DATE: April 7, 1959

SUBJECT: Determination of Tetravalent Uranium in Thorium Oxide-Uranium Oxide Mixtures, Parts I, II and III

TO: See Distribution

FROM: Oscar Menis

ABSTRACT

For the determination of milligram quantities of uranium (IV) in thorium oxide-uranium oxide mixtures which may also contain uranium (VI), it was necessary to devise a means of dissolving the sample so as to prevent any air oxidation of the uranium (IV) to uranium (VI). For this determination, the conventional potassium dichromate, volumetric method was used with the innovation that the sample was dissolved under reflux in 7 M H₃PO₄ which contained an excess of standard dichromate solution. Following the dissolution of the sample, this excess was determined by back titration with a standard solution of iron (II). Barium diphenylaminesulfonate was used as the indicator. In Parts I and II of this report, initial tests on the dissolution of samples of thorium oxide-uranium oxide in hot HClO₄ and hot HCl, respectively, are described.

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DETERMINATION OF URANIUM (IV) CONTENT IN THORIUM OXIDE-URANIUM OXIDE MIXTURES

Part I: Stability of Ceric Sulfate in Hot 6 M Perchloric Acid

D. L. Manning

Purpose

To ascertain if ceric sulfate is stable in 6 M HClO₄ under reflux conditions.

Introduction

Uranium (IV) as UO₂ can be determined by dissolving the sample in approximately 5 per cent HClO₄, maintained at ~80°C, which contains an excess of standard ceric sulfate. The excess ceric sulfate is then back titrated with a standard solution of iron (II).

When thorium oxide-uranium oxide mixtures are encountered, however, the sample is not dissolved by the above treatment. The validity of the uranium (IV) measurement is therefore based upon a leaching process which may or may not dissolve all the UO₂.

A more reliable technique would be to dissolve the entire sample in the ceric solution and then back titrate the excess ceric sulfate. In order to do this, however, it is necessary to reflux the ThO₂-UO₂ mixture in ~6 M HClO₄ which contains a few drops of 10 per cent HF solution. A reflux period of about 30 minutes is required. It is necessary, then, to determine if ceric sulfate is stable under these conditions; i.e., no loss of the oxidizing power of ceric sulfate is indicated.

Experimental and Discussion

A portion of a standard solution of ceric sulfate was refluxed in 6 M HClO₄ (inert atmosphere maintained) for 30 minutes. On subsequent titration of the ceric sulfate with iron (II), it was revealed that ceric sulfate is not stable under these conditions inasmuch as the oxidizing power of the ceric solution decreases 40 per cent.

Conclusion

In view of the instability of ceric sulfate in hot 6 M HClO₄, any uranium (IV) measurement based upon dissolving the sample and determining the milliequivalents of cerium (IV) reduced, as a measure of uranium (IV), would not be valid.
Part II: Dissolution of Thorium Oxide-Uranium Oxide Mixtures in Hot Concentrated HCl Under an Inert Atmosphere

Purpose

To investigate the feasibility of determining uranium (IV) by dissolving the thorium oxide-uranium oxide mixture in boiling HCl under an inert atmosphere and then titrating the uranium (IV) with ceric sulfate.

Experimental

A 100-ml, round-bottom flask equipped with a side arm for the introduction of an inert gas was used in conjunction with a water-cooled condenser for dissolving the samples by refluxing in an inert atmosphere. Known amounts of uranium oxide, 30 ml of concentrated HCl, and a few drops of 10 per cent HF were added to the flask; helium was passed through the flask for 5 minutes at a flow rate of approximately 20 ft³ per hour to displace the air. The sample was then dissolved by heating to boiling while maintaining a helium atmosphere in the flask. Following dissolution of the sample and cooling, the solution was transferred to a 150-ml beaker, 50 ml of water was added, and the dissolved uranium (IV) was titrated with standard ceric sulfate to a ferroin end point.

Table I

Determination of Uranium (IV) by Dissolution in Hydrochloric Acid and Subsequent Titration with Cerium (IV)

<table>
<thead>
<tr>
<th>Substance</th>
<th>Milligrams</th>
<th>Ceric Sulfate to End Point, ml</th>
<th>Uranium (IV), mg</th>
</tr>
</thead>
<tbody>
<tr>
<td>UO₂</td>
<td>35.0</td>
<td>4.92</td>
<td>30.9</td>
</tr>
<tr>
<td>UO₂*</td>
<td>37.0</td>
<td>5.27</td>
<td>32.6</td>
</tr>
<tr>
<td>U₃O₈</td>
<td>49.4</td>
<td>2.07</td>
<td>14</td>
</tr>
<tr>
<td>U₃O₈*</td>
<td>75.6</td>
<td>3.20</td>
<td>21.4</td>
</tr>
</tbody>
</table>

Coefficient of Variation V 3%

* Approximately 200 mg ThO₂ was added to the uranium oxide prior to dissolving the sample.
Discussion

It is indicated from the data in Table I that the HCl dissolution method(2) is applicable to the determination of milligram quantities of uranium (IV) in thorium oxide. The coefficient of variation for the data obtained so far appears to be about 3 per cent. The method has the advantage that the uranium (IV), after dissolution, can be measured by a direct titration instead of resorting to an indirect measurement involving a back-titration. The disadvantage, however, which actually outweighs the above mentioned advantage is the necessity of maintaining an inert atmosphere to prevent air oxidation of uranium (IV) to uranium (VI). Thorium does not interfere with the titration of uranium (IV) with ceric sulfate. The only change in the procedure is a longer heating period for dissolution when a thorium oxide-uranium oxide mixture is present. Whereas 10 minutes of heating is sufficient to dissolve on the order of 30 mg of UO₂ or U₃O₈, a period of 30 to 45 minutes is required to dissolve mixtures containing the same amount of uranium and 200 to 300 mg of thorium oxide.

Conclusion

The uranium (IV) content of thorium oxide-uranium oxide mixtures can be measured by dissolving the sample in boiling HCl under an inert atmosphere and the titrating the uranium (IV) with ceric sulfate. The coefficient of variation is about 3 per cent. The disadvantage of the procedure is that it is not easily adapted to the analysis of a large number of samples because the dissolution of the samples must be carried out under an inert atmosphere.
Part III: Dissolution of Thorium Oxide-Uranium Oxide Mixtures in a Boiling Acidic Solution of K₂Cr₂O₇

Purpose

To determine uranium (IV) in uranium oxide-thorium oxide mixtures by dissolving the sample in a boiling acidic solution of K₂Cr₂O₇, then titrating the excess K₂Cr₂O₇ with iron (II) according to the conventional potassium dichromate, volumetric method.³

Apparatus and Reagents

- Flask for Refluxing, round-bottom, 100-ml capacity.
- Condenser, water cooled.
- Heating Mantle.
- Variac.
- Potassium Dichromate, 0.0585 N. Dissolve 1.433 g of Baker's, reagent-grade K₂Cr₂O₇ in 500 ml of water.
- Ferrous Ammonium Sulfate, 0.05 N. Dissolve 12 grams of ferrous ammonium sulfate dihydrate in 500 ml of water. Add 10 ml of HClO₄ and dilute to 500 ml.
- Barium Diphenylaminesulfonate Indicator. Dissolve 25 mg of barium-diphenylaminesulfonate in 100 ml of water. Add 1 ml of concentrated H₂SO₄. Filter the solution to remove the BaSO₄ precipitate.
- Phosphoric Acid, concentrated.
- Perchloric Acid, concentrated.

Procedure

The uranium content of synthetic thorium oxide-uranium oxide mixtures was determined following the step-wise procedure below. These data are shown in Table II. The results from the analysis of representative samples are given in Table III.
Steps

1. Transfer from 200 to 600 mg of the thorium oxide-uranium oxide sample to a round-bottom flask.

2. Add 10 ml of conc. H_2PO_4 and 10 ml of the standard K_2Cr_2O_7 solution. Add 4 drops of 10 per cent HF.

3. Assemble the flask for reflux and boil until the sample has dissolved. Set the Variac dial to 70.

4. After the sample has dissolved, remove the heating mantle, condenser, and transfer the solution to a 150-ml beaker. Rinse the flask with 20 ml of water and also add this water to the beaker.

5. Add 2 drops of indicator solution and titrate the excess K_2Cr_2O_7 with the iron (II) solution until the color changes from purple to green.

6. Calculate the milligrams of uranium (IV) per gram of sample from the following formula:

\[
\frac{\text{ml of } K_2Cr_2O_7 \text{ added to flask}}{\text{ml of } K_2Cr_2O_7 \text{ for back titration}} \times \frac{\text{ml Fe}^{+2} \text{ for back titration}}{N \text{ of } K_2Cr_2O_7} \times \frac{119}{\text{wt. sample, g}}
\]
Table II

Determination of Uranium (IV) by Dissolution in a Phosphoric Acid Solution of K$_2$Cr$_2$O$_7$ and Back-Titrating the Excess of Potassium Dichromate with Iron (II)

Conditions:

<table>
<thead>
<tr>
<th>Sample, mg</th>
<th>Phosphoric acid, ml</th>
<th>K$_2$Cr$_2$O$_7$, 0.0585 N, ml</th>
<th>Indicator</th>
<th>Reflux time, minutes</th>
</tr>
</thead>
<tbody>
<tr>
<td>UO$_2$</td>
<td>ThO$_2$</td>
<td>Iron (II) for Back Titration*, ml</td>
<td>Uranium (IV), mg</td>
<td>Per Cent</td>
</tr>
<tr>
<td>26.1</td>
<td>458</td>
<td>8.32</td>
<td>23.0</td>
<td>22.3</td>
</tr>
<tr>
<td>28.3</td>
<td>442</td>
<td>7.72</td>
<td>25.0</td>
<td>27.0</td>
</tr>
<tr>
<td>35.5</td>
<td>360</td>
<td>7.00</td>
<td>31.3</td>
<td>31.1</td>
</tr>
<tr>
<td>35.9</td>
<td>336</td>
<td>7.00</td>
<td>31.6</td>
<td>31.1</td>
</tr>
<tr>
<td>42.4</td>
<td>534</td>
<td>6.30</td>
<td>37.4</td>
<td>37.6</td>
</tr>
<tr>
<td>47.5</td>
<td>500</td>
<td>4.70</td>
<td>41.9</td>
<td>43.4</td>
</tr>
</tbody>
</table>

$\overline{X}$ 101

Coefficient of Variation $\overline{V}$ 3%

* Iron (II) titer

6.30 ml iron (II) = 5.00 ml K$_2$Cr$_2$O$_7$
Table III

Determination of Uranium (IV) in Samples of Thorium Oxide-Uranium Oxide Mixtures

Conditions:

<p>| | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Phosphoric acid, ml</td>
<td>10</td>
<td>K$_2$Cr$_2$O$_7$, 0.0585 N, ml</td>
<td>10</td>
</tr>
<tr>
<td>Indicator</td>
<td></td>
<td>barium diphenylaminesulfonate</td>
<td></td>
</tr>
<tr>
<td>Reflux time, minutes</td>
<td></td>
<td>30 to 45</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sample</th>
<th>Weight, mg</th>
<th>Iron (II) for Back-Titration, ml</th>
<th>Uranium (IV) Milligrams per Gram of Sample</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>332</td>
<td>6.90</td>
<td>95</td>
</tr>
<tr>
<td></td>
<td>422</td>
<td>5.35</td>
<td>95</td>
</tr>
<tr>
<td>2</td>
<td>353</td>
<td>6.45</td>
<td>96</td>
</tr>
<tr>
<td></td>
<td>661</td>
<td>1.25</td>
<td>95</td>
</tr>
<tr>
<td>3</td>
<td>535</td>
<td>4.40</td>
<td>85</td>
</tr>
<tr>
<td></td>
<td>257</td>
<td>3.38</td>
<td>86*</td>
</tr>
</tbody>
</table>

* After correcting for the standard addition of 49 mg of UO$_2$ to the sample.

Discussion

That the procedure is applicable to the measurement of uranium (IV) in thorium oxide is evident from the data in Tables II and III. The coefficient of variation based on the determination of uranium (IV) in known mixtures appears to be about 3 per cent. It was established that a solution composed of K$_2$Cr$_2$O$_7$ in 6 M HClO$_4$ or in a mixture of HClO$_4$ and H$_3$PO$_4$ could likewise be used for sample dissolution. The solution composed of K$_2$Cr$_2$O$_7$ in 7 M H$_3$PO$_4$ appeared to dissolve the thorium oxide-uranium oxide mixtures in the shortest period of time, however. This was probably due in part to the formation of a soluble thorium phosphate complex in the boiling 7 M H$_3$PO$_4$ solution.

The solutioning of the samples by refluxing is not essential although this technique is recommended. No attention is required during the heating period which may vary from about 20 minutes to 1 hour in extreme cases. If open beakers are used, care must be exercised to prevent the mixtures from bumping or spattering, evaporating to small volumes or possibly to dryness. Occasionally a highly refractive sample is encountered which will not dissolve when treated according to the procedure reported herein. When this occurs, the uranium (IV) content can be determined after dissolving the sample in HCl as described in Part II of this report. A solution of K$_2$Cr$_2$O$_7$
in HCl is not satisfactory due to the possibility of the reduction of the
K2Cr2O7, and also the possible volatilization of chromyl chloride by solutions
of hot HCl. The K2Cr2O7 is stable, however, under reflux conditions, in
either 7 M H3PO4, 6 M HClO4, or a mixture of two acids.

Possible interferences include any substance that will reduce the K2Cr2O7
in the same manner as uranium (IV). For this application, however, the
contaminants in the thorium oxide-uranium oxide mixtures were in the parts per
million range and no significant error was introduced.

Conclusion

The procedure whereby the sample is subjected to boiling 7 M H3PO4 which
contains an excess of K2Cr2O7 can be used to dissolve most thorium oxide-
uranium oxide mixtures. Following dissolution, the uranium (IV) content can be
evaluated from a back-titration of the excess K2Cr2O7 with iron (II). The
coefficient of variation of the method is 3 per cent for an order of magnitude
of 30 mg of U (IV).

References

1. C. J. Rodden, Analytical Chemistry of the Manhattan Project,
(1951), pp. 323, 327.
3. C. J. Rodden, Analytical Chemistry of the Manhattan Project,

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