should not exceed 1 gram of the organic acid, as the subsequent removal of larger amounts is troublesome. $\text{H}_2\text{S}$ is passed into the solution to reduce the Fe and $\text{NH}_4\text{OH}$ added to slight alkalinity, followed by a further treatment with $\text{H}_2\text{S}$ to completely precipitate $\text{FeS}$. The solution should be faintly alkaline (litmus), otherwise more ammonia
should be added. After filtration and washing of the ferrous sulphide with very dilute colorless ammonium sulphide, the Ti is entirely in the iron-free filtrate.

Since difficulty is experienced in precipitating Ti in the presence of tartaric acid, except when cupferron is used, the organic acid is oxidized by addition of 15 to 20 c. c. of concentrated H₂SO₄ to the sample, placed in a 500 c. c. Kjeldahl flask. The solution is evaporated to incipient charring of the tartaric acid. After this has been cooled slightly, about 10 c. c. of fuming HNO₃ are added cautiously, a few drops at a time, and when the violent reaction has subsided the flask is heated gradually under a hood. A vigorous reaction takes place, accompanied by much effervescence, foaming, and the evolution of copious brown fumes. The organic matter gradually disappears, the effervescence becomes steady and finally ceases, and white fumes of SO₃ are given off. The solution is cooled and the pale yellow sirup poured into 100 c. c. of cold water. The flask is washed out and the rinsing added to the main solution. The solution is filtered if cloudy.

**Precipitation of TiO₂.**

Ammonia is added until the solution is nearly neutral, a point where the solution is slightly turbid, the precipitate dissolving when stirred vigorously. If a trace of Fe is suspected, about 1 c. c. of 10 per cent ammonium bisulphate is added. Five c. c. of glacial acetic acid, followed by 15 grams of ammonium acetate or its equivalent in solution, is added and the volume of the solution made up to about 350 c. c. The solution is brought rapidly to boiling and maintained in ebullition for about three minutes. The Ti will precipitate in white flocculent and readily filterable condition. The precipitate is washed first with water containing acetic acid, then with pure water. The filter and the precipitate are ignited cautiously over a low flame and finally blasted over a Meker blast for 20 minutes. The residue is weighed as TiO₂.

In the presence of large amounts of alumina and phosphoric acid the residue above obtained is fused with sodium carbonate in a platinum dish and the fusion leached by boiling with pure water. Alumina and phosphoric acid go into solution as soluble sodium salts and TiO₂ remains insoluble in the residue but must be redissolved and again precipitated with NH₃OH to free it from sodium salts. The ignited insoluble residue is TiO₂.

**Precipitation of Titanium with Sodium Thiosulphate or SO₂ Analysis of Ferro-Alloy.**

This procedure is described by Johnson (9), pages 43 and 44, as follows:

When ferrotitanium of low titanium content, 8 per cent titanium for example, dissolves almost completely in sulphuric acid, proceed in the following manner: Dis-
solve from 0.4 to 0.5 gram of drillings in 30 c. c. 1:3 sulphuric acid. Filter and keep the insoluble residue, if any. After washing it free from blue iron test with potassium ferricyanide; it is fused with 20 times its weight of sodium carbonate. 
(Use 1:10 sulphuric acid for washing.)

Nearly neutralize the filtrate and washings with 1:3 ammonia water. Dilute to 300 c. c. with water. Add to the cold solution 5 grams of sodium thiosulphate dissolved in water. Boil gently for half an hour and filter, using paper pulp. Wash with sulphuric acid water (2 c. c. of concentrated sulphuric acid to 500 c. c. of water) until no test for iron is obtained. The washed precipitate is ignited and fused with 20 times its weight of sodium carbonate. Keep the fusion molten at a bright red heat for 40 minutes. Dissolve in water in a platinum dish, add ashless paper pulp, filter, wash 30 times with sodium carbonate water. Heat the filtrate to boiling in a beaker, add hydrochloric acid drop by drop to the filtrate, and note if a white precipitate forms at any time before the filtrate becomes acid. If a precipitate forms, roast the sodium titanate to free it from pulp, and fuse again as before, filter, wash, and treat the now aluminum-free titanate as follows:

Spread filter and residue in a small dish and cover it with about 30 c. c. of 1:3 sulphuric acid. It is heated on a water bath for half an hour, or until all but the filter pulp is in solution. The pulp is filtered out and washed 30 times with dilute (1:20) sulphuric acid water and then with water until the washings no longer show a test for sulphuric acid with barium chloride solution. Burn this washed pulp to make sure that all titanate is dissolved. The filtrate and washings are nearly neutralized with ammonia, 5 grams of sodium thiosulphate are added, and the titanate acid is precipitated and washed as before with sulphuric acid wash. It is given 40 washings and ignited as TiO₂ plus a little SiO₂. The residue is treated with from 5 to 10 drops of concentrated sulphuric acid. The crucible is filled about three-fourths full of c. p. hydrofluoric acid and freed from silica as in steels. The weight thus obtained being the pure TiO₂, is multiplied by 60.04 and divided by the weight taken for analysis, to obtain the percentage of titanium.

The small insoluble residue obtained from the first solution of the drillings in 1:3 sulphuric acid is fused with 20 times its weight of sodium carbonate. The melt is dissolved in water and washed 30 times with sodium carbonate water. The filter and residue are spread out in a small dish with 20 c. c. 1:3 sulphuric acid and heated on a water bath for 30 minutes to dissolve the titanate of soda. The paper pulp is then removed by filtration, and the filter is washed 30 times with 1:20 sulphuric acid. The filtrate and washings from the pulp are made nearly neutral with ammonia water, 5 grams of "thio" are added, and the solution is boiled gently for half an hour. The titanate acid thus obtained is combined with the main precipitate obtained in like manner with sodium thiosulphate. It is roasted with it just before it is fused the first time with Na₂CO₃ to remove alumina.

**PLAIN TITANIUM STEEL.**

The procedure for plain titanium steel is described by Johnson (9), page 54, as follows:

If the titanium content is 0.05 per cent or over, weigh 0.500 gram of drillings into a 10 by 1 inch tube. Also weigh 0.500 gram of a plain carbon steel that contains no titanium by the qualitative test. Add to the latter enough of the standard ferrotitanium to bring the amount of titanium present in this standard mixture to within about 0.95 per cent of the titanium content of the test. If the test is likely to be about 0.15 per cent Ti, then the standard should either be about 0.10 per cent Ti, or 0.20 per cent Ti. The nearer the standard is to the test, in titanium content, the better.

Dissolve the drillings in 10 c. c. of dilute sulphuric acid. Add 5 c. c. of concentrated nitric acid and boil off red fumes. Cool, rinse the standard into a glass-stoppered
TITANIUM. 289

comparison tube of about 15 to 16 mm. outside diameter and with the graduated part about 38 cm. long. Add to the solution in the comparison tube 5 or 6 c. c. of hydrogen peroxide. Stopper the tube and mix the contents thoroughly. Transfer the test to the other comparison tube and treat it in like manner. If there is a great difference in color between standard and test, results will only be roughly approximate and the work should be repeated, preparing a new mixture of standard FeTi and plain carbon steel to imitate the test within the 0.05 limit or closer.

INSOLUBLE FERROTITANIUM.

The method described by Johnson (9), page 60, is as follows:

Instead of decomposing this type of ferrotitanium by the bisulphate fusion, 1 gram of the finely ground sample can be fused in a platinum crucible with a mixture of 10 grams of sodium carbonate and 2 grams of niter. The melt is dissolved out in a platinum dish with water and is then transferred to a casserole before acidulating the water solution. An excess of HCl is then added to the water solution. The crucible is rinsed off with water into the casserole and cleaned by warming in it a little HCl. The cleanings are added to the acidulated solution in the casserole, which is heated with a cover on it until all action is over. The contents of the casserole are evaporated twice to dryness, dissolved in HCl, heated with 100 c. c. of water, filtered, and washed after each evaporation. The combined filters from the two evaporations will contain all of the silica and a little of the titanium; these are washed carefully, weighed, and evaporated with HF and 5 drops of concentrated H₂SO₄, and the silica obtained from the loss of weight. The residue remaining in the crucible is fused with 20 times its weight of Na₂CO₃, dissolved in HCl, and added to the filtrate from the second evaporation to dryness to remove silicon. This filtrate and washings now contain all of the Ti, P, Al, Fe, and S in the sample. The filtrate can be diluted to a definite volume and one-half reduced with stannous chloride and titrated with standard dichromate solution for iron, paying no attention to the Ti present, as Ti has no effect on the dichromate.

SO₂ METHOD OF SEPARATION.

The SO₂ method is described by Washington (19) as follows:

Although the colorimetric method is by far the simplest, most expeditious, and capable of extreme accuracy yet occasion may arise for the determination of TiO₂ in the gravimetric way. While the use of this is not advised, a brief description may be given.

The best gravimetric method is that of F. A. Gooch (6) which is fully described by Hillebrand (8), to whom the reader may be referred. While rather complicated, it is very accurate, although Hillebrand has shown that it is not to be used when zirconia is present in the rock.

An approximate determination of TiO₂ may be made in the solution after the titration of total iron by an old and well-known method. This consists in diluting the solution in a 1000 c. c. beaker to about 500 c. c., adding ammonia or solution of sodium carbonate till a permanent precipitate just forms, then 4 c. c. of concentrated sulphuric acid and 100 c. c. of solution of sulphur dioxide, diluting to 750 c. c. and boiling for several hours, the water lost by evaporation being replaced with hot water containing SO₂ added from time to time. The titanium is precipitated as metatitanic acid, collected on a filter, ignited, and weighed as TiO₂.

As thus precipitated, the TiO₂ is almost always contaminated by notable amounts of alumina and ferric oxide, which fall with it, and the operation should be repeated after bringing the ignited precipitate into solution by fusion with acid potassium sulphate and dissolving in hot water containing some sulphuric acid. It may happen, on the other hand, that the precipitation of titanium is incomplete, if the liquid con-
tains too much free acid. Another source of error is the tendency of the precipitated metatitanic acid to adhere firmly to the sides of the beaker, from which it is removable with difficulty.

Allen (1) has suggested a method for the precipitation of Ti by means of phenyl hydrazine. He uses this method for the separation of Al, Ti, and Zr from Fe. The precipitation takes place from dilute HCl solution. The method of procedure is the same as that used for Zr (see p. 307).

Brown (2) has used cupferron for the precipitation of Fe, Zr, and Ti away from Al. As the Ti and Zr are separated together, the method need not be given here. An abstract of Brown's paper is given on page 309 in the chapter on zirconium.

VOLUMETRIC METHODS.

COLORIMETRIC METHOD WITH H₂O₂.

Washington (19) describes in detail the colorimetric determination of Ti by means of H₂O₂, as first proposed by Weller. Since all of the standard textbooks on analytical chemistry describe this method and it is given later, it is only treated briefly here.

This method depends on the yellow to brown coloration of a solution of titanic acid when H₂O₂ is added, due to the formation of TiO₂, the depth of tint being proportional to the amount of Ti present. A solution containing a known amount of TiO₂ per cubic centimeter is made up and the tint given to this solution by H₂O₂ is used as a standard. The amount of Ti is estimated in the solution for analysis by treating it with a similar amount of H₂O₂ and comparing the depth of color in the two solutions either in ordinary color comparison tubes or in any standard form of colorimeter such as the Schreiner, Duboscq, or Kober.

The color is best compared when it is of deep straw yellow; that is, when the Ti present corresponds to about 2 mg. in 100 c. c. Even minute quantities of hydrogen fluoride and large quantities of sodium sulphate, potassium sulphate, or phosphoric acid bleach the color white. U, V, Mo, and chromates interfere with the peroxide. Fe interferes, if present in large quantities, but the yellow color may be discharged with phosphoric acid.

DETERMINATION BY TITRATION.

Titanium may be determined by several methods of titration. Newton (15) gives the following method for titration with KMnO₄:

Titanic acid is reduced by Zn, an excess of ferric sulphate is added, and the ferrous salt formed by reduction by titanous salt is titrated with standard KMnO₄. The method is more accurate than direct titration of the titanous salt with KMnO₄.

Reaction: Ti₄⁺(SO₄)₁₂+Fe₂O₃(FeOOH)₁₂=2Ti(SO₄)₂+2FeSO₄

or TiCl₃+FeCl₃=TiCl₄+FeCl₂.
TITANIUM.

PREPARATION OF THE SAMPLE.

One to two grams of the ore is decomposed by HF and H₂SO₄ or by fusion with potassium bisulphate or a combination of the two according to the methods already described. Members of the H₂S group, if present, may be removed by this reagent. If Fe is present, it may be determined by boiling off the H₂S in the filtrate containing Fe, Ti, etc., and allowance made in the titration for Ti. If other interfering elements are present in this filtrate, titanic acid may be precipitated by boiling the slightly acid solution (sulphurous acid) according to directions given for the gravimetric method. The washed oxide is dissolved in strong H₂SO₄ and diluted as directed below.

The solution is washed into a 100 c. c. flask and diluted with water so that it will contain 10 per cent of H₂SO₄. This acid holds titanic acid in solution and at the same time is insufficient to oxidize the reduced TiO₂. Sufficient Zn to cause complete reduction is added and a rubber stopper carrying a Bunsen valve tube and a thistle tube with a glass stopcock is inserted in the neck of the flask. The H evolved expels the air and reduces the TiO₂ to the titannous form. Fe, if present, is also reduced. Gentle heat is applied until the excess Zn dissolves. The solution is cooled and an excess of ferric sulphate added through the thistle tube, followed immediately by cold distilled water, until the flask is filled to the neck. The contents of the flask is poured into a No. 6 beaker containing 150 to 200 c. c. of cold distilled water, and the ferrous iron, formed by the reducing action of titannous salt, is titrated with 1/10 N KMnO₄ solution.

1 c. c. 1/10N KMnO₄ = 0.00481 gram Ti, or 0.00801 gram TiO₂.

VOLUMETRIC METHOD BY REDUCTION OF TITANIUM AND TITRATION WITH A FERRIC SALT.

DETERMINATION OF TITANIUM IN FERROCARBON TITANIUM.

Dissolve one-half gram of the sample in a 6-inch porcelain evaporating dish in a mixture of 10 c. c. of water, 10 c. c. of H₂SO₄, 5 c. c. of HCl, and 5 c. c. of HNO₃.

Evaporate the solution to fumes of sulphuric anhydride, take up by boiling with 50 c. c. of water and 10 c. c. of HCl, filter, and wash with hot water and HCl. The filtrate and washings should be about 100 c. c. in volume.

Prepare the modified Jones reductor for use by first passing through it a little hot dilute H₂SO₄, followed by hot water, finally leaving enough hot water in the reductor to fill to the upper level of the zinc.

Now introduce the hot titanic solution prepared as described above, drawing about 100 c. c. of water from the reductor into the original beaker to bring the solution to about the upper level of the zinc. The water thus removed will not contain any Ti if the operation has been conducted as described, but it serves as a safeguard and it is also convenient to acidify this water with 10 c. c. of H₂SO₄ and reserve it on the hot plate to be used as an acid wash after the reduction of the sample solution.

Allow the Ti solution to remain in the reductor for 10 minutes. While the solution is being reduced connect the receiving flask to the
reductor and displace the air completely by CO$_2$, conveniently drawn from a cylinder of the liquefied gas.

When the reduction is complete connect the receiving flask with the suction pump, and while the flow of CO$_2$ continues draw out the reduced solution, following it by the reserved acid wash and then three or four 100 c. c. washes with hot water. By means of the stopcock so regulate the displacement of the sample solution and the washing of the zinc that the reductor is always filled with a solution or water to the upper level of the zinc.

When the washing is complete, gradually release the suction to prevent air being drawn back into the receiving flask. Disconnect the flask, add 5 c. c. of potassium thiocyanate solution as indicator, and titrate immediately with standard ferric ammonium sulphate solution, adding the solution rapidly until a brownish color is produced which will remain for at least 1 minute.

This method is well adapted for determining Ti in other Ti products, suitable means being employed for bringing the Ti into H$_2$SO$_4$ solution.

DETERMINATION OF TITANIUM WHEN INTERFERING ELEMENTS ARE PRESENT.

If Cr, V, or Mo is present in the steel, fuse the residue insoluble in HCl or the calcined phenylhydrazine precipitate containing the interfering element with a mixture of Na$_2$CO$_3$ and a little sodium nitrate.

Dissolve the fusion in water, filter, and wash. The residue on the filter will contain the Ti, free from interfering elements. Bring the residue into H$_2$SO$_4$ solution and determine the Ti as usual.

COLORIMETRIC DETERMINATION OF TITANIUM WITH THYMOL.

According to Lehner and Crawford (11), TiO$_2$ dissolved in H$_2$SO$_4$ is colored red by addition of thymol, the depth of color being directly proportional to the amount of Ti present. The intensity of the color is claimed by Lehner and Crawford to be 25 times that produced by TiO$_2$ with the same amount of Ti.

As with H$_2$O$_2$, fluorides destroy the color, hence must be absent. Dilution with water has no effect until the concentration of H$_2$SO$_4$ falls below 79.4 (sp.gr. 1.725). The color then fades in direct proportion to dilution. Warm solutions are lighter in color than cold solutions with the same amount of Ti, hence the standard and the sample compared with it must have the same temperature. The color fades on heating but returns on cooling. Chlorides, phosphates, and tin seem to have no effect. W interferes, as it intensifies the color of the solution in direct proportion to the amount present and must be removed or allowance made by adding an equivalent amount to the standard or subtracting the equivalent blank.
Colorimetric methods using phenol, phenolcarboxylic and dihydroxymaleic acid have been proposed, but the strong acid necessary for the reactions and the sensitivity of these reagents to small amounts of Fe have proved a serious handicap to their use.

The thymol (1 per cent solution) is dissolved in a little glacial acetic acid containing 10 per cent ethyl alcohol, and this solution is added to concentrated H₂SO₄. Addition of the thymol directly to the acid gives a colored solution. The reagent should be protected from strong light, otherwise it will become colored.

About 0.3 gram of the material is fused with potassium acid sulphate (K₂H₂O₄) and the melt dissolved in concentrated H₂SO₄. Enough thymol reagent is added so that at least 0.0006 gram thymol is present for every 0.0001 gram TiO₂. Concentrated H₂SO₄ is added to bring up the volume to 50 or 100 c. c. in a Nessler tube exactly as in the colorimetric determination of titanium with H₂O₂. The depth of color is compared with a standard solution of Ti dissolved in concentrated H₂SO₄, which is added to 5 c. c. of thymol solution also made up to a convenient volume with concentrated H₂SO₄. The procedure is the same as that described in the H₂O₂ method (see p. 290).

**TITRATION WITH METHYLENE BLUE.**

According to Neuman and Murphy (14), titanium chloride may be easily reduced to TiCl₃ and this very accurately titrated with methylene blue.

The principle of the method is shown by the following equation:

$$C_{16}H_{15}N_3S\text{Cl} + \text{TiCl}_3 = C_{16}H_{15}N_3S + \text{TiCl}_4.$$ 

The methylene blue is decolorized in the titration much the same as KMnO₄ is decolorized by ferrous iron.

Methylene blue is made up in a 1/50 N to 1/25 N solution. The commercial product is about 83 per cent pure. Pure TiO₂ is made by heating with HF and H₂SO₄ to remove the SiO₂. The silica-free material is fused with potassium bisulphate and the Ti precipitated by convenient means. The SO₃ precipitation or the acetate hydrolysis could be used on this substance with success. The precipitated TiO₂ is ignited, weighed, and a given amount again put into solution for the titration. This solution is reduced in HCl contained in an Erlenmeyer flask with a stick of zinc suspended in the solution by a platinum wire. The flask contains a two-holed rubber stopper, so that after the reduction is completed (in about 10 minutes) CO₂ may be passed in and out of the flask again through a Bunsen valve.

When the solution is ready, it is heated nearly to boiling and the methylene blue is run in until a distinct coloration persists after a little shaking.
It is claimed that Ti can be titrated in this way, even in the presence of large amounts of Fe, and accurate results realized. In a strong HCl solution, Al, Si, Ca, Na, K, Mg, Zn, Se, As, P, etc., do not interfere with this titration, though vanadous and tungsten salts interfere with the reaction. The reaction is better in HCl than in other acids.

**VOLUMETRIC METHOD FOR ESTIMATING TITANIUM AND IRON.**

A volumetric method for the estimation of titanium and iron in the presence of each other is suggested by Hibbert (7) and Monnier (13).

The Ti salt is placed in an Erlenmeyer flask and reduced with Zn and HCl. The flask has a three-holed rubber stopper, one having a Bunsen valve, and the other holes being temporarily closed with glass rods which can easily be removed. A stick of zinc is suspended by a platinum wire in the hydrochloric titanium solution for about 20 minutes, and after the solution has been boiled, one of the glass rods is removed from the rubber stopper and CO₂ passed in. The second rod is then removed and the zinc withdrawn from the solution and washed down, after which the titration is made with methylene blue. The methylene-blue solution is standardized with titanous chloride solution.

The writer titrates K₂TiF₄·H₂O, and apparently this method is not affected by fluorides as with the H₂O₂ determination.

When Ti and Fe are together, the Ti is titrated with methylene blue, the ferrous iron not reducing this indicator. The ferric iron is determined from a separate sample by reducing with TiCl₂ and titrating with KCNS as an indicator.

Winch and Chand-Ratreya (20) have described the determination of titanium and iron in rutile by titration with K₂Cr₂O₇ solution.

**METHODS OF ANALYSIS SELECTED FOR ORES AND ALLOYS.**

A method of analysis for Ti to be used on an alloy must be such that the Ti can be determined in the presence of Fe, Al, V, Cr, Ni, Co, Zr, Si, P, C, etc., or can be separated from the interfering substances.

**PREPARATION OF SAMPLE.**

The alloys are broken up as far as possible in a steel mortar, while the ores or slags are pulverized to pass a 100-mesh sieve before the analysis is undertaken.

**METHOD OF SOLUTION AND SEPARATION OF SILICA.**

Alloys (0.5 gram) are dissolved in aqua regia. When there is an insoluble residue from the aqua regia treatment other than silica, it is sometimes necessary to filter this off, dry, ignite, and fuse with
six parts KHSO$_4$ in a covered platinum crucible. The SiO$_2$ should remain insoluble by this method and is filtered off and determined in the usual manner. After the solution has been brought to fumes of SO$_3$ to eliminate traces of SiO$_2$, the solution is diluted to 500 c. c. for analysis.

With ores or slags, 1 gram of the substance is fused carefully with 10 to 12 parts of KHSO$_4$ in a platinum crucible. The crucible must be covered and the heating started very gently, but finally, as the fusion will permit without loss, the temperature is raised to a dull-red heat and maintained thus for about one-half hour. The cooled fused mass is extracted with dilute HCl or dilute H$_2$SO$_4$. If the fusion is incomplete, a second KHSO$_4$ fusion is required on the residue which has been filtered off and ignited in a platinum crucible. The combined filtrates are evaporated to fumes of SO$_3$ and the SiO$_2$ filtered off and determined in the usual manner by volatilization with H$_2$SO$_4$ and HF. There is always a nonvolatile residue remaining, which should again be taken up with KHSO$_4$ and the solution obtained from this fusion put in with the solution obtained above. This should be made up to 500 c. c. in a volumetric flask, so that aliquots may be taken for analysis.

When slags carrying much SiO$_2$ are analyzed and difficulty is experienced in dissolving the sample, Scott's (17) method gives good results but eliminates the possibility of determining SiO$_2$. One gram of the slag is heated in a platinum dish with 5 c. c. of water, 5 c. c. of concentrated H$_2$SO$_4$, 2 c. c. of concentrated HNO$_3$, and 10 c. c. of HF. These reagents are added in the order mentioned and the solution evaporated to fumes of SO$_3$ to eliminate the SiO$_2$. The solution is diluted to 500 c. c. in a volumetric flask.

This last method of solution is the most rapid for analytical work, though care should be taken to eliminate any fluorides introduced if the H$_2$O$_3$ method is used in the determination of Ti.

When SiO$_2$ is determined, it might be suggested that after it has been filtered from the original solution, dried, and ignited, it should be moistened with H$_2$SO$_4$ and reignited before weighing. After weighing, the HF and H$_2$SO$_4$ treatment is used for volatilization of the SiO$_2$. If this is not done and the percentage of SiO$_2$ is very small, there is often an increase in weight after ignition with HF and H$_2$SO$_4$ instead of a decrease.

The procedure from this point varies with the conditions, depending on whether or not phosphates, vanadium, etc., are present in the solution.

**SEPARATION OF TITANIUM FROM INTERFERING ELEMENTS BY MEANS OF PHENYL HYDRAZINE.**

The acid solution (100 c. c. portion) is heated nearly to boiling (about 90° C.) and ammonium hydroxide added until a slight
permanent precipitate is formed. Dilute 1:1 HCl is now added from a burette drop by drop until the precipitate which has formed just redissolves and the solution is perfectly clear. Then add a few drops (about 5) of the dilute HCl. Add 3 c. c. of phenyl hydrazine, which has been dissolved in 10 c. c. of hot water. Stir thoroughly and filter immediately through a quantitative paper. Wash thoroughly with hot water and dry and ignite the precipitate in a platinum crucible. Fuse the residue in the platinum crucible with 5 to 10 grams of Na₂CO₃ and 1 gram of KNO₃. After cooling, dissolve the fused mass in hot water and filter. The residue on the filter paper contains the Ti and Zr, free from any of the interfering substances, unless large amounts of Fe are present, and is ready for the determination of Ti.

**H₂O₂ METHOD FOR DETERMINING SMALL AMOUNTS OF TITANIUM IN THE PHENYL HYDRAZINE PRECIPITATE.**

If the amount of Ti is not over a few milligrams, the colorimetric method with H₂O₂ gives good results. The phenyl hydrazine precipitate obtained as described above is ignited gently in a platinum crucible to destroy the carbonaceous matter of the paper, the crucible cooled, and the residue fused with 5 to 10 grams of KHSO₄. The fusion is completed in a very few minutes, after which it is cooled, dissolved in water, filtered, and the solution made up to the 100 c. c. mark in a volumetric flask. Fifty c. c. of this solution is then placed in a Nessler tube, beside which is placed another Nessler tube filled to the 50 c. c. mark with pure water. To each solution 5 c. c. of H₂O₂ solution is added and the contents well mixed. The first tube containing the Ti solution will show a red coloration. To the second tube is added, a fraction of 1 c. c. at a time, a standard solution of TiO₂ in H₂SO₄ (1 mg. TiO₂ per c. c.) until the color in the two tubes just matches after the contents is mixed thoroughly. If the color in the solution to be analyzed is equivalent to more than a few cubic centimeters of the standard TiO₂ solution, the former solution is too concentrated and should be diluted with water before another trial is attempted. There are several colorimeters on the market that give excellent results with this method. Any of these colorimeters are satisfactory for this determination, which is described in detail in all of the more complete texts on quantitative analysis.

**PREPARATION OF STANDARD TiO₂ SOLUTIONS.**

1. FROM K₂TiF₆

The standard TiO₂ solution is best made from K₂TiF₆·H₂O, which can be procured in a fairly pure condition.

Pure K₂TiF₆ is prepared in the following manner if c. p. TiO₂ is not available: Rutile, which has been pulverized as finely as possible, is fused with four parts of NaOH and one part of Na₂O₂ in a nickel
crucible for about 20 minutes at as high a temperature as possible without much spattering. After cooking, the mass is disintegrated with a small amount of water and washed into a beaker. Enough H₂SO₄ is added to make the solution about 10 per cent and this is digested for a short time near the boiling point, diluted, and filtered away from the SiO₂ and undecomposed mineral. This solution, which should contain about 0.1 gram TiO₂ per 100 c. c., is neutralized with ammonia until a small amount of permanent precipitate has formed. SO₂ is then passed into the boiling-hot solution for a few minutes until the Ti is all precipitated, the precipitate is allowed to settle and, as far as possible, washed by decantation with hot sulphurous acid, after which it is filtered, using a Buchner funnel.

After the TiO(OH)₂ has been dried on the paper it is easily broken off into a platinum dish. This, or c. p. TiO₂ if available, is dissolved in an excess of HF and sufficient pure potassium carbonate added to the HF solution in the platinum dish to precipitate the Ti as K₂TiF₆. It is necessary to have enough HF present to prevent the precipitation of titanium hydroxide when K₂CO₃ is added. After this has stood overnight, the salt is filtered off through a rubber funnel, thoroughly washed with dilute HF, and dried. If large quantities of K₂TiF₆ are to be prepared, lead dishes should be used for the crystallization, and no glass must come in contact with the HF solutions. The salt is purified by redissolving in hot diluted HF solution, filtering, allowing to cool, and recrystallizing.

The purified K₂TiF₆ is dissolved in concentrated H₂SO₄ and heated to fumes of SO₂. Great care must be taken to remove all fluorides by heating for some time. The solution obtained is diluted (at least 0.1 gm. TiO₂ to 100 c. c.) and NH₄OH added to precipitate the Ti(OH)₄, which is filtered, washed repeatedly with hot water, dried, and ignited. One-half gram of this TiO₂ is obtained in solution by fusion with KHSO₄ and diluted to 500 c. c. volume, the solution containing about 5 per cent H₂SO₄. Each cubic centimeter of this solution will contain 0.001 gram of TiO₂. If the purified K₂TiF₆ is gently ignited to a very dull red to remove all moisture and HF, it can be used directly for the preparation of the standard solution. One and one-half grams of this salt, heated with concentrated H₂SO₄ to remove all fluorides and made up to 500 c. c. with dilute H₂SO₄, gives a solution containing 0.001 gram of TiO₂ per cubic centimeter.

2. BY DIRECT PRECIPITATION.

A fairly pure solution of titanium sulphate may also be prepared in the following manner: The solution is first prepared by fusing the ore with NaOH, or Na₂O₂, or by any other fusion agent. After extracting the fused mass with water, making acid with H₂SO₄,
carrying down to fumes, and filtering to eliminate the SiO₂, the total hydroxides are precipitated with ammonia, filtered, and washed. The precipitate is dried and gently ignited in a platinum crucible, after which it is fused with Na₂CO₃, containing a little potassium nitrate. The fused mass is cooled and thoroughly extracted with hot water, filtered, and thoroughly washed. The Ti remains insoluble, while the Al and most interfering substances other than Fe are in the filtrate. The residue and paper are again gently ignited and this time fused with KHSO₄ and the Ti solution, after extracting the mass with dilute acid, is filtered free from any insoluble residue. The Ti is separated from the Fe by precipitation either with SO₂ or phenyl hydrazine. This precipitate will be found to be sufficiently pure for all ordinary purposes of standardization.

**METHYLENE-BLUE METHOD OF TITRATION.**

For solutions containing 1 mg. or more of TiO₂ (that is, 0.1 per cent of TiO₂ in a 1-gram sample) the titration method using methylene blue has given excellent results. Two solutions must be made up for this titration, methylene blue 1/25 N and pure titanium chloride solution.

Methylene blue (C₁₆H₁₈N₃SCl) is made up by dissolving 15 grams of the indicator in 1 liter of solution. This is standardized against a Ti solution of known concentration. The standardization of the methylene blue is accomplished by using either the carefully dried K₂TiF₆ or a standardized Ti(SO₄)₂ solution made as described above, although fluorides do not seem to interfere with this titration. If K₂TiF₆ is used, it is best to remove the fluorides by heating with H₂SO₄, however, before the reduction.

Measure out a quantity of standard solution equivalent to about 0.06 gram of TiO₂ into 100 c. c. of 1:5 HCl. Reduce the hot solution either in a Jones reductor or in a flask with zinc under CO₂ gas. The best way to accomplish this latter is to place the solution in a 300 c. c. Erlenmeyer flask having a two-holed rubber stopper. One of the holes holds a glass tube which is fitted with a Bunsen valve for the exit of gases through which passes a platinum wire which holds a stick of Zn suspended in the HCl solution. There should be a vigorous evolution of H₂, which escapes through the Bunsen valve, the other hole being temporarily closed. After 20 minutes, CO₂ gas is passed into the flask and the Zn is withdrawn when a layer of CO₂ has been formed over the surface of the solution. The Zn is washed, the wash waters falling into the flask. The methylene-blue solution is run in until the blue color persists after thorough shaking. The value of the methylene-blue solution is calculated from the equation:

\[ C₁₆H₁₈N₃SCl + TiCl₃ = C₁₆H₁₈N₃S + TiCl₄. \]
When the value of the methylene blue is established, the solutions to be tested for Ti are reduced and titrated as before and the percentage of Ti calculated. The methylene-blue solution keeps well in brown glass bottles; and if many determinations are to be made a fairly large volume can be made up and standardized at one time.

In alloys, ores, etc., when V, W, and Mo are absent from the solution the Ti and Fe may be titrated by this method in the presence of each other with considerable accuracy. One portion of the solution is reduced with Zn and HCl as before and the Ti titrated with methylene blue, the Fe not decolorizing the indicator.

A second portion of the solution is titrated for Fe. The iron in this solution is oxidized by adding KMnO₄ till the solution is just pink in color. The solution is heated to 90° C., a few drops of methylene blue is added, and TiCl₃ solution added until the indicator is decolorized. The titration is best done under CO₂ gas, which can be had by throwing a piece of magnesite into the HCl acid solution before the titration is commenced.

There are occasions where it might be desirable to separate Ti and Al from Fe and possibly Th, if it is present. This is accomplished by adding a little at a time to a solution from which the SiO₂ has been separated 10 grams of ammonium salicylate (18) dissolved in 50 c. c. of water. The solution should be boiling and should be as nearly neutral as possible. The solution is boiled for about 20 to 30 minutes, filtered, and washed with 5 per cent ammonium salicylate until the precipitate is white. It is often necessary to repeat this precipitation, and when the amount of Ti is large and the Zr is small it is better to employ the phosphate method for precipitating the zirconium.

BIBLIOGRAPHY ON TITANIUM.


ZIRCONIUM. 1

INTRODUCTION.

Zirconium occurs mainly in two minerals, baddeleyite, ZrO₂ (ZrO₂, 96.5 per cent), and zircon, ZrSiO₄ (ZrO₂, 61 to 67 per cent). Most of the baddeleyite ore is found at São Paulo, Brazil. It is sold in this country in a natural mixture with zircon, under the trade name of Zirkite, and contains about 75 per cent ZrO₂. Many placer deposits derived from the disintegration of granitic rocks carry zircon. (See Dana (8).) In this country a deposit of zircon sand has been located at Pablo Beach, Fla., and as much as 3 per cent of some of the auriferous sands of Idaho and other States have been found to be zircon mixed with monazite.

Considerable attention has been directed toward zirconium in recent years on account of reports that this element gave unusual properties to ferro-alloys. (See Meyer (26).) Nickel-zirconium alloy has been suggested by Cooper for knife blades and cutting tools, inasmuch as it is said to be noncorrosive and nonstaining.

Zirconium oxide (zirconia) has been investigated as a refractory because the melting point of this compound is about as high as that of any other known oxide. Zirconium salts also have some importance; they have been used for weighting silk, as mordants in dyeing, and for many other purposes.

With these new investigations of zirconium and its increased commercial uses, there have also been attempts to improve the methods of determining this element, but at the present time there is much to be desired in the speed and accuracy of these methods. Recently three of these schemes of procedure were tried to see how closely they checked. On a sample of zirkite containing 73 per cent ZrO₂, the sodium thiosulphate method of precipitation yielded 83 per cent ZrO₂, the phosphate method yielded 75 per cent, and the sodium iodate method yielded 45 per cent. Evidently a novice would have great difficulty in deciding whether this ore contained 40 per cent ZrO₂ or twice as much. Moreover, the methods of separating zirconium from other elements are satisfactory only when proper precautions are observed.

METHOD OF SOLUTION OF ORES AND ALLOYS.

TREATMENT WITH ACIDS.

The alloys of Zr may contain many metals, such as Fe, Ti, Si, Ni, Al, etc. The ores contain mainly Si, Fe, Al, and Ti, but may be

1 This chapter has been recently (1923) revised by E. L. Mack of the Ithaca field office of the Bureau of Mines. The author acknowledges his indebtedness to Dr. Mack for this revision.
associated with many other elements, such as those in monazite or the black sands of California.

Zr metal is insoluble in all acids except aqua regia and HF. The former dissolves the metal very slowly, while HF dissolves the metal with considerable ease and rapidity. Most of the ferro-alloys and Ni alloys dissolve in aqua regia, but they do not yield to treatment with a single acid such as HCl or H₂SO₄.

Ores of Zr are insoluble in practically all acids except after long and continued digestion with H₂SO₄ or with HF. Even then American zircons are not completely decomposed. Meyer (26) claims that there are two varieties of zircon, one soluble in HF and the other insoluble. The insolubility of these ores depends largely on the locality whence they come. The oxide, ZrO₂, if not ignited to too high a temperature, will dissolve with ease in hot concentrated H₂SO₄, but if it has been ignited to a very high temperature for any length of time it becomes insoluble in H₂SO₄, and is only slowly brought into solution with HF. It is recommended, therefore, that the alloys be treated with aqua regia in making solutions, but if this process fails, with HF, the fluorides being volatilized by subsequent treatment. The ores should be obtained in solution by fusion methods.

TREATMENT BY FUSION.

SODIUM CARBONATE OR SODIUM POTASSIUM CARBONATE MIXTURE.

It has been recommended that zircon be fused with three to six parts of Na₂CO₃ or NaKCO₃ mixture or the two mixed with a little KNO₃. In any one of these three methods it was found that only about 50 per cent of the zircon had been decomposed after fusion for one hour, and this method, therefore, unless repeated several times, should not be used.

SODIUM HYDROXIDE AND SODIUM PEROXIDE.

NaOH (3 parts) mixed with Na₂O₂ (1 part) and heated gently with 100-mesh zircon in a nickel dish, yields clear and complete fusion in about 20 minutes. This process seems the simplest and most rapid method of completing the decomposition of zircons, but yields the Zr in the form of insoluble sodium zirconate, Na₂ZrO₄; it is likely that the Ti goes into solution as a pertitanate.

SODIUM HYDROXIDE AND SODIUM CARBONATE.

A mixture of three parts of NaOH and one part of Na₂CO₃ in a nickel crucible will completely decompose the most difficult American zircons in about one hour of fusion and leaves Ti and Zr together as titanates and zirconates, insoluble in water, a condition often desirable in present methods of procedure.
SODIUM OR POTASSIUM BISULPHATE.

Sodium bisulphate or sodium pyrosulphate in the ratio of 10 parts to 1 of the ore, even after heating gently to dull-red heat and maintaining this temperature for one hour, does not always yield good results with American zircons. Some Brazilian zirkites may be decomposed by this method, whereas American zircons require two, and sometimes three, fusions for complete solution.

FLUORIDE FUSIONS.

The fusion of zircon sand with NaF or KF in the ratio of five to one of ore in a platinum dish is complete in about one-half hour. These fusions must be heated to about 900° to get clear liquid fusion and are not to be recommended because of the difficulties involved in the determination of the SiO₂. HF mixed with NaF gives good results.

SODIUM CARBONATE AND BORAX.

The fusion of zircon sand with four parts of Na₂CO₃ and one part of borax can be successfully accomplished by long-continued heating, maintaining a temperature sufficient for clear fusion. This temperature is much higher than with the other methods.

FUSION RECOMMENDED FOR SOLUTION OF ORES.

1. As has been stated, a mixture of NaOH and Na₂O₂ in a nickel dish in the ratio of one part of ore to three of NaOH and one of Na₂O₂ yields the quickest and most satisfactory results. When Ti and Zr are determined together and it is desired to separate these along with the Fe away from such interfering substances as phosphates, vanadium, and tungsten, it is recommended that the fusion be made with three parts of NaOH to one part of Na₂CO₃ in a nickel dish. When fusion is complete, the residue is cooled and extracted with water; the Zr remains as sodium zirconate, Na₂ZrO₃, the Ti as sodium titanate, Na₂TiO₃, and Fe as Fe₂O₃; these can be filtered away from and washed free of interfering elements.

2. If the ore is not too refractory, fusion with KHSO₄ gives fairly good results. The finely powdered ore is placed in a platinum crucible with 10 parts of KHSO₄. The lid of the crucible is adjusted so that the contents may be observed, but there will be very little loss through splattering. At first the mixture is heated very gently; later the temperature is raised gradually until a dull-red heat is attained. The fusion should be continued for about 20 minutes to one-half hour. The mass is cooled and extracted with hot water. The SiO₂ remains insoluble, but the Zr and other elements go into solution.

Lundell and Knowles (25) have found borax to be the most effective and most universally applicable of any of the suggested fluxes. They
RECOMMEND fusions of 0.3 gram of ore in 4 grams of borax and subsequent decomposition of the cooled melt in 150 c. c. of dilute HCl (1:5). If Al, Ca, or Mg is to be subsequently determined the boric acid should be expelled from this solution as methyl borate in the usual manner.

QUALITATIVE ANALYSIS.

DETECTION OF ZIRCONIUM.

Concentrated H₂O₂ (perhydrol) precipitates a white voluminous zirconium peroxide, Zr₂O₅(?) from slightly acid solutions. The H₂O₂ must be concentrated to cause precipitation.

SO₄ or Na₂S₂O₃ precipitates Zr as hydrated zirconium oxide from boiling slightly acid solutions of its salts, but this reaction is shown by some other metals and, without supplemental tests, it should not be accepted as indicating the presence of Zr.

Turmeric paper, after being moistened with a HCl solution of Zr salts and dried, shows a characteristic red-brown color reaction which is similar to the borate test with turmeric paper.

If a solution containing 20 per cent by weight of H₂SO₄ throws down a precipitate on the addition of a large excess of disodium phosphate (Na₂HPO₄) in the presence of H₂O₂, it may be taken as conclusive evidence of the presence of Zr. No other metal is known whose phosphate is insoluble in acid of this concentration. Data on the best conditions for the precipitation of the phosphate may be found in papers by Biltz and Mecklenberg (5), Nicolardot and Reglade (27), and Lundell and Knowles (25).

Phenyl hydrazine precipitates hydrated zirconium oxide from slightly acid solution, but this reaction is also shown by several other metals whose properties resemble those of Zr.

Cupferron throws down Zr from a solution containing 5 to 10 per cent (by volume) of H₂SO₄ (sp. gr. 1.82) as a white curdy precipitate of unknown composition. Other elements, including Cu, Fe, Ti, Th, Pb, Ag, Hg, Sn, Bi, Ce, W, U (quadrivalent), and V, interfere with this test. Great care should be used in drawing conclusions from the fact that a precipitate appears when cupferron is added to a given solution. The cupferron compounds of many of the metals mentioned above could easily be mistaken for the Zr compounds. On the other hand, the cupferron compounds of some of these metals are highly colored and could easily be identified by an experienced observer.

Sodium iodate precipitates hydrated zirconium oxide from slightly acid solutions as a white curdy precipitate, readily soluble in strong acids. The facts that this reaction is very sensitive to changes in acidity of the solution and that the iodates of some of the other metals are quite insoluble tend to make it of no practical value in detecting the presence of Zr.
The treatment of a solution for the detection of Zr depends to some extent upon the fusion method used in preparing the solution. If Zr only is desired, the solution obtained by any of the fusion methods is made (10 per cent) acid with H₂SO₄, a few c. c. of H₂O₂, and a few c. c. of Na₂HPO₄ solution added. If Zr is present, a white, flocculent, voluminous precipitate is formed. The addition of H₂O₂ is necessary only when Ti is present, the purpose being to oxidize the Ti to the hexavalent condition (TiO₂). Hexavalent titanium is not precipitated by phosphoric acid. It may be added that Ti will be found to accompany Zr almost universally; it will therefore be wise to adopt, as a routine measure, the addition of H₂O₂ when testing for Zr by the phosphate method.

If it is desired to make a complete analysis and include many other elements with which Zr is often alloyed or found, such as Ni, Fe, Al, Ti, and Si, it is recommended that the alloy be dissolved in aqua regia or the ore fused with three parts of NaOH and one part of Na₂O₂. The fused mass is extracted with dilute H₂SO₄ and the SiO₂ separated from this solution or from the aqua regia solution of the alloy. The hydroxides of Fe, Al, Ti, and Zr are precipitated with ammonia, filtered, and washed free of Ni, which is tested for in the filtrate. The solution is then made very slightly acid with HCl and SO₂ passed into the boiling hot solution. This precipitates the Zr, Ti, and Al, but leaves most of the Fe in the solution. The precipitated hydroxides are redissolved in hot 1:1 HCl and again precipitated with strong NaOH solution. This solution is warmed gently for a short time and the hydroxides of Zr and Ti filtered and washed free of the sodium aluminate solution. The Zr and Ti may be identified in a number of different ways, the simplest being to dissolve the hydroxides obtained above in 10 per cent H₂SO₄ solution, add H₂O₂ which turns the solution red if Ti is present, and then add Na₂HPO₄ solution. If a white or greenish white flocculent precipitate occurs, this indicates the presence of Zr. If V, Cr, W, or Mo is present, Na₂O₂ should be used along with the NaOH in separating the Al and other elements.

Browning, Simpson, and Porter (7) have suggested a method for the qualitative separation of Fe, Ti, Zr, and Ti. The hydroxides of the elements are dissolved in H₂SO₄, the solution made faintly alkaline with NaOH, and Na₂HPO₄ added. The solution containing the precipitate is acidified with H₂SO₄ containing H₂O₂. The precipitate remaining insoluble is ZrOHPO₄. In the filtrate, the Fe and Ti are precipitated with NaOH and filtered off. The Ti is precipitated

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*Some doubt may remain as to whether or not the proposed methods of separation of Zr from other elements will effect separation from the new element "halmium" (72). In the absence of the method of separation promised by Coster and Hevesy (Nature, vol. 111, 1923, p. 182), the authors are not able to make a positive statement at the present time.*
from this filtrate by acidifying with H₂SO₄ and boiling with Na₂SO₄ solution. The Ti precipitates as TiOHPO₄, a white, voluminous, gelatinous precipitate.

Should the original substance contain phosphates, it should be fused with a mixture of NaOH and Na₂CO₃ and the fused mass, after cooling, thoroughly extracted with hot water, filtered, and washed. In this process, zirconium hydroxide is left on the filter paper, but most of the Al, SiO₂, and phosphates are removed in the filtrate. This fusion treatment may also be used to separate V, W, etc., which offer difficulties in the colorimetric tests for Ti.

**QUANTITATIVE DETERMINATION OF ZIRCONIUM.**

**INSOLUBLE COMPOUNDS OF ZIRCONIUM.**

The following compounds of Zr have low enough solubility so that at one time or another they have been used in the gravimetric estimation of Zr:

(a) The hydrated oxide, ZrO(OH)₂ (β).
(b) The phosphate, Zr₅(PO₄)₄ (β).
(c) The cupferron compound, Zr(C₆H₅N₂O₂)₄.
(d) The selenite, Zr(SeO₄)₂.

None of these compounds has the properties which would allow the separation of Zr directly from the metals with which it commonly occurs. Hence, it usually becomes necessary to remove these accompanying elements with suitable precipitants before the precipitation and estimation of the Zr is attempted. Moreover, these accompanying metals are numerous and have chemical characteristics with which the average investigator is unfamiliar. For these reasons, the analytical chemistry of Zr has become seemingly very complicated. Methods of analysis have been proposed without due provision for the related metals which nearly always accompany Zr; therefore many of these methods are worthless or of very limited applicability. One of the worst features of the situation is that most of the literature makes little or no attempt to point out the advantages and disadvantages of the various methods or to indicate the classes of Zr-bearing material to which they are likely to be applicable.

For these reasons a review of the more widely known methods and an attempt to indicate their applicability have been deemed desirable, in an endeavor to enable the reader to select later a method appropriate to the conditions under which he is working.

**METHODS BASED ON THE PRECIPITATION OF ZIRCONIUM AS HYDRATED OXIDE.**

Several precipitants have been used for throwing down Zr as the hydrated oxide, the more common ones being ammonia, phenylhydrazine, and sodium iodate. Sulphur dioxide or sodium thiosul-
phate precipitate basic compounds which are similar enough to the hydrated oxide to permit consideration under the same head.

PRECIPITATION BY AMMONIA.

Addition of NH₄OH to solutions of Zr salts precipitates hydrated zirconium oxide as a white flocculent precipitate very similar in appearance to hydrated aluminum oxide. The precipitate, which is somewhat difficult to filter, can be washed with hot water, or with water containing a little ammonia (since it is insoluble in excess of the precipitant), ignited at high temperature over the blast lamp, and weighed as zirconium oxide (ZrO₂).

Unfortunately, nearly all of the elements with which Zr is ordinarily found and from which separation is necessary for analysis are also precipitated by ammonia; the value of this method for analytical purposes is thus limited practically to cases where Zr is free from substances precipitable by ammonia, that is, in the analysis of pure Zr salts. Occasionally precipitation by ammonia is employed to separate Zr from metals whose oxides are soluble in excess of ammonia. Ni and Cu can be separated from Zr in this way and the method has been used in the analysis of certain Zr alloys.

PRECIPITATION BY PHENYL HYDRAZINE.

The addition of phenyl hydrazine to solutions of Zr salts, under proper conditions of acidity, causes a complete precipitation of the Zr as hydrated oxide.

Attempt has been made, notably by Allen (1), to use this reaction for analytical purposes, the Zr being weighed as oxide after thorough ignition. The drawback to this method is that the reagent also precipitates, either partly or completely, the following metals: Ti, Al, Cr, Ce, U, and V. Some of these are usually present with Zr and contaminate any precipitate obtained by this method. Moreover, if Fe occurs in appreciable quantities, the Zr precipitate obtained by phenyl hydrazine will be contaminated. Some investigators have thought that this contamination might be avoided by careful adjustment of the acidity or by bringing the Fe to the ferrous condition, but experiment does not confirm these suppositions. The phenyl hydrazine method for the precipitation of Zr can not be recommended as reliable and easily handled. If circumstances necessitate its use, the precipitate should be examined very carefully for contamination by the metals mentioned and appropriate corrections made in the weight of Zr recorded.

PRECIPITATION BY SODIUM IODATE.

In feebly acid solutions Zr is precipitated when sodium iodate is added. Davis (9) has used this reaction in the separation of Al
from Zr, the Zr precipitate obtained being ignited and weighed as oxide. However, the sensitivity of this reaction to slight changes in the acidity of the solution is so great as to make it absolutely useless for practical purposes.

**Precipitation by Sodium Thiosulphate.**

Chance (7a) precipitated Zr and Ti together by adding sodium thiosulphate to boiling slightly acid solutions of these metals, and weighed them as oxides, after ignition.

This method has been used to some extent in the analysis of certain Zr materials, but will not separate Zr and Ti from Al. Moreover, unless the Fe content of the solution is very low there will be serious contamination by this metal. Other metals less frequently present will interfere, notably Cr, W, V, and Co.

The facts mentioned tend to lessen the usefulness of this method for general analytical purposes.

**Precipitation by Sulphur Dioxide.**

Baskerville (3) has proposed the precipitation of Zr and Ti by boiling slightly acid solutions with SO₂. The precipitate can be ignited and weighed as the mixed oxides of Zr and Ti.

This method has inherent faults very similar to those mentioned in connection with sodium thiosulphate precipitation. Some of the metals most commonly associated with Zr are not separated from it and fixing the acidity of the solution at the proper point is extremely difficult.

**Methods Based on the Precipitation of Zirconium as Phosphate.**

When alkali phosphates are added to solutions of Zr salts, the Zr is precipitated as a zirconium phosphate, the exact composition of the precipitate being uncertain. The precipitate is very insoluble, even in the presence of large amounts of mineral acid. Bailey (2) first used the phosphate in the separation and quantitative determination of Zr. Later Hllebrand (19) used this method in determining small amounts of Zr occurring in rocks, the precipitation of any accompanying Ti being prevented by adding H₂O₂ to the solution.

Early users of the phosphate method usually washed the precipitate with water, disregarding the fact that this causes hydrolysis and resulting serious loss of P₂O₅ from the precipitate. If the water-washed precipitate is ignited to constant weight and the Zr content calculated on the assumption that its composition is represented by the formula ZrP₂O₇, it is evident that the results will be seriously in error if appreciable amounts of Zr are being handled. Hllebrand (19) recognized this and specifically stated that—

For the small amounts (of Zr) usually met with it is safe to assume that the ignited phosphate contains 50 per cent of ZrO₂ (51.8 by theory). If the amount is rather large,
it may be safer as shown by Schiotz (29) to fuse with sodium carbonate, leach, ignite, fuse with pyrosulphate, reprecipitate by ammonia, and weigh as ZrO₂.

The phosphore method has been carefully investigated recently and proper conditions for its employment very clearly ascertained. Nicolardot and Regla (27) worked out the separation of Zr from Al, Cr, and Fe. Wunder and Jeanneret (32) have also used the method for the precipitation of Zr as a phosphate. Lundell and Knowles, (24, 25, and 25a), of the United States Bureau of Standards, in simultaneous investigations thoroughly tested the phosphate method and considered the possibility of its application to the analysis of Zr ores and Zr steel. They concluded that, by proper attention to the conditions under which the zirconium phosphate is precipitated and handled, the method will give reasonably accurate separations from Al, Fe, Cr, Ti, Ce, and Th. Nevertheless, they questioned (25a) the advisability of using the phosphate method in Zr steel analysis because of very serious contamination of the phosphate precipitate by Fe and because separate samples were necessitated for the determination of Al and Ti. They also objected to using this method on Zr ores because of uncertainties introduced by various factors, including (1) incomplete data as to the interference of such elements as U, (2) the tendency of zirconium phosphate to hydrolyze upon washing, and (3) difficulties during ignition owing to decrepitation.

METHODS BASED ON THE PRECIPITATION OF ZIRCONIUM BY CUPFERRON.

When cupferron (the ammonium salt of nitroso-phenyl-hydroxylamine) is added to cold solutions of Zr salts containing up to 10 per cent mineral acid, the Zr is thrown down as a white curdy precipitate of unknown composition. This precipitate, which will also contain any Ti present in the solution, can be ignited and weighed as mixed Zr and Ti oxides. The precipitate can then be brought into solution, the Ti estimated colorimetrically, and the weight of Zr found by difference.

The precipitation by cupferron was first utilized for the quantitative determination of Zr by Schröder (29a), and has since been used by Thornton (30a), Brown (6), Ferrari (13), and Baudisch and King (4). The effect of possible interfering elements and the use of the method in steel and ore analysis have been reviewed fully by Lundell and Knowles (25).

The precipitate obtained by the action of cupferron on Zr and Ti salts has very desirable properties for analytical chemistry. It is very insoluble, even in mineral-acid solutions of 10 per cent acidity; it is easily flocculated and consequently filters and washes well; and it can be ignited readily and weighed as a compound of definite and known composition, that is, the oxide. Unfortunately, cupferron precipitates the following metals, either partly or completely, in
addition to Zr and Ti: Cu, Fe, Th, Pb, Ag, Hg, Sn, Bi, Ce, W, U (quadrivalent), and V. Hence the method ordinarily can not be used to separate Zr directly from solution without previous provision for the removal of metals that would contaminate the cupferron precipitate. If the absence of these interfering metals can be demonstrated, the problem of analysis becomes somewhat simplified. However, in dealing with Zr ores, the presence of all the metals mentioned should be assumed until their absence is conclusively proved. The furnace history of Zr steel is usually available, therefore the alloying elements are known and intelligent provision can be made for the elimination of those which interfere with the precipitation of cupferron.

At first thought, the necessities outlined above would seem so to complicate the procedure of the cupferron method as to minimize its possible usefulness. However, careful appraisal of all the factors involved will lead to the conclusion that the cupferron method offers the best solution of the problem of Zr analysis.

Lundell and Knowles, of the United States Bureau of Standards, have worked out the details of this method very carefully, making thorough provisions for the elimination and determination of every element known to occur with Zr. They have adapted their scheme to ores (25) and to steels (25a). The method has been used extensively at the Bureau of Standards and, with slight modification at the Ithaca, N. Y., laboratory of the Bureau of Mines. Detailed instructions for the analysis are given on page 312.

**Methods Based on the Precipitation of Zirconium by Selenious Acid.**

Nilson (27a) noticed that when selenious acid is added to moderately acid solutions of Zr or Ti salts, basic selenites are precipitated as flocculent compounds, which change into crystalline normal salts on heating the solution containing an excess of selenious acid.

Smith and James (20) have attempted to apply this method to the analysis of Zr materials. Their findings show that it may be possible to separate satisfactorily Zr from Ti, Al, small amounts of Fe, and the rare earths.

Although the method is very promising, data are lacking on the interference of such metals as Mn, W, U, V, Cu, Pb, Bi, Co, Zn, Gl, Ta, and Cb, many of which are frequently encountered in Zr analysis.

Until such information has been compiled, the selenite method can not be recommended for routine use. It is hoped that the missing data will soon be made available.

**Miscellaneous Methods Large of Historical Interest.**

Several other methods for the separation of Zr have been devised. Many are unsound theoretically, others are promising but have not
been developed thoroughly, and some can be applied only to very special conditions. Reference is made here to certain of these methods, in order that a comprehensive résumé of data on Zr determination may be available.

Streit and France (30) precipitated Zr by boiling a neutralized sulphate solution with a 50 per cent excess of acetic acid. This method does not give a satisfactory separation from Fe and probably from many other metals. Bailey (2) and Geisow and Horkheimer (14) precipitated Zr as ZrO$_3$ or Zr$_2$O$_5$ by perhydrol (a strong solution of H$_2$O$_2$).

Walker (31) has separated Zr and U by H$_2$O$_2$. The method may prove valuable in special cases.

Havens and Way (17) tried to separate Fe from Cr, Zr, and Ge by passing hydrogen chloride over the oxides. The method is valueless for analytical purposes.

Gutbier and Hüller (15) claim to have made a quantitative separation of Fe and Zr by precipitating them together as hydroxides and igniting; on reduction with H the Fe is reduced to the metal but the ZrO$_3$ is unchanged. The value of this method has never been demonstrated.

Knorre (23) separated Fe from Zr and other metals by precipitating with nitroso-beta-naphthol.

Hartwell (16) found that certain separations of Zr, Ce, La, Nd, Pr, and Th could be made by using the chloranilines and betamethylene tetramine.

Dittrich and Freund (10) have tried to separate Zr from Ti, Fe, and Th by ammonium salicylate.

Dittrich and Pohl (11) weighed Ti and Zr together, estimated the Ti colorimetrically and found the Zr by difference.

Headden (18) has published a paper on the separation and estimation of the fluorides of Cb, Ta, Ti, and Zr.

Ferguson (12) and Johnson (21) have suggested methods for the determination of Zr in steel. Both methods leave much to be desired, because they are based upon the separation and weighing of the Zr as phosphate.

Kelley and Meyers (22) have developed a method for the analysis of alloys containing mainly Ni and Zr. It was devised for works-laboratory use and may give accurate enough results under such conditions. However, since the method completely ignores the presence of Ti in the Zr precipitate and attempts the determination of Fe in this precipitate by titration after reduction with Zn, not much can be expected from it.

**RECOMMENDED METHOD FOR THE ANALYSIS OF ZIRCONIUM ORES.**

The author strongly recommends that the following method, in full, be applied to the analysis of Zr ores. After the operator has
become thoroughly familiar with the method and with the types of ores he is handling, certain slight modifications will suggest themselves as feasible, either because certain elements are known to be absent from the ore, or because the degree of accuracy desired is less than that contemplated by the unmodified method. If any doubt exists, however, it is strongly urged that all precautions be taken and the sample be assumed to carry all the elements with which Zr is commonly associated.

The following procedure is that used at the United States Bureau of Standards and is fully discussed by Lundell and Knowles (25), who point out that it provides for the elimination of interference by the following elements which have been found in Zr ores: Titanium, silicon, thorium, cerium, iron, aluminum, scandium, yttrium, erbium, didymium, beryllium, calcium, magnesium, sodium, potassium, lithium, uranium, phosphorus, tantalum, manganese, zinc, cobalt, tin, lead, copper, and bismuth. Furthermore, they state that Cr and Ni do not interfere in a cupferron precipitation, that W causes no trouble since it is removed before the final precipitation, and that only V would require special treatment. Since this element has not been reported as having been encountered in Zr ores, no trouble need be expected from it.

**PROCEDURE.**

Fuse 4 grams of borax in a platinum crucible, cool, and place on top of the fused mass a 0.300-gram sample of ore which has been ground to approximately 100 mesh. Cover the crucible and fuse thoroughly over a Meker burner, stirring occasionally with a platinum wire, which is allowed to remain in the crucible during the fusion. When decomposition of the ore is complete,* remove the platinum wire to the beaker used for the solution of the melt.

Dissolve the cooled melt in 150 c. c. of 1:5 HCl, gently warming on the steam or water bath.

Transfer the solution to a platinum dish, add 20 c. c. of 1:1 H₂SO₄, and evaporate on the hot plate until heavy fumes of SO₂ escape. Cool, dilute to 100 c. c., filter off the impure SiO₂, wash with hot water, and reserve for subsequent treatment.

Digest the filtrate and washings (preferably over night) to throw down interfering amounts of P in the form of zirconium phosphate. If a precipitate appears, filter, wash with 5 per cent ammonium nitrate solution, and reserve the paper and residue. Treat the filtrate and washings as described below.

Add approximately 5 grams of ammonium chloride, then NH₄OH in slight excess. Boil the solution for one or two minutes, filter,

---

* This operation ordinarily requires no more than one-half hour. If determinations of other elements, such as Al, Ca, and Mg, are wished, the substitution of sodium peroxide as a fusion medium is desirable, since otherwise all boric acid must be expelled by a methyl alcohol-HCl treatment after solution of the melt.
wash with 2 per cent ammonium nitrate solution, and discard the filtrate. (If a determination of such elements as Cu, Mn, Zn, Ca, and Mg is desired, a double precipitation should be performed and the combined filtrates treated as in ordinary analysis. When extreme accuracy is desired, due attention should be paid to the slight recoveries of Cu, Co, Zn, and Mn subsequently made.)

Dissolve the precipitate in 100 c. c. of hot 5 per cent H$_2$SO$_4$, wash thoroughly with hot water, and reserve the filtrate and washings.

Ignite the filter paper and the reserved papers containing the impure SiO$_2$ and zirconium phosphate in the original platinum crucible. Moisten the ash with water, add 1 c. c. of 1:1 H$_2$SO$_4$ and 5 c. c. of HF, and evaporate to complete the expulsion of H$_2$SO$_4$. Fuse the residue with a small amount of Na$_2$CO$_3$, digest the melt in water, and filter off the insoluble residue. Wash the residue with hot water, ignite it in a platinum crucible, fuse it in potassium pyrosulphate, dissolve the cooled fusion in hot 5 per cent H$_2$SO$_4$, and add the solution to the reserved solution. These steps remove phosphoric acid and recover any Zr, that accompanies the SiO$_2$ or that has been precipitated by NH$_4$OH as phosphate and subsequently resists solution in 5 per cent H$_2$SO$_4$.

Dilute or neutralize with NH$_4$OH until the solution contains approximately 1 per cent (by volume) of H$_2$SO$_4$, and pass H$_2$S through the solution until convinced of the complete precipitation of any "H$_2$S metals" or of the absence thereof. If a precipitate is obtained, filter it off, and wash well with a 1 per cent H$_2$SO$_4$ solution saturated with H$_2$S.

The treatment of the acid solution with H$_2$S, instead of ammonium sulphide, is carried out for the following reasons: (1) It shows up immediately the presence of members of the H$_2$S group. (2) Unless the Fe is reduced before precipitation as sulphide, Ti will be in part thrown down also. The sulphide precipitate may contain Sn, Cu, Pb, and Bi, together with some platinum resulting from attack on the crucible during the various previous operations. If desired, these may be determined after the recovery and inclusion of the Cu present in the filtrate from the NH$_4$OH precipitation.

Keep the volume of the filtrate at approximately 200 c. c. To the solution add powdered tartaric acid in amount equal to five times the aggregate weight of the bases to be held in solution, make the solution ammoniacal, and saturate it with H$_2$S. Filter through the equivalent of an S. and S. blue-ribbon No. 589 paper, wash with dilute ammonium sulphide-ammonium chloride solution, and refilter through a new paper, if traces of iron sulphide are detected.

---

3 It is advisable to carry out this step whether or not the filtrate appears perfectly clear. Almost invariably a small amount of iron sulphide will be caught on the second filter.
in the filtrate. All of the Fe in the sample taken, together with any Mn, Zn, and Co which came down with the NH₄OH precipitate, are caught at this point as sulphides. If a determination of Fe alone is desired, the simplest procedure would consist in solution of the sulphide in H₂SO₄, elimination of H₂S, reduction in a Jones reductor, and titration with permanganate.

Carefully acidify the filtrate to a total acidity of 10 per cent H₂SO₄ (by volume) in 400 c. c., boil to expel H₂S, filter off any precipitate of sulphides which may appear, and cool the solution to between 5° and 14° C.

Precipitate with an excess of a cold 6 per cent water solution of cupferron. An excess of the precipitant is indicated by the formation of a fine white precipitate, which redissolves, instead of a curdy one, which persists. Filter, after a five-minute digestion, using an ashless filter paper and a platinum cone, with gentle suction. Thoroughly wash the precipitate with cold 10 per cent (by volume) HCl.

Clear filtrate and washings indicate complete precipitation of Zr and Ti, while cloudy or opalescent ones indicate the reverse. The latter occasionally develop, and no satisfactory explanation has been found. Under these circumstances, recovery must be made as follows: Evaporate the solution to a small volume and destroy the organic matter by digestion with HNO₃, finally heating until fumes of H₂SO₄ appear. Cool, dilute, filter off any SiO₂ resulting from attack on glassware, and repeat the precipitation with cupferron in a 10 per cent H₂SO₄ solution, as directed above.

Carefully dry and ignite the paper, precipitate in a tared platinum crucible, and finally ignite over a blast lamp or its equivalent. Cool in a desiccator and weigh as mixed oxides of Zr, Ti, and rare earth. Fuse the mixed oxides with potassium pyrosulphate, take up in 10 per cent (by volume) of H₂SO₄, dilute to exactly 100 c. c., and divide into two 50 c. c. portions.

**DETERMINATION OF TITANIUM IN PORTION 1.**

If the percentage of Ti is low, determine it by the Weller colorimetric method, when the percentage is high, reduce to titanium.

---

11 The color of the cupferron precipitate is an excellent indication of the amount of Ti present, since Zr precipitates are pure white while the Ti precipitates are yellow. A brownish tint indicates Fe or, less likely, V.

12 Although V has not been reported as a constituent of Zr ores, it may be worth while to call attention to the fact that V is partly precipitated by cupferron in 10 per cent acid solution. If V is present in the ore either of the following procedures may be followed: Substitution of a peroxide fusion of the ore for the recommended borax fusion, followed by a water extraction of the cold melt and filtration to eliminate V, at the start of the analysis; fusion, with Na₂CO₃, of the weighed oxides obtained in the above method, followed by water extraction and filtration to separate V from Zr, Ti, and the rare earths. The determination of Ti and the rare earths would then be performed, as directed in the above method, on the ignited, water insoluble residue, while the determination of V₂O₅ would be carried out by acidifying the Na₂CO₃ filtrate with H₂SO₄, reducing to V₂O₅ in a Jones reductor containing ferric alum solution in the receiver, and then titrating to V₂O₅ with a standard KMnO₄ solution.

13 The Weller method will be found described in any standard textbook on quantitative analysis.
sesquioxide in a Jones reductor containing ferric alum-phosphoric acid in the receiver and then oxidize to titanium dioxide by titration with standard KMnO₄ solution.

Determination of the rare earths in portion 2.

Determine the rare earths in portion 2 by Hillebrand's method as follows (19): Precipitate the hydroxides with an excess of KOH, decant the liquid, wash by decantation with water once or twice and then slightly upon the filter, wash the precipitate from the paper into a small platinum dish, treat with HF, and evaporate nearly to dryness. Take up in 5 c. c. of 5 per cent (by volume) HF. If no precipitate is visible, rare earths are absent. If a precipitate is present, collect it upon a small filter held by a perforated platinum or rubber cone and wash it with from 5 to 10 c. c. of the same acid. Wash the crude rare-earth fluorides into a small platinum dish, burn the paper in platinum, add the ash to the fluorides, and evaporate to dryness with a little H₂SO₄. Dissolve the sulphates in dilute HCl, precipitate the rare-earth hydroxides by ammonia, filter, redissolve in HCl, evaporate the solution to dryness, and treat the residue with 5 c. c. of boiling 5 per cent oxalic acid solution. Filter after 15 minutes, collect the oxalates on a small filter, wash with not more than 20 c. c. of cold 5 per cent oxalic acid solution, ignite, and weigh as rare-earth oxides, which are to be deducted from the weight of the cupferron precipitate.

Recommended method for analysis of zirconium steel.

The method of analysis outlined below has been developed and used extensively in the course of an investigation of the properties of Zr and other alloy steels conducted jointly by the Bureau of Standards, the Bureau of Mines, and the Bureau of Ordnance of the Navy Department. It has been but slightly modified from the method originally described by Lundell and Knowles (25a).

The method provides for the routine determination of Zr, Ti, and Al in steel and insures the elimination of interference by the following alloying elements which are frequently present in steels of this class: W, Cr, V, P, Cu, Mo, Ni, Co, Ce, and U.

Extensive experience with this method, in comparison with several others, has shown it to be unquestionably the most reliable and accurate one available at the present time. It is strongly recommended that a procedure based upon the principles of this method be used in the determination of Zr in steel.

Procedure.

Depending upon the Zr content, use 3 to 5 grams as a sample. Dissolve this with 15 c. c. of water and 15 c. c. of HCl (sp. gr. 1.2),
adding from time to time 1-c. c. portions of HNO₃, until solution is complete. This operation is best carried out in a covered porcelain casserole.

Evaporate the solution to dryness on the hot plate. Take up in 25 c. c. of HCl (sp. gr. 1.2), again evaporate to dryness, and bake thoroughly on the hot plate. Allow the residue to cool and take up with 30 c. c. of HCl (sp. gr. 1.2) and 40 c. c. of water, digesting on the hot plate to hasten the operation. Filter through a rapid paper, washing thoroughly with hot 5 per cent (by volume) HCl, and combine and reserve the filtrate and washings.

Ignite the filter in a platinum crucible,¹⁴ cool, add 2 c. c. of H₂SO₄ (sp. gr. 1.82), and an excess of HF. Evaporate, on the hot plate, until copious fumes of H₂SO₄ are given off. Cool, and take up in the smallest possible quantity of HCl (1:1) and later add to the acid extract obtained from the ether separation described below.

Evaporate the reserved filtrate to a volume of 25 to 40 c. c., and cool by placing the beaker in ice water. Add 200 c. c. of ether and mix the two layers by rapid stirring with a small glass rod. Allow to stand until the two layers have completely separated and both are perfectly clear. Decant off the ether layer, which contains most of the Fe, and discard. Add 100 c. c. more ether and repeat the operation. The last few cubic centimeters of the ether layer may conveniently be pipetted off. This method of making the ether separation will be found to have marked advantages over the conventional procedure, in which the solutions are handled in closed funnels that resemble ordinary separatory funnels. The method described avoids the serious mechanical losses which are practically unavoidable when the concentrated aqueous solution must be transferred one or more times from one vessel to another. Moreover, the solutions are easily cooled and kept cool; this helps to insure an efficient separation of Fe.

Heat the aqueous residue from the ether extraction to boiling, to expel dissolved ether, and add a few cubic centimeters of HNO₃ to insure the oxidation of any ferrous Fe in solution. Heat the solution to boiling and pour it, with constant stirring, into 135 c. c. of hot 20 per cent NaOH solution in a 600 c. c. Pyrex beaker. This 20 per cent NaOH solution should be as pure and as free from carbonates as possible. It should be filtered through an asbestos mat several times before being used. It must be perfectly clear and throw down practically no precipitate on long standing. The reagent should be tested for substances precipitable by NH₃ and, when these are found, appropriate corrections made in the Al figures.

¹⁴ The dehydration of the SiO₂ precipitate has been found to be more complete when H₂SO₄ is substituted for HCl. It is therefore recommended that Si be determined in a separate sample of the steel, using the H₂SO₄ method.
Allow the precipitate to settle for several hours (preferably overnight),\(^{15}\) filter on ashless paper, without washing, but allow the filter to drain until no more liquid drops from the funnel. Reserve the alkaline filtrate if a determination of Al is intended. Replace the filter in the beaker in which the original precipitation took place, add 25 c. c. of HCl (sp. gr. 1.2), and dilute to a volume of 125 c. c. Heat the solution to near boiling and stir rapidly to assist in breaking up the filter into pulp. Filter through an ashless paper, washing until substantially free from Fe and combining and reserving the filtrates and washings for subsequent analysis.

Dry the filter containing the filter pulp and its contained zirconium phosphate (formed from the P in the original sample) and ignite in platinum, fuse the ash with Na\(_2\)CO\(_3\), digest the cooled melt in water, filter the residue through a rapid paper, and wash with water; and finally dissolve the residue from the filter with hot HCl (1:1) and add to the reserved acid solution for subsequent treatment.

**DETERMINATION OF ALUMINUM.**

If a determination of Al is desired, treat the reserved filtrate from the NaOH treatment by the method of Lundell and Knowles (25a).

**DETERMINATION OF ZIRCONIUM AND TITANIUM.**

To the reserved HCl solution add 2 grams of powdered tartaric acid, make quite strongly ammoniacal, and saturate the solution for 10 minutes with H\(_2\)S. Filter through a rapid paper and, if the solution is not perfectly clear, refilter through a closer paper. Wash by decantation and on the filter with dilute ammonium sulphide-ammonium chloride solution. The precipitate of ferrous sulphide will also contain manganese sulphide, cobalt sulphide, and nickel sulphide, if these metals were carried by the steel.

Neutralize the filtrate with H\(_2\)SO\(_4\) (1:1) and add 60 c. c. in excess. Dilute to 300 c. c. and warm on the water bath until the precipitated S and sulphides are coagulated. The sulphides which appear at this point are sulphides of those metals which are soluble in ammonium sulphide. Filter and wash with H\(_2\)SO\(_4\) and cool the filtrate with ice water. If U is known to be present in the steel, interference from it can be avoided by boiling the solution at this point to insure freedom from H\(_2\)S, adding KMnO\(_4\) solution to a faint pink, cooling, and proceeding with the cupferron precipitate as described.

---

\(^{15}\) The conditions of precipitation are such as to throw down a small portion of the Fe as very finely divided hydrated iron oxide. If the solution is filtered soon after the precipitation is made this portion will pass through the filter and contaminate the subsequent Al\(_2\)O\(_3\) precipitate; standing tends to flocculate this portion and to allow removal with the bulk of the Fe.
Add an excess \(^\text{16}\) of a cold 6 per cent water solution of cupferron and filter through an ashless paper supported by a platinum cone, using gentle suction if desired. Wash the precipitate thoroughly by decantation and on the filter with cold 10 per cent HCl.

Dry the precipitate and ignite in a tared platinum crucible over a Meker burner or blast lamp and weigh as mixed zirconium and titanium oxides. If the presence of V in the steel is suspected, make a \(\text{Na}_2\text{CO}_3\) fusion of the oxides obtained by cupferron precipitation, dissolve in water, and filter, reserving both filtrate and residue. Acidify the filtrate with \(\text{H}_2\text{SO}_4\) run through a Jones reductor in the conventional manner, receiving the solution in ferric alum-phosphoric acid mixture and titrating with standard \(\text{KMnO}_4\). Calculate the \(\text{V}_2\text{O}_5\) present on the basis of its being oxidized by the \(\text{KMnO}_4\) from \(\text{V}_2\text{O}_5\) to \(\text{V}_2\text{O}_6\). Make an appropriate correction in the weight of mixed oxides found. Ignite the reserved insoluble residue in the original crucible and proceed with the determination of Ti as described.

To the ignited oxides in the crucible add 5 c. c. of \(\text{H}_2\text{SO}_4\) (sp. gr. 1.82) and 5 c. c. of HF and warm until the oxides are completely in solution, adding other portions of HF if necessary. Evaporate on the hot plate until fumes of \(\text{H}_2\text{SO}_4\) are given off. Cool and dilute to 100 c. c. in a volumetric flask. Determine the Ti present in an aliquot portion by Weller’s colorimetric method,\(^{17}\) and estimate the small amount of Fe present as oxide by colorimetric comparison with standard solutions of known iron content to which potassium sulphocyanate have been added. This comparison may conveniently be made in a Schreiner colorimeter. Appropriate corrections may then be made for titanium and iron oxides and the weight of zirconium oxide found by difference.

**BIBLIOGRAPHY ON ZIRCONIUM.**


\(^\text{16}\) The presence of an excess of cupferron is shown when the precipitation of heavy curds ceases and there appears a fine silky precipitate which dissolves away from the point of high local concentration.

\(^{17}\) If the metals Th or Ce are known to be present, they can be recovered and estimated by Hillebrand’s method, which is described on page 315.


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### INDEX.

#### A.  

<table>
<thead>
<tr>
<th>Allanite. See Orthite.</th>
<th>Page.</th>
<th>1-18</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alloys, determination and separation</td>
<td>10-18</td>
<td></td>
</tr>
<tr>
<td>Arsenic, determination and separation</td>
<td>200</td>
<td></td>
</tr>
<tr>
<td>Autunite, as source of uranium</td>
<td>200</td>
<td></td>
</tr>
<tr>
<td>occurrence</td>
<td>200</td>
<td></td>
</tr>
</tbody>
</table>

#### B.  

<table>
<thead>
<tr>
<th>Baddileyte, as source of zirconium</th>
<th>301</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Brookite, as source of titanium</td>
<td>281</td>
<td></td>
</tr>
<tr>
<td>Bureau of Mines method, for determination of uranium in carnotite ores</td>
<td>224-227</td>
<td></td>
</tr>
</tbody>
</table>

#### C.  

<table>
<thead>
<tr>
<th>Calcium vanadate, as source of vanadium</th>
<th>239</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Carnotite, as source of uranium</td>
<td>199</td>
<td></td>
</tr>
<tr>
<td>occurrence</td>
<td>199-200</td>
<td></td>
</tr>
<tr>
<td>treatment for radium</td>
<td>196</td>
<td></td>
</tr>
<tr>
<td>Carnotite ores, analysis, for uranium</td>
<td>262-263</td>
<td></td>
</tr>
<tr>
<td>for vanadium</td>
<td>262-263</td>
<td></td>
</tr>
<tr>
<td>volumetric method</td>
<td>227-230</td>
<td></td>
</tr>
<tr>
<td>Carnotite residues, treatment, for radium</td>
<td>196</td>
<td></td>
</tr>
<tr>
<td>Cerite, as source of cerium</td>
<td>19</td>
<td></td>
</tr>
<tr>
<td>Cerium, chemistry, bibliography</td>
<td>66-70</td>
<td></td>
</tr>
<tr>
<td>determination, colorimetric</td>
<td>50</td>
<td></td>
</tr>
<tr>
<td>gravimetric, by precipitation with oxalic acid</td>
<td>43</td>
<td></td>
</tr>
<tr>
<td>by precipitation with potassium iodate</td>
<td>43</td>
<td></td>
</tr>
<tr>
<td>qualitative, by ammoniacal silver nitrate</td>
<td>27</td>
<td></td>
</tr>
<tr>
<td>by bromine on precipitated rare-earth hydroxides</td>
<td>27</td>
<td></td>
</tr>
<tr>
<td>by hydrogen peroxide</td>
<td>26</td>
<td></td>
</tr>
<tr>
<td>by lead peroxide and nitric acid</td>
<td>27</td>
<td></td>
</tr>
<tr>
<td>by tartaric acid and hydrogen peroxide</td>
<td>27</td>
<td></td>
</tr>
<tr>
<td>volumetric, by alkaline permanganate</td>
<td>46</td>
<td></td>
</tr>
<tr>
<td>by ferricyanide and permanganate</td>
<td>44</td>
<td></td>
</tr>
<tr>
<td>by hydrogen peroxide and permanganate</td>
<td>45</td>
<td></td>
</tr>
<tr>
<td>by iodometric method</td>
<td>44</td>
<td></td>
</tr>
<tr>
<td>by Lindsay Light Co. method</td>
<td>49</td>
<td></td>
</tr>
<tr>
<td>by sodium bismuthate and permanganate</td>
<td>47</td>
<td></td>
</tr>
<tr>
<td>double sulphate, with potassium or sodium, properties</td>
<td>24</td>
<td></td>
</tr>
<tr>
<td>in monazite sand, determination</td>
<td>63-66</td>
<td></td>
</tr>
<tr>
<td>metallic, properties</td>
<td>23</td>
<td></td>
</tr>
</tbody>
</table>

**Cerium—Continued.**  

| Page. |  
|-------|-------|
| separation, from common metal bases | 30    |
| from rare earths, by bismuth tetroxide | 39    |
| by bromide | 38    |
| by bromine | 38    |
| by chlorine gas | 38    |
| by cuprous oxide | 40    |
| by lead dioxide | 39    |
| by persulphate | 39    |
| by potassium permanganate | 37    |
| by sodium peroxide | 39    |
| from thorium and rare earths, by alkali sulphates | 35-37 |
| from titanium and zirconium | 30    |

**uses.**  

| Page. |  
|-------|-------|
| Cerium and thorium, separation from titanium and zirconium, by fluorides and double fluorides | 40    |
| Cerium and yttrium earths, separation from thorium, by sodium sulphite | 41    |
| by solubility of double oxalate of thorium | 41    |
| Cerium dioxide, properties | 25    |
| Cerium earths, decomposition | 20-21  |
| solution and precipitation | 21-22  |

**See also Cerite; Lanthanum; Monazite sand; Neodymium; Orthite; Praseodymium; Samarium.**

| Cerous carbonate, properties | 24    |
| Cerous hydroxide, properties | 23    |
| Cerous oxalate, properties | 23    |
| Cerous sulphate, properties | 24    |
| Chrome-vanadium steels, properties | 240, 268 |
| Chrome-vanadium-molybdenum steels, properties | 240    |
| Chromium, separation and determination | 10-18  |
| Cuprodioselodite, as source of vanadium | 239   |

#### E.  

<table>
<thead>
<tr>
<th>Electroscope, accessories</th>
<th>181</th>
</tr>
</thead>
<tbody>
<tr>
<td>alpha-ray, use</td>
<td>178</td>
</tr>
<tr>
<td>view of</td>
<td>178</td>
</tr>
<tr>
<td>amberoid insulation, description</td>
<td>176-177</td>
</tr>
<tr>
<td>figure showing</td>
<td>177</td>
</tr>
<tr>
<td>description</td>
<td>174-178</td>
</tr>
<tr>
<td>figure showing</td>
<td>175</td>
</tr>
<tr>
<td>emanation chamber, calibration</td>
<td>180-181</td>
</tr>
<tr>
<td>gamma-ray, view of</td>
<td>178</td>
</tr>
<tr>
<td>interchangeable, use, in emanation method</td>
<td>178-180</td>
</tr>
<tr>
<td>use, in detecting radioactivity</td>
<td>174</td>
</tr>
<tr>
<td>in detecting uranium</td>
<td>201</td>
</tr>
</tbody>
</table>

321
<p>| F. | Elzi, P. F., amberoid insulation for electroscope | Page. 176 |
| E. | Emanation chamber. See Electroscope. | |
| F. | Ferberite, as source of tungsten | 131 |
| F. | Ferrotungsten, decomposition, methods. determination. See Tungsten steels and alloys. | 134 |
| F. | Ferrotungsten alloys, determination. See Tungsten steels and alloys. | |
| F. | Ferrovanadium, decomposition, methods | 243 |
| H. | Hübnerite, as source of tungsten | 131 |
| I. | Ilmenite, as source of titanium | 281 |
| J. | Jackson, V. T., acknowledgments to | 49, 63 |
| J. | Jones redutor, use, in determining molybdenum | 113-120 |
| J. | In determining uranium | 256 |
| L. | Lanthanum, use in combination with cerium | 20 |
| L. | Lindsay Light Co., method for determination of cerium | 49 |
| L. | In monazite sand | 63-66 |
| M. | McCoy, H. N., acknowledgment to | 49 |
| M. | Mesothorium, as source of radium | 173 |
| M. | properties | 24 |
| M. | Metager, F. J., work cited | 49 |
| M. | Miner, H. R., acknowledgment to | 53 |
| M. | Molybdenite, as source of molybdenum | 71 |
| M. | Molybdoc ocher. See Molybdite. | |
| M. | Molybdite, as source of molybdenum | 71 |
| M. | Molybdenum, analysis, qualitative, methods | 72-74 |
| M. | chemistry, bibliography | 125-130 |
| M. | determination, gravimetric, by precipitating and weighing, as lead molybdate | 96-109 |
| M. | by removal of barium, stronium, and calcium | 104-105 |
| M. | by removal of chromium | 101 |
| M. | by removal of iron | 101 |
| M. | by removal of lead | 99 |
| M. | by removal of phosphorus, arsenic, and antimony | 100 |
| M. | by removal of tungsten | 105-107 |
| M. | by removal of uranium, zirconium, and titanium | 105 |
| M. | by removal of vanadium | 105, 107-108 |
| M. | In presence of vanadium | 6 |
| M. | In presence of vanadium, chromium, and nickel | 5 |
| M. | quantitative, acidimetric | 94 |
| M. | by iodine | 92 |
| M. | by iodine liberated from molybdate solution | 94 |
| M. | by precipitation as lead molybdate | 87 |
| M. | by precipitation as mercurous molybdate | 86-87 |
| M. | Molybdenum—Continued. | Page. 322 |
| M. | Determination—Continued. | |
| M. | Quantitative—Continued. | |
| M. | by precipitation as sulphide | 83-86 |
| M. | by titration with ferric chloride | 91-92 |
| M. | by titration with lead acetate | 88-89 |
| M. | by titration with methylene blue | 91 |
| M. | by titration with potassium iodate | 93 |
| M. | by titration with potassium permanganate | 89-91 |
| M. | by volatilization | 94 |
| M. | colorimetric | 93 |
| M. | electrolytic | 94 |
| M. | volumetric, decomposition by fusion | 111-113 |
| M. | by removal of chromium, vanadium, and tungsten | 111 |
| M. | by removal of copper, arsenic, tin, and antimony | 111 |
| M. | occurrence | 71 |
| M. | precipitation by lead acetate, effect of sulphuric acid | 102-104 |
| M. | separation, quantitative, from alkaline earths and fixed alkalies | 81 |
| M. | from aluminium, chromium, iron, zinc, nickel, cobalt, manganese, zirconium, titanium, and rare earths | 80 |
| M. | from arsenic, antimony, tin, and tungsten | 78-79 |
| M. | from lead, mercury, bismuth, copper, and cadmium | 78-79 |
| M. | from silver, lead, and mercury | 78 |
| M. | separation and determination | 10-18 |
| M. | Molybdenum ores. See Molybdenite; Molybdate; Powellite; Wulfenite. | |
| M. | Molybdenum products, decomposition, by acid. | 74-76 |
| M. | by alkaline leaching | 76 |
| M. | by fusion | 76 |
| M. | uses | 71 |
| M. | Monazite, occurrence | 19 |
| M. | treatment | 19 |
| M. | Monazite sand, as source of cerium | 19 |
| M. | as source of thorium | 20 |
| N. | Neodymium, used in combination with cerium. | 20 |
| N. | Nickel-zirconium alloy, uses | 301 |
| O. | Octahedrite, source of titanium | 261 |
| O. | Orthite, as source of cerium | 19 |
| P. | Patronite, as source of vanadium | 230 |
| P. | Perovskite, as source of titanium | 261 |
| P. | Phosphorus, analysis of material containing | 11-12 |
| P. | separation and determination | 10-18 |
| P. | Pitchblend, as source of uranium | 199 |
| P. | examination, for radium | 180 |
| P. | occurrence | 199 |
| P. | treatment, for radium | 195-196 |
| P. | Powellite, as source of molybdenum | 71 |
| P. | Prazoedymium, used in combination with cerium | 20 |</p>
<table>
<thead>
<tr>
<th>R.</th>
<th>Page.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Radioactivity, determination, by alpha-ray method.</td>
<td>182-184</td>
</tr>
<tr>
<td>Radium, bibliography.</td>
<td>187-188</td>
</tr>
<tr>
<td>determination, by fusion, blanite-fusion method.</td>
<td>192-193</td>
</tr>
<tr>
<td>carbonate method.</td>
<td>190-191</td>
</tr>
<tr>
<td>direct-fusion method.</td>
<td>191-192</td>
</tr>
<tr>
<td>figure showing fusion boat.</td>
<td>190</td>
</tr>
<tr>
<td>in solution.</td>
<td>188-190</td>
</tr>
<tr>
<td>measurement, by emanation method.</td>
<td>185-188</td>
</tr>
<tr>
<td>by gamma-ray method.</td>
<td>184-185</td>
</tr>
<tr>
<td>Radium chloride liquids, treatment of.</td>
<td>197</td>
</tr>
<tr>
<td>Radium emanation, apparatus for boiling of.</td>
<td>193-197</td>
</tr>
<tr>
<td>figure showing.</td>
<td>194</td>
</tr>
<tr>
<td>Roscoelite, as source of vanadium.</td>
<td>239</td>
</tr>
<tr>
<td>Rutile, as source of titanium.</td>
<td>281</td>
</tr>
<tr>
<td>S.</td>
<td></td>
</tr>
<tr>
<td>Samarium, use in combination with cerium.</td>
<td>20</td>
</tr>
<tr>
<td>Sandstones, vanadiumiferous, analysis, for vanadium.</td>
<td>264</td>
</tr>
<tr>
<td>Scheelite, as source of tungsten.</td>
<td>131</td>
</tr>
<tr>
<td>Scholl method, for determination of uranium in carnottite.</td>
<td>230-231</td>
</tr>
<tr>
<td>Silica, acid decomposition for materials containing.</td>
<td>13</td>
</tr>
<tr>
<td>Slag, from tungsten steels, decomposition methods.</td>
<td>136</td>
</tr>
<tr>
<td>T.</td>
<td></td>
</tr>
<tr>
<td>Thorianite, as source of thorium.</td>
<td>20</td>
</tr>
<tr>
<td>Thorite, as source of thorium.</td>
<td>20</td>
</tr>
<tr>
<td>Thorium, as source of radium.</td>
<td>173</td>
</tr>
<tr>
<td>chemistry, bibliography.</td>
<td>65-70</td>
</tr>
<tr>
<td>determination, gravimetric, by ammonium oxalate.</td>
<td>60</td>
</tr>
<tr>
<td>by fumaric acid.</td>
<td>58-60</td>
</tr>
<tr>
<td>by hydrogen peroxide method.</td>
<td>55</td>
</tr>
<tr>
<td>by lead carbonate.</td>
<td>56</td>
</tr>
<tr>
<td>by metanitrobenzoic acid.</td>
<td>57</td>
</tr>
<tr>
<td>by potassium azidite.</td>
<td>56</td>
</tr>
<tr>
<td>by potassium iodate in nitric acid solution.</td>
<td>61</td>
</tr>
<tr>
<td>by precipitation of thorium salt from mineral acid solution.</td>
<td>61</td>
</tr>
<tr>
<td>by precipitation of thorium salt from neutral solution.</td>
<td>52-61</td>
</tr>
<tr>
<td>by sebacic acid.</td>
<td>56</td>
</tr>
<tr>
<td>by sodium hypophospate in HCl solution.</td>
<td>62</td>
</tr>
<tr>
<td>by sodium pyrophosphate in HCl or (\text{H}_2\text{SO}_4) solution.</td>
<td>63</td>
</tr>
<tr>
<td>by sodium thiosulphate.</td>
<td>53</td>
</tr>
<tr>
<td>by Websbach Co. method.</td>
<td>53-55</td>
</tr>
<tr>
<td>qualitative, by electrophore and spectroscopic examination.</td>
<td>29</td>
</tr>
<tr>
<td>by hydrogen peroxide.</td>
<td>28</td>
</tr>
<tr>
<td>by potassium iodate.</td>
<td>28</td>
</tr>
<tr>
<td>by pyrophosphate.</td>
<td>28</td>
</tr>
<tr>
<td>by sebacic acid.</td>
<td>28</td>
</tr>
<tr>
<td>by sodium thiosulphate.</td>
<td>28</td>
</tr>
<tr>
<td>volumetric, by molybdate titration.</td>
<td>51</td>
</tr>
<tr>
<td>properties.</td>
<td>24-25</td>
</tr>
<tr>
<td>Thorium—Continued.</td>
<td></td>
</tr>
<tr>
<td>separation, from cerium.</td>
<td>30</td>
</tr>
<tr>
<td>from cerium earths, by carbonate.</td>
<td>42</td>
</tr>
<tr>
<td>from cerium and rare earths, by hydrogen peroxide.</td>
<td>31</td>
</tr>
<tr>
<td>by hypophosphates.</td>
<td>40</td>
</tr>
<tr>
<td>by potassium iodate from strong nitric acid solution.</td>
<td>33</td>
</tr>
<tr>
<td>by pyrophosphate.</td>
<td>34</td>
</tr>
<tr>
<td>by sebacic acid.</td>
<td>34</td>
</tr>
<tr>
<td>by sodium thiosulphate.</td>
<td>31-33</td>
</tr>
<tr>
<td>from cerium and yttrium earths, by solubility of double oxalate of thorium.</td>
<td>41</td>
</tr>
<tr>
<td>from common metal bases.</td>
<td>30</td>
</tr>
<tr>
<td>from titanium and zirconium.</td>
<td>30</td>
</tr>
<tr>
<td>uses.</td>
<td>20</td>
</tr>
<tr>
<td>Thorium acetate, properties.</td>
<td>26</td>
</tr>
<tr>
<td>Thorium and cerium, separation from titanium and zirconium, by fluorides and double fluorides.</td>
<td>40</td>
</tr>
<tr>
<td>Thorium carbonate, properties.</td>
<td>25</td>
</tr>
<tr>
<td>Thorium dioxide, properties.</td>
<td>25</td>
</tr>
<tr>
<td>Thorium ears, decomposition and solution, and precipitation.</td>
<td>21-22</td>
</tr>
<tr>
<td>See also Thorianite; Thorite.</td>
<td></td>
</tr>
<tr>
<td>Thorium fluoride, properties.</td>
<td>25</td>
</tr>
<tr>
<td>Thorium hydroxide, properties.</td>
<td>25</td>
</tr>
<tr>
<td>Thorium oxalate, properties.</td>
<td>25</td>
</tr>
<tr>
<td>Thorium peroxide, properties.</td>
<td>25</td>
</tr>
<tr>
<td>Thorium phosphates, properties.</td>
<td>25</td>
</tr>
<tr>
<td>Thorium sulphate, properties.</td>
<td>25</td>
</tr>
<tr>
<td>Titane, as source of titanium.</td>
<td>281</td>
</tr>
<tr>
<td>Titanium, analysis, quantitative.</td>
<td>286-294</td>
</tr>
<tr>
<td>bibliography.</td>
<td>299-300</td>
</tr>
<tr>
<td>determination, in presence of tungsten.</td>
<td>8</td>
</tr>
<tr>
<td>in presence of zirconium and iron.</td>
<td>9</td>
</tr>
<tr>
<td>qualitative.</td>
<td>284-285</td>
</tr>
<tr>
<td>volumetric.</td>
<td>290-294</td>
</tr>
<tr>
<td>in ores and alloys, separation by phenyl hydrate.</td>
<td>293-295</td>
</tr>
<tr>
<td>separation of silica.</td>
<td>294</td>
</tr>
<tr>
<td>separation, from other elements.</td>
<td>285-286</td>
</tr>
<tr>
<td>gravimetric, by alkali acetates.</td>
<td>286-290</td>
</tr>
<tr>
<td>separation and determination.</td>
<td>10-18</td>
</tr>
<tr>
<td>treatment by fusion, by potassium bisfluoride.</td>
<td>284</td>
</tr>
<tr>
<td>by sodium carbonate and borax.</td>
<td>284</td>
</tr>
<tr>
<td>by sodium carbonate and potassium carbonate mixture.</td>
<td>283</td>
</tr>
<tr>
<td>by sodium hydroxide and sodium carbonate.</td>
<td>283</td>
</tr>
<tr>
<td>by sodium hydroxide and sodium peroxide.</td>
<td>283-284</td>
</tr>
<tr>
<td>by sodium or potassium bisulphate.</td>
<td>284</td>
</tr>
<tr>
<td>uses.</td>
<td>282</td>
</tr>
<tr>
<td>Titanium ores and alloys, solution, by acids.</td>
<td>283</td>
</tr>
<tr>
<td>See also Brookite; Ilmenite; Octahedrite; Perovskite; Rutile; Titane.</td>
<td></td>
</tr>
<tr>
<td>Titanium and vanadium, determination, simultaneous.</td>
<td>9</td>
</tr>
<tr>
<td>Titanium oxide solutions, standard, preparation.</td>
<td>296-299</td>
</tr>
<tr>
<td>Torbernite, as source of uranium.</td>
<td>200</td>
</tr>
<tr>
<td>occurrence.</td>
<td>200</td>
</tr>
<tr>
<td>Topic</td>
<td>Page</td>
</tr>
<tr>
<td>-------</td>
<td>------</td>
</tr>
<tr>
<td>Uranium—Continued.</td>
<td></td>
</tr>
<tr>
<td>in ferrouranium and alloy steels, determination</td>
<td>231-233</td>
</tr>
<tr>
<td>in metals, determination</td>
<td>221-223</td>
</tr>
<tr>
<td>in ores, determination, colorimetric</td>
<td>220</td>
</tr>
<tr>
<td>gravimetric</td>
<td>214-218</td>
</tr>
<tr>
<td>radioactive</td>
<td>220-221</td>
</tr>
<tr>
<td>volumetric</td>
<td>219-220</td>
</tr>
<tr>
<td>separation, from alkalis and alkaline earths</td>
<td>201</td>
</tr>
<tr>
<td>from beryllium, chromium, and zirconium</td>
<td>205-206</td>
</tr>
<tr>
<td>from iron, aluminum, and nickel</td>
<td>204-205</td>
</tr>
<tr>
<td>from molybdenum and tungsten</td>
<td>206</td>
</tr>
<tr>
<td>from phosphorus and arsenic</td>
<td>205</td>
</tr>
<tr>
<td>from vanadium</td>
<td>207</td>
</tr>
<tr>
<td>separation and determination</td>
<td>10-18</td>
</tr>
<tr>
<td>uses</td>
<td>200</td>
</tr>
<tr>
<td>Uranium analyses, bibliography</td>
<td>234-237</td>
</tr>
<tr>
<td>Uranium and vanadium, estimation, simultaneous analysis</td>
<td>8</td>
</tr>
<tr>
<td>Uranium ores, vanadiferous, analysis, volumetric</td>
<td>227-230</td>
</tr>
<tr>
<td>See also Autunite; Carnotite; Pitchblende; Torbernite.</td>
<td></td>
</tr>
<tr>
<td>Uranium ores and metals, decomposition</td>
<td>200-201</td>
</tr>
<tr>
<td>U. S. Bureau of Standards, method for determining molybdenum</td>
<td>121-125</td>
</tr>
</tbody>
</table>

V.

Vanadanite, as source of vanadium | 239 |

Vanadium, bibliography | 278-280 |

determination, colorimetric | 261-262 |

electrolytic | 262 |

gravimetric, as ammonium vanadate | 252 |

as barium pyrovanadate | 253 |

as lead acetate | 252-253 |

as manganese vanadate | 253 |

by mercuric nitrate | 251-252 |

in presence of molybdenum | 6 |

in presence of tungsten | 6 |

in presence of uranium | 6 |

in presence of uranium and zirconium | 6-8 |

qualitative, by hydrogen peroxide | 244 |

volumetric, by electrometric titration | 237 |

by ferrous sulphate titration | 256-257 |

by iodometric titration | 257-259 |

by potassium ferricyanide titration | 259 |

by potassium permanganate titration | 254-256 |

by stannous chloride titration | 261 |

by titanium chloride titration | 259-260 |

in ferrovanadium, determination | 270 |

in iron, determination, electrometric | 269 |

gravimetric | 270 |

in iron and steel, determination, qualitative | 245 |

in iron ores, rocks, and slags, determination | 265-266 |

in iron, steel, and ferrovanadium, determination, methods | 275-277 |

in ores, determination, methods | 270-275 |

in rocks and minerals, determination, qualitative, by HCl | 244-245 |

U.

Uranium, analysis, bibliography | 234-237 |

as source of radium | 173, 199 |

determination, colorimetric | 214-218 |

gravimetric | 208-211 |

qualitative, chemical method | 202 |

radioactive method | 201 |

quantitative | 206-233 |

volumetric | 211-213 |

in carnallite, determination, Scholl method | 230-231 |

in complex carnallite ores, determination | 224-227 |
### VANADIUM—Continued.

<table>
<thead>
<tr>
<th>Subject</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>in steel, determination, electrometric</td>
<td>299</td>
</tr>
<tr>
<td>ferrous sulphite method</td>
<td>266-267</td>
</tr>
<tr>
<td>gravimetric</td>
<td>270</td>
</tr>
<tr>
<td>in HCl method</td>
<td>268</td>
</tr>
<tr>
<td>in vanadiferous sandstones, determination</td>
<td>254</td>
</tr>
<tr>
<td>occurrence</td>
<td>239</td>
</tr>
<tr>
<td>separation, from alkalies</td>
<td>250</td>
</tr>
<tr>
<td>from aluminum</td>
<td>247</td>
</tr>
<tr>
<td>from arsenic and antimony</td>
<td>248</td>
</tr>
<tr>
<td>from chromium</td>
<td>247-248</td>
</tr>
<tr>
<td>from iron</td>
<td>146-147</td>
</tr>
<tr>
<td>from molybdenum</td>
<td>250-251</td>
</tr>
<tr>
<td>from phosphorus pentoxide</td>
<td>248</td>
</tr>
<tr>
<td>from silica</td>
<td>249</td>
</tr>
<tr>
<td>from tungsten</td>
<td>251</td>
</tr>
<tr>
<td>from uranium</td>
<td>250</td>
</tr>
<tr>
<td>from zirconium and titanium</td>
<td>251</td>
</tr>
<tr>
<td>separation and determination</td>
<td>10-18</td>
</tr>
<tr>
<td>uses</td>
<td>240</td>
</tr>
</tbody>
</table>

### VANADIUM AND TITANIUM, ESTIMATION, SIMULTANEOUS

<table>
<thead>
<tr>
<th>Subject</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vanadium and uranium, estimation, simultaneous</td>
<td>8</td>
</tr>
</tbody>
</table>

### VANADIUM BRONZES, DECOMPOSITION, METHODS

<table>
<thead>
<tr>
<th>Subject</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vanadium iron, analysis, HCl method</td>
<td>268</td>
</tr>
<tr>
<td>Vanadium metal, analysis</td>
<td>266</td>
</tr>
<tr>
<td>Vanadium ores, decomposition, by fusion</td>
<td>242-243</td>
</tr>
<tr>
<td>by mineral acids</td>
<td>241-242</td>
</tr>
</tbody>
</table>

### VANADIUM ORES, ANALYSIS, DECOMPOSITION, BY MINERAL ACIDS

<table>
<thead>
<tr>
<th>Subject</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>See also Calcium vanadate, red: Cuprodescliozite; Patronite; Roscoelite;</td>
<td></td>
</tr>
<tr>
<td>Vanadanite: Zinc descliozite</td>
<td></td>
</tr>
</tbody>
</table>

### VANADIUM ORES CONTAINING CHROMIUM, ANALYSIS, FOR VANADIUM

<table>
<thead>
<tr>
<th>Subject</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vanadium oxide, as source of vanadium</td>
<td>239</td>
</tr>
<tr>
<td>Vanadium pentoxide, separation, from barium, calcium, zinc, and lead</td>
<td>249</td>
</tr>
<tr>
<td>Vanadium steel, analysis, colorimetric</td>
<td>268</td>
</tr>
<tr>
<td>decomposition</td>
<td>243</td>
</tr>
</tbody>
</table>

### W.

<table>
<thead>
<tr>
<th>Subject</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Welsbach Co., method, for gravimetric determination of thorium</td>
<td>53-55</td>
</tr>
<tr>
<td>Wilson, C. T. R., electroscope</td>
<td>175</td>
</tr>
<tr>
<td>Wolframite, as source of tungsten</td>
<td>131</td>
</tr>
<tr>
<td>Wulfenite, as source of molybdenum</td>
<td>71</td>
</tr>
</tbody>
</table>

### Y.

<table>
<thead>
<tr>
<th>Subject</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yttrium and cerium earths, separation from thorium, by sodium sulphite</td>
<td>41</td>
</tr>
<tr>
<td>by solubility of double oxalate of thorium</td>
<td>41</td>
</tr>
</tbody>
</table>

### Z.

<table>
<thead>
<tr>
<th>Subject</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zine descliozite, as source of vanadium</td>
<td>239</td>
</tr>
<tr>
<td>Zircon, as source of zirconium</td>
<td>301</td>
</tr>
<tr>
<td>Zirconia. See Zirconium oxide</td>
<td></td>
</tr>
<tr>
<td>Zirconium, analysis, qualitative</td>
<td>304</td>
</tr>
<tr>
<td>quantitative, insoluble compounds</td>
<td>306-311</td>
</tr>
<tr>
<td>bibliography</td>
<td>318-320</td>
</tr>
<tr>
<td>separation, from other elements</td>
<td>305-306</td>
</tr>
<tr>
<td>separation and determination</td>
<td>10-18</td>
</tr>
<tr>
<td>Zirconium ores, analysis, recommended method</td>
<td>313-315</td>
</tr>
</tbody>
</table>

### See also Baddeleyite; Zircon; Zirkite

<table>
<thead>
<tr>
<th>Subject</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zirconium ores and alloys, treatment, by acids</td>
<td>301-302</td>
</tr>
<tr>
<td>by fusion, by fluoride</td>
<td>303</td>
</tr>
<tr>
<td>by sodium carbonate and borax</td>
<td>303</td>
</tr>
<tr>
<td>by sodium carbonate or sodium potassium carbonate mixture</td>
<td>302</td>
</tr>
<tr>
<td>by sodium hydroxide and sodium carbonate</td>
<td>302</td>
</tr>
<tr>
<td>by sodium hydroxide and sodium peroxide</td>
<td>302</td>
</tr>
<tr>
<td>by sodium or potassium bisulphate</td>
<td>303</td>
</tr>
<tr>
<td>Zirconium oxide, use as refractory</td>
<td>301</td>
</tr>
<tr>
<td>Zirconium steel, analysis, recommended method</td>
<td>315-318</td>
</tr>
</tbody>
</table>

### Zirkite, as source of zirconium

<table>
<thead>
<tr>
<th>Subject</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zirkite, as source of zirconium</td>
<td>301</td>
</tr>
</tbody>
</table>