ANALYTICAL PROCEDURE MANUAL FOR A RADIUM RECOVERY PROCESS

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I. A B S T R A C T

This manual is a complete compilation of analytical procedures used in the laboratory-scale separation of radium from sulfate-insoluble residues from African pitchblende processing. Included in five alternate procedures are quantitative analyses for silica, lead, copper, molybdenum, barium, nickel, calcium, magnesium, radium, moisture, water-solubles, nitrate, silver, manganese, zinc, carbon dioxide, sulfate, and chromium.

II. INTRODUCTION

This analytical procedure manual is a revised and enlarged edition of the manual employed by the Analytical Group while working on the separation of radium from the sulfate insoluble residues from African pitchblende processing. The manual serves as a record of analytical procedures used. It may also serve as a source of tested procedures if, at some future time, the process should be used on a pilot-plant scale. In general, existing analytical procedures were adapted to the problem at hand.

The Silica Method, Barium Method I, and Barium Method II are sections on general separation procedures which may be applied to the uranium residue or to intermediates of a similar nature. Determinations, starting directly with the original sample, are grouped under the section, Analyses Made Directly on Residue Sample. The final section, Analyses of Special Samples, deals with separations and determinations of special process samples which do not lend themselves readily to the more general procedures.

III. SILICA METHOD

DETERMINATION OF SILICA

Step A. Mix a 0.2000 g. sample with two g. of anhydrous Na_2CO_3 on glazed, black paper. Brush carefully into a platinum crucible. Add a little more Na_2CO_3 to the glazed paper, and brush this into the crucible to aid in removing any particles of sample adhering to the paper.

Place the crucible on a silica triangle over a Meker burner, cover the crucible, and bring the temperature up slowly. Slow evolution of moisture is important to prevent "boiling-over" of the mixture. After the reaction has quieted down and the mixture has caked or shrunken, bring the temperature to full heat, with only the oxidizing part of the flame touching the crucible. An electric muffle at 950°C may be used for the latter heating.

When the molten mixture has no appearance of solids on the bottom or turbidity, tip and rotate the crucible to spread out the melt on the sides as it freezes. Place the crucible and the lid in a 250 ml. beaker containing 50 ml. water; and boil gently a few minutes, adding sufficient water to cover the crucible. Remove the beaker from the heat. Pick out the crucible, and rinse the outside into the beaker. Loosen adhering flakes in the crucible with a policeman and rinse into the beaker. Make sure that all of the material has been removed from the crucible before setting it aside. Now clean the crucible cover in a like manner. Return the beaker to the hot plate and boil gently, breaking up any large particles with a stirring rod. When the insoluble residue is completely broken up, filter on Whatman No. 40 paper, and wash six times with hot water. Reserve the filtrate for Step D.

Step B. The residue on the filter paper from the water leach of the sodium carbonate fusion (Step A) is dissolved in HClO_4 as follows: Punch a hole in the filter paper, and wash thoroughly with hot 2N HClO_4 into a clean beaker. Then wash the paper six times with hot water to remove all HClO_4 . Place the paper in the original platinum crucible to await other silica residues for ignition (Step F).

Step C. The precipitate is now digested in the beaker (Step B) for ten minutes by gently boiling. Break up any lumps with a stirring rod. Filter while hot on No. 40 paper, wash three times with 0.1N HClO_4 , and six times with hot water. Place the paper and residue in the original platinum crucible for Step F. The filtrate is reprocessed for residual silica in Step E.

Step D. Neutralize the water leach filtrate (Step A), with conc. HClO_4 , and add one ml. in excess. Cover with a ribbed watch glass. Place the beaker on a steam bath or 130°C hot plate to evaporate the water. Now heat strongly on the hot plate until fumes of HClO_4 are evolved. Continue heating for five minutes to dehydrate the silica. Cool, add 50 ml. of water, and boil gently for five minutes. Filter on No. 40 paper, and wash three

times with hot 0.1N HClO_4 , directing the wash stream around the top of the paper. Wash six times with hot water. Reserve the filtrate for Step H or for the determination of molybdenum (Step K). Fold the filter paper over the residue, and place in the original platinum crucible for Step F.

Step E. The filtrate from Step C contains a little silica and must be dehydrated for more complete recovery by dehydration and re-solution. Follow the procedure in Step D. Reserve the filtrate for Step H. Fold the filter paper over the residue and place in the original platinum crucible for Step F.

Step F. The platinum crucible now contains the four filter papers from Steps B, C, D, and E. If washing has been insufficient, residual HClO_4 will cause spurting and loss of some of the residue when charring. The filter papers may be dried in the oven or over a Meker burner by directing the flame against the bottom of the crucible (placed in an inclined position on a silica-covered triangle). Allow the paper to char, not flame. Then raise the temperature until the char glows. When the char is almost consumed, ignite with the full flame to constant weight. Two 30-minute heatings should be sufficient. After cooling in a desiccator, accurately weigh the crucible to obtain the weight of impure silica. Place the platinum crucible in an air bath over a hot plate (The air bath is made by placing the platinum crucible in a nichrome triangle, supported by a nickel crucible. There should not be physical contact between the two crucibles). Add one ml. water, one-half ml. HClO_4 , and ten ml. HF. The silica is volatilized as SiF_4 and H_2SiF_6 . Prevent bubbling by keeping the temperature low. Evaporate to 0.5 ml., cool, add one ml. water and two to three ml. HF, and continue the volatilization of silica. Raise the temperature to fume off the HClO_4 . Now place the platinum crucible over a Meker burner, and ignite to constant weight for 30 minutes. Cool in a desiccator, and weigh.

The difference in weight is calculated as pure silica.

$$\text{Per cent SiO}_2 = \frac{(\text{wt. of crucible and crude silica}) - \text{wt. of crucible and HF residue)} \times 100}{\text{wt. of sample}}$$

The residue in the platinum crucible is reserved for Step G.

SEPARATION OF HYDROGEN SULFIDE GROUP

Step G. Fuse the platinum crucible residue obtained from the volatilization of silica, if weighable, with at least five times its weight of anhydrous Na_2CO_3 . Use the same precautions as in Step A. Leach the melt with water as for silica. The filtrate is reserved for Step H.

Step H. Combine the filtrates from Steps D, E, and G. Neutralize the solution with 6N NH_4OH (alkacid paper); then acidify one normal with acetic acid to pH2. (If molybdenum is to be determined, use a pressure flask for this precipitation.) While the solution is hot, precipitate the lead and

other hydrogen sulfide-group metals with a moderate stream of H_2S . Continue the gas flow until the precipitate coagulates and tends to settle. Filter on an asbestos pad in a Gooch crucible, and wash six times with hot, 0.01 normal acetic acid saturated with H_2S . Now test the filtrate for completeness of precipitation by saturating again with H_2S . The precipitate is reserved for the determination of lead (Step I) and copper (Step J). Silver and molybdenum may also be present.

ELECTROLYTIC DETERMINATION OF LEAD

Step I. Dissolve the sulfide precipitate from the Gooch crucible (Step H) by digestion in a beaker with hot, 6N HNO_3 . When solution is apparent, due to the complete disappearance of the black precipitate, remove the crucible from the beaker, and rinse the crucible thoroughly with hot water. Filter off the asbestos, using filter paper or another Gooch crucible, and wash thoroughly with hot water.

Evaporate the solution to a small volume, and add 15 ml. conc. HNO_3 . Add 0.5 ml. conc. H_2SO_4 to make the electrolytically-deposited PbO_2 more adherent. Any slight precipitate of PbSO_4 in the solution is disregarded, since it will dissolve and be deposited during electrolysis. Now dilute to 100 ml.

Connect a clean, weighed platinum gauze electrode to the positive (+) terminal of the Fisher Electroanalyzer and a platinum spiral or gauze electrode to the negative (-) terminal. Now bring the beaker of solution under the electrodes after adding a magnetic stirring piece, and adjust the level to permit ample clearance of the stirrer and the electrodes when in motion. Cover the beaker with a split watch glass. Turn on the current, and adjust the amperage to 1.5 to 2.0 at two volts or more. Turn on the magnetic stirrer to permit moderate stirring without much vibration. Continue the electrolysis for 1.5 hours. Test for completeness of deposition by adding a little water, and, after 15 minutes, noting if any deposit is formed on the freshly-immersed gauze of the anode. If no deposit is formed, the electrolysis is complete. If a deposit is formed, electrolyze 15 minutes more and test again.

When the deposition is complete, lower the beaker slowly while rinsing the anode thoroughly with water from a wash bottle. Now turn off the current. Reserve the lead-depleted solution for the determination of copper. (Step J). Dip the gauze anode into a beaker of water and then into a beaker of acetone to remove the water. Let drain. Dry the anode with its deposit of PbO_2 in an oven at 120°C for one-half hour. Cool in a desiccator, and weigh.

Calculation:

$$\text{Per cent lead} = \frac{(\text{wt. of anode and PbO}_2 - \text{wt. of anode})}{\text{wt. of sample}} \times 100 \times 0.866$$

Clean the anode by placing in 6N HNO_3 and adding a little H_2O_2 .

The residual solution and any deposit on the cathode are reserved for the copper determination (Step J).

ELECTROLYTIC DETERMINATION OF COPPER

Step J. Use the lead-depleted solution (Step I) for the determination of copper. Dissolve the trace of dark deposit on the cathode in a few ml. of hot HNO_3 , and combine with the lead-depleted solution. Add three ml. conc H_2SO_4 , and heat until fumes of SO_3 are evolved. Cool, and dilute with water to 75 to 100 ml. Add two ml. of conc. HNO_3 . Add about 0.2 g. urea to remove HNO_2 which interferes with the deposition.

Now place a clean, weighed, gauze electrode on the negative terminal (cathode) of the Fisher Electroanalyzer and a spiral wire electrode on the positive terminal (anode). Place a magnetic stirrer in the beaker, and position the beaker on the stirring base so that the stirring piece rotates freely beneath the electrodes. A motor stirrer may be used with the resistance at a maximum. Regulate the current to three to four amperes. The voltage should be two to four volts. Electrolyze for 45 minutes. After the blue copper color of the solution has entirely disappeared, rinse the cover glass and any spray on the sides of the beaker into the solution. This raises the level of the electrolytic solution. After electrolyzing the solution another 15 minutes, determine if deposition is complete by examining the newly-immersed portion of the cathode. If deposition has continued, raise the liquid level once more, and electrolyze an additional 15 minutes.

When electrolysis is complete, slowly lower the beaker while washing the electrodes with water from a wash bottle. Wash thoroughly, since any acid solution left on an electrode will redissolve the deposit. Finally, dip the plated electrode in a beaker of water, then rinse - first with alcohol and then with acetone - to remove soluble material and water. Rinsing may be done with wash bottles or by dipping into beakers containing these solvents. Dry for two to three minutes in a 100°C oven. Cool in a desiccator, and weigh.

Calculation:

$$\text{Per cent copper} = \frac{(\text{wt. of electrode and copper} - \text{wt. of electrode})}{\text{wt. of sample}} \times 100$$

To clean the plated electrode, immerse in 6N HNO_3 until the deposit appears to be entirely removed; wash with water, alcohol, and acetone.

DETERMINATION OF MOLYBDENUM¹

All of the molybdenum remains in the water leach from the Na_2CO_3 fusion. Use the solution obtained after the removal of silica by HClO_4 digestion (Step D).

Step K. To the filtrate from Step D, add two g. of tartaric acid or a tartrate to hold tungsten and vanadium in solution during subsequent operations. Saturate the hot solution with H_2S . A purple solution indicates considerable vanadium. Molybdenum gives a yellow to orange solution, becoming brown on prolonged reaction and reduction.

Acidify the solution slowly with 1:1 H_2SO_4 , while continuing the passage of H_2S . The molybdenum precipitates as a brown floc. Filter off the precipitate, and wash six times with hot water. The filtrate contains the reduced molybdenum and must be reprocessed. Make the filtrate alkaline with NH_4OH , and boil five minutes. Add a few drops of H_2O_2 , and saturate with H_2S . Acidify, and filter as before, using a second filter.

Place both filters with precipitates back in the original beaker, cover, and add five ml. H_2SO_4 and ten ml. HNO_3 until all paper is destroyed, and heat strongly to completely remove HNO_3 . Cool, wash down the cover and sides of the beaker, and fume again. Repeat washing and fuming once more. Molybdenum can now be determined by one of the following methods:

1. Volumetric analysis with potassium permanganate (Step L).
2. Gravimetric analysis as lead molybdate (Step M).

Step L. Interfering elements arsenic and antimony are now removed. Cool the above H_2SO_4 solution, dilute to 15 ml. with water, and add three ml. of four per cent $CuSO_4$. Now add, a little at a time, five g. of 30-mesh zinc, and cover the beaker. Cool if the action becomes too violent. Allow the action to proceed at $50^\circ C$ for 15 minutes. All the copper and interfering elements are precipitated. Make sure the solution is acid (red to alkacid paper), and filter off the precipitate. Wash six times with cold water.

To the filtrate, add 20 ml. of 1:1 H_2SO_4 . Pour the hot solution (50° to $75^\circ C$) through the Jones reductor. The lower tip of the reductor should reach nearly to the bottom of a one-liter receiver containing 35 ml. of a ferric solution (add 100 g. $NH_4Fe(SO_4)_2 \cdot 18H_2O$ to 50 ml. of 1:1 H_2SO_4 , 500 ml. of water, 150 ml. of 85% H_3PO_4 , and dilute to one liter). Slow passage (five minutes) through the reductor is necessary. Now wash the reductor with 100 ml. of hot, 1:20 H_2SO_4 . The molybdenum is reduced to the trivalent state by the Jones reductor.

Titrate the hot solution immediately with standard $KMnO_4$ solution, 0.1 to 0.01 normal.

A blank run is made with 150 ml. of water and five ml. H_2SO_4 , using the same procedure starting with the addition of 30-mesh zinc.

Calculation:

$$\text{Per cent molybdenum} = \frac{(\text{ml. X N of permanganate}) \times 0.03198 \times 100}{\text{wt. of sample}}$$

Step M. Fume the molybdenum-sulfuric acid solution obtained from the sulfide precipitation (Step K) to a moist residue and dissolve in hot water. Use a little HCl to aid in solution if necessary. Now, neutralize the solution with NH_4OH , using methyl orange indicator; make just pink with HCl and add three drops in excess. The volume is about 300 ml. Add 20 ml. of ammonium acetate-acetic acid solution (250 ml. of saturated ammonium acetate and 150 ml. of glacial acetic acid diluted to one liter). Heat to boiling and titrate dropwise with lead acetate solution (18 g. lead acetate and 15 ml. glacial acetic acid diluted to one liter) with constant stirring. Tannic acid is used as an outside indicator. At the end point, one drop of tannic acid with one drop of solution no longer gives a yellow color. Add 1.5 ml. excess lead acetate solution. After the addition of a little paper pulp, boil five minutes. Allow to digest below the boiling temperature until the precipitate has settled.

Filter and wash the precipitate with diluted ammonium acetate-acetic acid solution (50 ml. diluted to one liter). Dry, and ignite to constant weight at a low red heat, 500° to 525°C . The precipitate is white or faintly yellowish. Cool in a desiccator and weigh.

Calculation:

$$\text{Per cent molybdenum} = \frac{(\text{g. lead molybdate}) (0.2613) \times 100}{(\text{wt. of sample})}$$

IV. BARIUM METHOD I

DETERMINATION OF BARIUM

The sulfate residue contains about 17 per cent lead which, despite the most careful technique, is destructive to platinum crucibles in NaCO_3 fusions. It is recommended that the bulk of the lead be removed before fusion.

Weigh a one g. sample into a platinum crucible. To remove lead, leach the sample in the crucible with a hot solution saturated with ammonium acetate and containing one per cent $(\text{NH}_4)_2\text{SO}_4$ to prevent solution of the barium. Fill the crucible $1/3$ full of acetate solution, and stir briefly with a small, glass stirring rod. Decant while hot into a funnel fitted with No. 40 Whatman filter paper. Repeat five times. Finally, wash the crucible and paper with hot water to remove the ammonium acetate. Discard the filtrate.

The filter paper is transferred to the platinum crucible, charred over a low flame, and burned off. Now mix the residue with five to seven g. anhydrous Na_2CO_3 containing 0.1 g. KNO_3 . Fuse in a muffle furnace, bringing the temperature from 500°C to 950°C , or fuse over a Meker burner. Remove the crucible cover, and lay it on a piece of clean asbestos. Remove the crucible from the heat; tip and rotate to spread the liquid over the sides while freezing. Cool partially, immersing the crucible in cold water. This assists in loosening the melt from the crucible. Fill the crucible $2/3$ full with water, and heat nearly to boiling on a low-temperature hot plate. While supporting the crucible with tongs, rub the sides and bottom with a rubber policeman to assist in dissolving the melt. Decant into a funnel fitted with Whatman No. 42 paper. Repeat the leaching and decanting until all the fusion cake is removed. Use 0.01M Na_2CO_3 for these latter leachings to prevent solution of the barium. Wash the crucible, its cover, and the residue on the paper six times with this solution. Discard the filtrate.

Place a clean 250 ml. beaker under the funnel, and pour 15 ml. portions of 0.05N HCl over the filter to dissolve the carbonate. When solution is apparently complete, wash the paper six times with hot water.

An insoluble residue on the paper indicates an incomplete fusion. In this case, place the paper in the original platinum crucible, burn off the paper and repeat the fusion and procedure as above. Combine the resulting HCl solution of the water-insoluble residue with the previous one.

The combined HCl solutions are evaporated to dryness to dehydrate any silica. Since most of the silica was removed in the water leachings of the fusion cake, there should be very little in this solution. After dehydration, add 15 ml. of 0.5N HCl and heat to redissolve the residue. More acid may be required. Dilute with hot water, filter off the flocculent silica, and wash with hot water.

If the silica is more than a trace, it will contain some barium which must

be recovered. Place the paper in the platinum crucible, and char. Ignite to a white residue. Add four drops of HClO_4 , and fill the crucible two-thirds full with HF . Volatilize the silica and HF below the boiling point. Finally, fume off most of the HClO_4 . Dissolve the residue in HCl , and combine it with the major barium solution. Any lead not previously removed will be found in the resulting solution. To remove lead and, incidentally, other hydrogen sulfide group metals, adjust the acidity to 0.2 normal with HCl (using a methyl violet spot test to a blue-green), heat and pass in H_2S until the precipitate coagulates. Filter on a Gooch crucible and wash six times with hot 0.1N HCl saturated with H_2S . Immediately, pass H_2S into the combined filtrate and washings for 10 minutes. Filter again if necessary through the same Gooch crucible, and wash as before.

Make the filtrate alkaline with NH_4OH (to a distinct odor), and heat to approximately 80°C . Pass in H_2S for 10 minutes and test the solution with alkacid paper. If the indicator is not blue or dark green, add more NH_4OH , and again pass in H_2S for five minutes. Filter the coagulated precipitate on a Gooch crucible and wash with freshly-prepared 0.06N NH_4OH for two minutes). The filtrate contains the alkaline earths and alkali metals. If the filtrate is colored, heat to boiling to bring down more precipitate, and filter again. The precipitate contains the R_2O_3 and ammonium sulfide-group metals. This precipitate can be reserved for determinations of elements in these groups (see Separation of R_2O_3 Group). It should be taken into solution immediately with hot HNO_3 or aqua regia for this purpose.

Dilute the combined HCl solutions containing all the barium to about 0.1N HCl heat to 90°C , and with vigorous stirring precipitate the barium with 10 ml. of 0.1M H_2SO_4 added drop by drop. Set the beaker on the steam bath for at least an hour to permit crystal growth. Allow to cool before filtering. Overnight standing does no harm.

Filtration is accomplished by decanting the supernatant liquid through a Whatman No. 42 filter paper. Test the first runnings of the filtrate with a few drops of the H_2SO_4 reagent for residual barium. If no turbidity occurs, it is best to start again with a new sample.

Fold the filter paper over the precipitate, place in a porcelain crucible, dry at 110°C , char off the paper, and ignite to constant weight at red heat over a Meker burner or in a muffle furnace at 700° to 800°C . Cool in a desiccator and weigh.

Calculation:

$$\text{Per cent barium} = \frac{(\text{wt. of crucible and BaSO}_4 - \text{wt. of crucible})}{\text{wt. of sample}} \times 0.5885 \times 100$$

The precipitate will contain a little CaSO_4 . Add five ml. conc H_2SO_4 to the precipitate in the crucible, and heat to apparent complete solution of the precipitate. Cool the crucible, and wash its contents into a 100 ml. beaker with 50 ml. water. BaSO_4 reprecipitates, leaving calcium in the solution.

Repeat the filtration, washing, ignition, weighing, and calculation.

SEPARATION OF THE R_2O_3 GROUP

The ammonium sulfide-group precipitate from the Determination of Barium is used for the R_2O_3 group. Dissolve the precipitate in hot 6N HNO_3 . (Addition of a little HCl may aid if the precipitate is difficult to dissolve.) Dilute, and filter into a 250 ml. beaker to remove any filter paper or asbestos.

Add two g solid NH_4Cl . Add a few drops of methyl red indicator, and, after gently boiling the solution, carefully add 1:1 NH_4OH (prepared fresh from the original stock bottle) until the indicator just changes to yellow. If the indicator color is obscured by the precipitate, remove the beaker from the hot plate and allow the precipitate to settle between each addition of NH_4OH to permit an accurate observation of the indicator color.

After neutralizing, remove the beaker from the hot plate and allow the precipitate to settle for three minutes. Filter on No. 40 paper by decanting the supernatant liquid, leaving as much of the precipitate in the beaker as possible. To the precipitate in the beaker, add boiling one per cent NH_4Cl wash solution (made slightly ammoniacal), stir, allow to settle, and decant into the filter. Repeat four times, and pour the precipitate into the funnel. Do not quantitatively transfer the precipitate to the filter. Reserve the filtrate for determinations in the ammonium sulfide group.

After the filter has drained, place the original beaker under the filter and pour 1:2 HCl through the filter to dissolve the precipitate. Wash the paper with hot water, and reserve the filter paper.

Dilute the dissolved precipitate solution to 200 ml., heat to boiling, and reprecipitate the R_2O_3 group with NH_4OH as above. Now place the reserved filter paper in the gently boiling solution, remove from the hot plate, and stir to disintegrate the paper. Filter on a fresh No. 40 paper, and wash six times with hot, slightly ammoniacal, one per cent NH_4Cl solution. Finally, transfer all the precipitate to the filter; use a policeman to rub loose any adhering particles clinging to the beaker.

Transfer the paper and precipitate to a porcelain or platinum crucible, char off the paper, and ignite to constant weight. Cool in a desiccator and weigh quickly, since this precipitate is somewhat hygroscopic. The precipitate contains Fe_2O_3 , Al_2O_3 , TiO_2 , etc.

Calculation:

$$R_2O_3 = \frac{(\text{wt. of crucible and precipitate} - \text{wt. of crucible}) \times 100}{\text{wt. of sample}}$$

SEPARATION OF THE AMMONIUM SULFIDE GROUP

The filtrate from the R_2O_3 group is made alkaline with $6N$ NH_4OH to a detectable odor, and two ml. more added. Heat to 80° to $90^\circ C$ and pass in H_2S for 10 minutes; test for alkalinity with alkacid paper. If neutral, add two ml. more of $6N$ NH_4OH , and pass in H_2S for five more minutes.

The precipitate is best filtered on a Gooch crucible. Boil the filtrate briefly if colored; usually, additional precipitate will be formed. Filter on the same Gooch crucible. Wash with freshly prepared, $0.06N$ $(NH_4)_2S$ (prepared by bubbling H_2S into $0.06N$ NH_4OH for two minutes).

After drying, the precipitate can be ignited at $800^\circ C$ to the mixed oxides and weighed as such. If the determination of nickel is desired, dissolve the precipitate while still wet. The precipitate will contain any manganese, cobalt, zinc, uranium, zirconium, or rare earths.

DETERMINATION OF NICKEL

The nickel determination is made on the ammonium sulfide-group precipitate.

The $(NH_4)_2S$, asbestos, and Gooch crucible are placed in a 150 ml. beaker and digested with aqua regia until all dark particles have disappeared. The Gooch crucible is then removed and washed. The asbestos is now removed by filtering on a Whatman No. 1 filter paper. The filtrate is evaporated to remove aqua regia. When the volume is five ml., add five ml. conc. HNO_3 and evaporate to a moist residue. Now add two ml. of HNO_3 . Dilute to 200 ml., and add seven g. of tartaric acid to complex the metals precipitated by NH_4OH . When the tartaric acid has dissolved, neutralize with conc NH_4OH and add one ml. in excess. Filter off any slight quantity of insoluble matter, and wash well with water, adding the water washings to the filtrate. Make the solution slightly acid to litmus with HCl , heat to $80^\circ C$, and add 20 ml. of a one per cent alcoholic solution of dimethylglyoxime. Add NH_4OH until its odor is slightly perceptible, and let stand overnight. Filter, using a tared filtering crucible (medium), and wash the precipitate with hot water until the washings appear chloride free. Test the filtrate for completeness of precipitation by addition of five ml. of dimethylglyoxime reagent. Dry the precipitate at $100^\circ C$ for one-hour periods until constant in weight. The precipitate contains 20.32 per cent nickel.

V. BARIUM METHOD II

DETERMINATION OF BARIUM

A two g. sample is weighed into a platinum crucible and treated with one ml. water, one ml. HClO_4 , and ten ml. HF . The silica is volatilized by heating the crucible in an air bath below a temperature that causes bubbling. When the liquid in the crucible has evaporated to one ml., cool, add one ml. of water, (swirl to mix) and ten ml. HF . Repeat the evaporation to remove residual silica. Do not ignite. Allow the crucible to cool.

Rinse the contents of the crucible into a 250 ml. beaker with water, rub the inside of the crucible with a policeman, and wash the crucible out thoroughly. Make the solution about 0.6N with HCl and digest for a half-hour just below boiling.

Filter to remove any residue, and reprocess the residue separately, starting at the beginning of this determination. Probably, the residue is mainly silica. Combine the solution obtained from this residue with the main solution. Add three g. of NH_4Cl to the solution, and adjust to 0.2 normal in acid, using the methyl violet spot test to a blue-green color.

Now pass H_2S into the hot solution until the precipitate coagulates. Dilute with an equal volume of cold water, and continue the addition of H_2S for another 20 minutes.

Filter on a Gooch crucible, and wash six times with hot 0.1N HCl solution saturated with H_2S . Immediately bubble H_2S into the combined filtrate and washings for ten minutes to remove any additional hydrogen sulfide-group elements. This procedure should completely remove silver, lead, copper, and any minor constituents present as hydrogen sulfide-group elements.

Reserve the hydrogen sulfide precipitate if the determination of molybdenum is desired.

Immediately, add five ml. conc. H_2SO_4 to the filtrate, and evaporate until SO_3 fumes are evolved. Dissolve the residue in water, and heat to aid solution of minor quantities of coprecipitated basic acetates, and ammonium sulfide-group elements. Filter on Whatman No. 42 paper the insoluble sulfates which contain the barium and part of the calcium. Wash six times with small quantities of warm water.

Place the filter paper in a platinum crucible, dry at a low temperature, char the paper, and then raise the temperature to red heat to complete the removal of char. If any dark particles remain moisten the residue with conc. H_2SO_4 , and fume until the char is removed.

Cool the crucible and add one ml. of water, two drops of conc H_2SO_4 , and ten ml. HF . Volatilize any silica by quiet evaporation as described at the beginning of this determination. Fume off the H_2SO_4 and ignite the residue.

Mix the residue with approximately ten times its weight of anhydrous Na_2CO_3 and fuse, as described under Determination of Silica. Remove from the heat, and rotate to bring the fusion up on the sides of the crucible while freezing. Cool to room temperature by dipping the bottom of the hot crucible partially in cold water. Now fill the crucible two-thirds full with water, and heat nearly to boiling. Rub the mixture with a policeman to promote solution. Decant the crucible contents through a No. 42 filter paper, and repeat the leaching of the flakes in the crucible twice more. Now rinse the residue completely into the funnel with 0.01M Na_2CO_3 , and wash six times with the Na_2CO_3 solution. Reserve the filtrate for calcium and magnesium.

Place a clean, 250 ml. beaker under the funnel, and pour repeatedly into the filter 15 ml. portions of 0.5N HCl to dissolve the carbonates. Then wash the paper with hot water. Dilute the solution to make it approximately 0.1 normal in HCl, heat to 90°C and precipitate the barium with ten ml. of 0.1N H_2SO_4 added drop by drop. Set the beaker on the steam bath for an hour to permit the crystals to grow. Allow the precipitate to settle (overnight settling does no harm) and decant the supernatant liquid through a No. 42 paper. Test this filtrate with a few drops of dilute H_2SO_4 for residual barium. If no turbidity occurs, place the beaker under the funnel and finish the filtration. If the first runnings of filtrate are cloudy, pour the filtrate repeatedly through the funnel until clear. Wash the precipitate eight times with warm water, fold the paper over the precipitate, place in a porcelain crucible, dry at 110°C , char off the paper, and ignite to constant weight at red heat. Reserve the filtrate for the determination of calcium and magnesium.

Place ten ml. of conc. H_2SO_4 on the residue, break up the precipitate with a rod, and heat until SO_3 fumes are evolved. Cool, and pour the crucible contents into 100 ml. of water. Filter, wash, and ignite the residue to constant weight. Reserve the filtrate for calcium and magnesium determination.

Calculation:

$$\text{Per cent barium} = \frac{(\text{wt. of crucible and BaSO}_4 - \text{wt. of crucible}) \times 0.5885 \times 100}{\text{wt. of sample}}$$

If the precipitate is large, it may still be contaminated with calcium. Add conc. H_2SO_4 to the crucible and heat to dissolve the precipitate.

Cool the crucible, and wash its contents into a 100-ml. beaker with 50 ml. water. BaSO_4 reprecipitates, leaving calcium in solution.

Repeat the filtration, ignition, and weighing.

DETERMINATION OF CALCIUM

This procedure follows the determination of barium. Evaporate the filtrates reserved from the barium procedure to a convenient volume, 100 to 150 ml. Add five g. NH_4Cl , and make alkaline with NH_4OH . Pass H_2S into the hot solution to remove any traces of heavy metals. Filter, and wash with 0.06M $(\text{NH}_4)_2\text{S}$ solution.

Make the filtrate obtained from the ammonium sulfide group acid to methyl red, and add 2.4 ml. excess of 1:1 HCl. Boil the solution to remove H_2S and to reduce the volume to 100 ml. Filter off any free sulfur causing turbidity.

Now readjust the acidity by neutralizing with NH_4OH ; add just enough 1:1 HCl to make the solution acid to methyl red, and add 2.4 ml. in excess.

To the cooled solution add 15 ml. of a saturated solution of ammonium oxalate and ten g. of solid urea. Heat on a hot plate for 15 minutes or until the indicator turns yellow; the coarse crystals of calcium oxalate which form are ready for filtration.

Filter on a Gooch crucible with an asbestos pad previously ignited at 500° to 525°C in the electric muffle furnace and weighed. Wash at least five times with ice-cold, 9.1 per cent ammonium oxalate solution until the filtrate is chloride free. Test a portion of each filtrate, acidified with dilute HNO_3 , using 0.1N AgNO_3 . Dry for an hour at 110°C , and then ignite in the electric muffle furnace for 40 minutes at 500° to 525°C . Cool in a desiccator, and weigh. Reignite for 25-minute periods until constant weight is obtained.

Reserve the filtrate if the determination of magnesium is desired.

Calculation:

$$\text{per cent calcium} = \frac{(\text{wt. of crucible and } \text{CaCO}_3 - \text{wt. of crucible}) \times 0.4004 \times 100}{\text{wt. of sample}}$$

DETERMINATION OF MAGNESIUM

The filtrate from the calcium oxalate precipitation is evaporated to dryness and heated with a free flame to remove ammonium oxalate.

Add five ml. of conc. HCl, and dilute to 150 ml. Add ten ml. of freshly prepared $(\text{NH}_4)_2\text{HPO}_4$ solution (25 g. $(\text{NH}_4)_2\text{HPO}_4$ per 100 ml. of solution). Add a few drops of methyl red, and cool in ice. Now add conc. NH_4OH very slowly and with constant stirring until the indicator just turns yellow. Avoid scratching the sides of the beaker with the stirring rod. Continue to stir for five minutes. If the indicator turns pink carefully add NH_4OH to make it just yellow. After five minutes add five ml. of conc. NH_4OH and stir

for two minutes. Set aside to settle overnight, or for at least four hours.

Filter off the precipitate using No. 1 Whatman paper. Wash the precipitate with a minimum quantity of ice-cold 1:20 NH_4OH . Use six to eight small washings.

To get a precipitate of the correct chemical composition, dissolve the washed precipitate in 50 ml. of warm 1:10 HCl , and wash the paper well with hot 1:100 HCl . Dilute the solution to 150 ml., add 0.5 ml. $(\text{NH}_4)_2\text{HPO}_4$ solution, cool in ice, and precipitate with NH_4OH exactly as described above. Allow to stand four hours or overnight, filter on a previously-prepared Gooch crucible, and ignite to constant weight at $1,100^\circ\text{C}$. Wash with ice-cold, 1:20 NH_4OH . Acidify the washings with HNO_3 , and test for chloride with 0.1N AgNO_3 . Wash until the filtrate gives a negative test for chloride.

Dry the crucible in an oven at 110°C , and then ignite in the muffle furnace. Gradually increase the temperature to $1,100^\circ\text{C}$. Heat for half-hour periods to constant weight.

Calculation:

$$\text{Per cent magnesium} = \frac{(\text{wt. of crucible and magnesium pyrophosphate} - \text{wt. of crucible}) \times 0.2184 \times 100}{\text{Wt. of sample}}$$

DETERMINATION OF MOLYBDENUM

For this determination use the hydrogen sulfide precipitate obtained in Determination of Barium. The precipitate, which contains principally lead sulfide, is placed in a 125 ml. pressure bottle with an asbestos mat. Rinse the crucible contents into the bottle with 3N NaOH . Add an equal volume of 2M Na_2S , and wire down the stopper. Heat the bottle gently by placing it on the steam bath for 30 minutes. Cool to room temperature (do not plunge the bottle into cold water, or it will likely break).

Open the bottle, and filter the contents through No. 42 paper. Wash the bottle and residue thoroughly with a 0.05M $\text{NaOH} - \text{Na}_2\text{S}$ solution. The filtrate, containing molybdenum, tin, and possibly antimony or arsenic, is poured rather slowly into 15 ml. of 6N H_2SO_4 to avoid spattering due to H_2S evolution. When evolution has apparently ceased, heat the solution to drive off residual H_2S . Now add two ml. HNO_3 and continue heating to complete the solution, to oxidize some of the sulfur, and to coagulate the residual sulfur which is filtered off on No. 1 filter paper after the solution is diluted to 50 ml. Wash the filter paper six times with 0.2N H_2SO_4 and discard the paper.

Cool the clear solution, dilute to 100 ml., and add two ml. 0.25N $(\text{NH}_4)_2\text{SO}_4 \cdot \text{FeSO}_4$ to reduce any vanadic and chromic acids. Cool in an ice bath to 5° or 10°C , and add 10 ml. alpha-benzoin oxime reagent*. Add bromine water until bromine color is distinct, and then three ml. more of alpha-benzoin oxime reagent. Allow to stand ten minutes to permit complete precipitation. Filter through Whatman No. 41H paper or S and S 589 black ribbon paper. Wash

the precipitate with 150 ml. of fresh, ice-cold alpha-benzoin oxime wash solution. Transfer the filter paper to a weighed porcelain crucible and char the paper at a low temperature. Place the crucible in the electric muffle furnace, and ignite at 500°C to 525°C. Cool in a desiccator, and weigh. Now treat the residue with five ml. of warm, 1:3 NH₄OH, filter, and wash the precipitate with warm 1:100 NH₄OH. Reserve the filtrate. Ignite the filter paper in the original crucible, using the same precautions as before. Cool in a desiccator, and weigh.

Deduct the weight of this insoluble residue from the weight of molybdic oxide.

Examine the filtrate and washings for tungsten by adding HCl until acidic, followed by cinchonine (10 per cent solution in 1:1 HCl), and digest the solution overnight at 90°C, keeping the beaker covered with a watch glass. A steam bath is suggested for the digestion. If a precipitate of tungsten is obtained, filter on No. 42 paper and wash with cinchonine wash solution (25 ml. of the cinchonine reagent solution diluted to one liter). Ignite the precipitate and paper as described above, cool in a desiccator, and weigh.

Deduct this weight from the weight of MoO₃.

Calculation:

$$\text{Per cent molybdenum} = \frac{(\text{wt. of MoO}_3 - \text{wt. of residue} - \text{wt. of WO}_3) \times 0.6665 \times 100}{\text{wt. of sample}}$$

* Two per cent solution of alpha benzoin oxime in 95 per cent ethanol.

† 50 ml. of the above reagent and 10 ml. of sulfuric acid diluted to one liter.

VI. ANALYSES MADE DIRECTLY ON RESIDUE SAMPLES

DETERMINATION OF RADIUM

The radium analysis of residues from African pitchblende processing requires the preparation of a proper solution, (2) which may be used in alpha counting by the aeration method. The method of Tompkins, et al., (3) for radium analysis by alpha counting was adapted to this procedure. The procedure adopted modifies the reported method of Thomas. (4)

A solution to be used for the determination of radium by the aeration method should contain no sulfates and no silicates since the determination is made on samples from which radon can be quantitatively removed. Precipitated silica absorbs radon and makes its quantitative removal difficult.

Procedure: Weigh a five g. sample into a 30 ml. platinum crucible. Add two ml. of 50% H_2SO_4 , and then fill two-thirds full with 48% HF. Heat the crucible gently to permit evaporation without any bubbling. When the liquid remaining is about two ml. cool the crucible, refill with HF, and resume heating. Do this once more. Most of the silica has now been removed. Now suspend the residue in water in the crucible, and treat with hot, saturated ammonium acetate containing a little $(\text{NH}_4)_2\text{SO}_4$. Stir, and decant through a Whatman No. 42 filter paper. The filtrate is discarded. Repeat the treatment of the residue with the hot $(\text{NH}_4)_2\text{SO}_4$ and finally with water. Most of the lead has now been removed. The filter paper is placed in the platinum crucible, charred, and ignited. The residue is again treated with H_2SO_4 and HF, as above. Cool. Pour the sulfuric acid-containing residue into water, and scrub out the platinum crucible. Filter, and ignite again as described above. This residue contains all of the barium and radium as sulfates.

Fuse the weighed residue with ten times its weight of anhydrous Na_2CO_3 . While the crucible is hot, remove the cover and place the cover in a beaker containing 50 ml. water. Remove the crucible from the heat, and tilt and rotate it to spread the melt over the sides of the crucible. Place the crucible in the water containing the crucible cover. Heat the beaker, and scrub the crucible to promote solution of the melt. Decant the liquid through a Whatman No. 42 filter paper. Continue this process until all the melt has disintegrated. Wash thoroughly with hot one per cent Na_2CO_3 solution to ensure complete removal of sulfates. The residue contains all of the radium and barium as carbonates. Dissolve the carbonates in dilute HNO_3 .

Residual lead must now be removed. Precipitate the lead, barium and radium by additional of H_2SO_4 to the above HNO_3 solution. Allow the precipitate to stand overnight; filter on Whatman No. 42 filter paper; and wash five times with hot water. Discard filtrate. Now pour over the filter 100 ml. of hot, saturated, ammonium acetate solution containing one % $(\text{NH}_4)_2\text{SO}_4$. This dissolves the residual lead. Wash the paper with hot water. Place the paper in the original platinum crucible, char, ignite, and fuse again with Na_2CO_3 .

Treat the fusion mixture as before, including final solution in HNO_3 .

Preparation for Alpha Counting: Transfer the HNO_3 solution of barium and radium to a small volumetric flask; dilute to the graduation mark; and mix thoroughly. Pipette 10 ml. of this solution into a 15 ml. centrifuge tube or equivalent-size test tube. Fit a two-hole rubber stopper that fits the test tube with an inlet capillary tube reaching to the bottom of the test tube and an exit tube for applying suction.

Now place the tube containing the sample and stopper in a thermostatic bath held at 85°C . Apply suction to the exit tube to bubble air slowly through the solution. Continue this aeration for a minimum of five hours. Overnight aeration does no harm. Then transfer the solution to a ten ml. volumetric flask. Wash the tube, capillary, and stopper, and add the washings to the flask. Dilute to the graduation mark, and mix well. Transfer ten lambda or more of the solution to a counting slide, and dry under a heat lamp. Alpha counts are made on a suitable instrument whose geometry is known.

DETERMINATION OF MOISTURE

A two g. sample is weighed into a previously dried and tared weighing bottle. The open bottle is placed in the 110°C oven overnight. The bottle is then transferred to a desiccator to cool. It is then weighed. Drying and weighing are continued until the weight remains constant.

Calculation:

$$\text{Per cent moisture} = \frac{(\text{loss in weight})}{\text{wt. of sample}} \times 100$$

DETERMINATION OF LOSS ON IGNITION

A porcelain crucible is cleaned and ignited to constant weight at 950°C in an electric muffle furnace. A one to two gram sample is then weighed into the crucible. The crucible is dried overnight at 110°C and immediately placed in the furnace, which is gradually heated. Raise the temperature to 950°C and hold this temperature for one hour. Remove the crucible, and place in a desiccator to cool.

Calculation:

$$\text{Per cent loss on ignition} = \frac{(\text{loss in weight})}{\text{wt. of sample}} \times 100$$

DETERMINATION OF WATER-SOLUBLES

The water-solubles were not determined on an analytical scale. The procedure given here is the one used in the bench-scale radium process. For

analytical purposes, the quantities used can be scaled down to optimum size.

Procedure: One pound of residue is added with constant stirring to one liter of water held at its boiling point in a two-liter beaker. The stirring is continued for a minimum of five minutes to prevent caking, to dissolve any soluble coarse particles, and to give time for the leaching of the solubles from the larger lumps. The mixture is allowed to settle briefly and then decanted into a Buchner funnel containing a Whatman No. 1 filter paper. The bulk of the residue is then stirred with 200 ml. of hot water and decanted. Repeat once more, and this time transfer the residue to the filter. Wash with small portions of hot water until 500 ml. has been used.

During the agitation and gentle boiling of the mixture, considerable frothing occurs. The froth is easily broken by cooling or by temporarily discontinuing the agitation.

The volume of the filtrate is now determined, and 25 ml. aliquots pipetted for dry-weight determinations. The aliquots are transferred to 30 ml. beakers or crucibles and evaporated down without boiling. When aliquot volumes are less than five ml., place the beakers or crucibles in the drying oven at 110°C and dry for 24 hours. Repeat the drying at two-hour intervals until constant weight is obtained.

Calculation:

Per cent water-solubles =

$$\frac{(\text{total volume of filtrate})}{25 \text{ ml.}} \times 100 \times \frac{(\text{wt. of container and residue} - \text{wt. of container})}{\text{wt. of residues extracted}}$$

This filtrate (water leach) is essentially a mixture of NaNO_3 and Na_2SO_4 . To determine its constituents, use the methods described elsewhere as well as the following:

ALKALI METALS To determine alkali metals, evaporate an aliquot of the water leach in a porcelain crucible with a liberal excess of H_2SO_4 . Then fume off the excess H_2SO_4 and ignite, raising the temperature from 500° to 700°C rather slowly to avoid splattering during the decomposition of the $\text{Na}_2\text{S}_2\text{O}_7$ intermediate. Repeat the ignition at 700°C until constant weight is obtained.

The yield obtained is for impure Na_2SO_4 . After the other metals in the solution have been determined, the value can be corrected for these minor impurities.

NITRATE Transfer exactly 50 ml. of the water leach sample into the distillation flask of the Devarda apparatus. Mix with 100 ml. of freshly boiled distilled water and sufficient solid NaOH to make the solution approximately

1/10 normal (9 or 10 pellets). Add approximately 1.5 g. of finely powdered Devarda's alloy.

Connect the flask to the all-glass distillation apparatus (Figure 1). Use as a receiver a 250 ml. Erlenmeyer flask containing a measured volume of standardized 0.1N HCl and five ml. of methyl red indicator solution. (Set aside an equal volume of standard acid solution as a blank). Make certain that the condenser tube extends well beneath the surface of the acid.

Turn on the condenser water; gently heat for 20 or 30 minutes; then gradually increase the heat and distill. Continue distillation until only about 2 ml. of solution remain in the distilling flask. To prevent suckback of the distillate, lower the receiving flask to insure that the delivery tube is out of the acid before the heat is removed. Rinse the tip of the condenser tube with freshly-boiled distilled water, catching the rinsings in the receiver. The nitrate nitrogen has been converted to ammonia, distilled, and has neutralized a part of the HCl in the receiver.

Slowly titrate the solution in the receiver with 0.1N NaOH or KOH to the methyl-red endpoint; color change is red to yellow. Subtract this titer from that of the blank. The difference represents the amount of acid neutralized by the ammonia distilled.

Calculations: One ml. of 0.1N HCl is equivalent to 6.2 mg. of nitrate ion. Report mg. of nitrate per 50 ml. of sample.

DETERMINATION OF LEAD POLAROGRAPHICALLY

A 60 to 70 mg. sample is digested in a 20 ml. beaker with two ml. of 50 % NaOH on a low temperature hot plate. The mixture is held at the boiling point for about five minutes while being triturated with a five mm stirring rod. Place five ml. of 1M NaOH in a 25 ml. volumetric flask, and then pour the hot, digested solution into the flask. Rinse the beaker several times with two to five ml. portions of hot 1M NaOH, and add these rinsings to the flask. Now add two ml. of 0.05M NaCl to the flask, and dilute to near the graduation mark. Mix thoroughly, and place in the thermostatic bath at about 35°C. When equilibrium has been reached (in about one-half hour), dilute to the graduation mark with one molar sodium hydroxide and mix thoroughly. Pour the solution into a 30 ml. beaker for the polarographic determination.

A standard lead solution is prepared from recrystallized and dried reagent-grade PbNO_3 . This solution should be of sufficient strength that one ml. contains at least the lead equivalent of the unknown sample. To prepare the standard for polarographic analysis, pipette two ml. of 50% NaOH into a 25 ml. volumetric flask. Add the required volume of standard lead solution (not more than one ml.), one ml. of 0.1M NaCl, and any water needed to make the volume of standard lead solution plus water equal one ml., dilute the mixture to near the mark with 1M NaOH, and mix thoroughly. Place in the thermostatic bath, and after one-half hour dilute to the mark and again mix thoroughly. A blank is prepared the same way as the standard.

The polarographic determination is made in an open 30 ml. beaker without removal of dissolved oxygen. A silver chloride electrode is used in place of the mercury pool electrode. The electrode is made by attaching a wire to a one by five cm. strip of silver. The strip is coated with AgCl by anodizing in 1M NaCl for 15 minutes with a ten milliamper current. Measurements are made with the Fisher Electropode. The reduction wave occurs in the 0.8 volt range. The flat portions of the polarographic curve are located and determinations made by the increment method with readings taken at 0.60 and 1.15 volts. The standard solution and the blank solution values are determined in an identical manner.

Calculation:

Microamperes for sample = Δu a for sample - Δu a for blank

Microamperes for standard = Δu a for standard - Δu a for blank

DETERMINATION OF SILVER AND COPPER

The sample (two g.) is weighed into a platinum crucible and treated with one ml. of water, one ml. HClO_4 , one ml. HNO_3 and ten ml. HF. The silica is volatilized by placing the crucible in an air bath (nickel crucible) and keeping the temperature below that causing bubbling. After the HF has evaporated, it is advisable to add another five ml. HF and then to evaporate to HClO_4 fumes. Do not ignite.

Digest the crucible in 100 ml. of hot water, make about 0.1 normal with HNO_3 , and filter. Wash any precipitate with hot water and treat by the following procedure:

Char the paper, and glow off the char in a platinum crucible. After cooling, volatilize the silica as above with smaller quantities of reagents. Any residue should be immediately soluble in water. Combine with the previous filtrate.

Add one ml. of 1:1 HCl to the clear solution, and stir. Heat nearly to boiling, stir, and allow to settle. Test the supernatant liquid with one ml. of 1:1 HCl for completeness of precipitation. If the reagent causes turbidity, add one more ml. HCl, heat nearly to boiling, and allow to settle. Test again for completeness of precipitation. When precipitation is complete, set aside, preferably overnight. Filter on a No. 1 paper; wash with 0.01N HNO_3 six times. Reserve the filtrate.

Place the original beaker under the filter, and dissolve the precipitate with warm 1:1 NH_4OH poured repeatedly over the paper, and, finally, wash the paper with fresh 1:1 NH_4OH . Then wash with hot water six times. Neutralize the filtrate with 1:1 HCl, and add a slight excess. Heat nearly to boiling, let settle, and test the supernatant with one ml. of 1:1 HCl as before. When the precipitation is complete, allow to settle overnight; filter, using a fine, sintered-glass crucible, wash with cold, 0.01N HNO_3 six times, and finally, wash twice with cold water. Dry in an oven at 110°C to constant

weight.

Calculation:

$$\text{Per cent silver} = \frac{(\text{wt. of crucible and AgCl} - \text{wt. of crucible})}{\text{wt. of sample}} \times 0.7526 \times 100$$

The crucible can be cleaned with hot 1:1 NH_4OH .

When the silver content is quite low, it may be concentrated and be more accurately determined as follows:

Instead of precipitating silver as AgCl as above, the silver is electro-deposited along with copper (see method under Determination of Copper, Electrolytic).

After it is weighed, the electrodeposit is dissolved in hot dilute HNO_3 . The gauze electrode should be washed, dried, and weighed to establish that the deposit of silver plus copper has been removed.

Now the solution is evaporated to a moist residue to remove excess HNO_3 , the residue taken up with a minimum of water (five ml.), and the silver precipitated with a minimum of HCl as in the above AgCl procedure.

For best results, the filtration is performed with a small, sintered-glass crucible and the precipitate is washed several times with small portions of 1:100 HCl and then washed with small portions of water until the filtrate is chloride free. Dry at 110°C , cool in a desiccator for 20 minutes, and weigh.

Calculate silver according to the aforementioned equation.

Subtract the weight of silver from the total deposit weight to obtain the copper content.

DETERMINATION OF MANGANESE⁽⁵⁾

An 0.5 g. sample is treated with HF and HClO_4 to volatilize silica.

To the aqueous extract in a 250 ml. Erlenmeyer flask, add five to ten ml. H_3PO_4 . Heat to complete solution if necessary. Remove from the heat, add 20 ml. HNO_3 to oxidize any reducing material, and boil for ten minutes. If chlorides are present, evaporate to fumes to remove them.

Dilute with water to 100 ml.; add 0.4 to 0.5 g. solid sodium periodate or potassium periodate or 0.5 to 0.6 g. of sodium paraperiodate ($\text{Na}_2\text{H}_3\text{IO}_6$); boil for five minutes, keep hot for ten minutes, cool, dilute to 250 ml. in a volumetric flask, and mix thoroughly. This solution should contain not more

than five mg. of manganese.

Prepare a standard solution of manganous salt, and use suitable aliquots for oxidizing for color comparison standards. These periodate standards are stable for two to three months. Compare in Nessler tubes or in a suitable colorimeter.

DETERMINATION OF ZINC⁽⁶⁾

Remove silica with HF and HClO_4 . Remove copper, lead, and tin at 0.3 normal acidity with H_2S precipitate in HNO_3 ; remove the HNO_3 from the solution by evaporating with an excess of conc. HCl . Reprecipitate copper, lead, and tin with H_2S as above. Filter, and add the second filtrate to the first.

Boil the combined filtrates to remove H_2S . Cool, add two ml. conc. H_2SO_4 and evaporate to SO_3 fumes to remove HCl . Cool, dilute to 50 ml., and transfer to a H_2S precipitation pressure flask. Add two g. citric acid (preferably from a filtered stock solution). Neutralize with NH_4OH , using methyl orange indicator. Now add 40 ml. formic mixture (30 ml. of 15M NH_4OH , 200 ml. of 23.6 molar formic acid, 250 g. $(\text{NH}_4)_2\text{SO}_4$ to one liter). The pH should now be between two and three. Check this with a suitable instrument.

Heat to 60°C and pass in H_2S while continuing the heating. When steam issues from the exit tube, close it off, and immediately remove from the heater. Maintain a slight H_2S pressure on the flask, and shake intermittently to saturate the solution with H_2S (20 to 40 minutes are required). A rapidly-settling precipitate of ZnS (white) indicates complete precipitation. Filter on paper, and wash with 0.01 normal formic acid (0.4 ml. of 23.6 molar acid per liter) which has been saturated with H_2S . Dry the filter paper in a tared porcelain crucible. Ash the paper very slowly. Ignite strongly. Cool, moisten the residue with 1:1 H_2SO_4 , volatilize the excess acid, and heat to constant weight in an air bath. The residue is ZnSO_4 .

Calculation:

$$\text{Per cent zinc} = \frac{(\text{wt. of residue in crucible}) \times 0.4050 \times 100}{\text{wt. of sample}}$$

DETERMINATION OF CARBON DIOXIDE⁽⁷⁾

For this determination use a Geissler alkalimeter. The loss in weight of the entire assembly represents the CO_2 in the sample.

Weigh the sample directly into the lower chamber of the alkalimeter. Connect the acid chamber (the one with the hooked tube entering the lower chamber). Close the stopcock to the acid chamber, and fill to near the top with 1:4 HCl or HNO_3 . Place just enough conc. H_2SO_4 in the exit chamber to make a seal. Weigh the entire apparatus to 0.1 mg. accuracy.

Clamp the apparatus or place in a suitable holder to prevent tipping over. Attach a drying tube containing $\text{Mg}(\text{ClO}_4)_2$ to the exit and one containing soda asbestos to the air inlet of the acid chamber.

To operate, open the stopcock allowing the dilute acid to flow into the sample in the lower chamber. When most of the acid has been added, close the stopcock. Complete the reaction by placing the entire apparatus in a dry beaker and setting it on the steam bath. Make sure that all the sample has mixed with the acid. After 30 minutes allow the alkalimeter to come to room temperature.

Now attach a small rubber tube to the side arm above the H_2SO_4 trap and open the acid stopcock. Suck air slowly and carefully through the apparatus until the liberated CO_2 has been replaced by air (five minutes). Weigh the whole apparatus. The loss in weight is the CO_2 .

For samples low in CO_2 it is necessary to perform the work with extreme care; protect the apparatus from dust and grease; make sure that the apparatus and contents have reached room temperature, and avoid any chance of loss while sweeping out with air.

VII. ANALYSES OF SPECIAL SAMPLES

ANALYSIS OF SODIUM HYDROXIDE LEACH

Lead, barium, and silica are the determinations to be made. The leach liquor is hot as it comes from the filter. It should be sampled and aliquots taken for analysis before the material cools. Otherwise, upon cooling, dense flakes of impure lead oxide form which are difficult to redissolve.

A known volume of the original hot filtrate is used. Decant the supernatant liquor as completely as possible. Add conc. NaOH or water plus NaOH pellets to the residue, and heat and stir to dissolve as much as possible. Decant the clear solution from the residual solids, and repeat the solution treatment until solution is complete. The NaOH solutions are then thoroughly mixed with the original solution, decanted, and the final volume determined. The ratio of the original to the final volume is determined for proper conversion of the analytical data. Aliquots of the final solution are taken before reprecipitation occurs for all the determinations to be made.

Determination of Silica Transfer ten ml. aliquots of the leach to 250 ml. beakers. Neutralize the solutions with dilute HCl, and then add 20 ml. in excess. Dehydrate the silica by evaporation, and heat overnight on a hot plate at 120°C. Cool, add ten ml. of dilute HCl, stir, digest for five minutes, dilute to 100 ml. with water, and continue the digestion until all but the flocculent silica has dissolved. Filter on a Whatman No. 30 filter paper; wash three times with hot, 1:100 HCl and then six times with hot water. Fold the paper over the impure silica, and place in a tared platinum crucible. The filtrate is evaporated and the remaining silica dehydrated without addition of more acid. The silica obtained from the solution of this second dehydration is filtered separately as before and added to the platinum crucible.

The paper is dried in a 110°C oven or over a low flame, charred and the char glowed off. Finally, the residue is ignited to constant weight, preferably in the 950°C electric muffle furnace. The weight difference is the crude silica.

Place the platinum crucible in an air bath. Add one ml. water and one ml. of 50 % H_2SO_4 , and then fill 2/3 full with HF. Place over a suitable heater, and volatilize the silica without any bubbling occurring. When the volume of residual liquid has been lowered to about one ml., cool; add ten ml. more of HF, and repeat the volatilization. When the volume has again reached one ml., gradually raise the temperature to fume off the excess H_2SO_4 . Finally, make the temperature as high as possible, or place in the electric muffle furnace and ignite at 950°C to constant weight. Cool, and weigh the nonsilicious residue.

The difference in weight of the crucible before and after the silica

volatilization is the weight of pure silica in the ten ml. NaOH leach aliquot.

Determination of Barium After volatilization of the silica, fuse the residue in the platinum crucible with one g. of Na_2CO_3 at 950°C in the electric muffle furnace. Cool, and leach the cake with hot water. When the cake has loosened, remove it from the crucible to the leaching beaker, and scrub the crucible with a policeman. Clean the platinum crucible cover. Decant the leachings on a Whatman No. 42 filter paper. Continue digestion of the cake, crushing the lumps with a stirring rod. When the melt has completely disintegrated, finish the filtration and wash six times with hot water. Discard the filtrate.

Place a clean beaker under the funnel, and repeatedly pour over the melt residue 15 ml. portions of 0.5N HCl to dissolve the carbonates. When solution is complete, wash the paper six times with hot water. This filtrate is now combined with the filtrate from the second dehydration for silica.

Removal of heavy metals is now necessary. Adjust the acidity to 0.2 normal, using HCl and NH_4OH and spot tests with methyl violet to a blue-green color. Place the solution in a pressure flask, and, while heating to boiling, pass in H_2S . When the solution boils, close the exit and immediately remove from the heater, leaving the flask under a slight H_2S pressure. Shake occasionally to maintain saturation of the liquid with H_2S . After 20 minutes, turn off the H_2S , and filter on an asbestos pad in a Gooch crucible. Wash with hot, 0.05N HCl saturated with H_2S . This procedure removes copper, lead, silver, and molybdenum.

The filtrate is immediately made alkaline to a distinct odor with NH_4OH and is saturated with H_2S while being heated to near boiling. After 10 minutes, test with alkacid paper. If below a pH of eight, add more NH_4OH and continue the addition of H_2S for five minutes more. Filter on an asbestos pad in a Gooch crucible, and wash six times with warm 0.06M $(\text{NH}_4)_2\text{S}$ solution. (This wash solution is prepared by passing H_2S into 0.06M NH_4OH for two minutes.) The filtrate is immediately boiled to remove $(\text{NH}_4)_2\text{S}$. It is then acidified with dilute HCl, and the boiling is continued until the solution is free from H_2S .

Precipitate the barium from the hot solution by the dropwise addition of ten ml. of 0.5N H_2SO_4 .

Allow to digest on the steam bath for one hour, and set aside to cool. Filter on Whatman No. 42 filter paper, and wash with cold water until the washings are chloride free.

Place the paper in a previously weighed porcelain crucible, char the paper, glow off the char, and ignite to a white residue to constant weight.

Calculation:

The increase in weight of the crucible times the factor, 0.5885, is the barium content of the sample.

The hydrogen sulfide precipitate from the above procedure may be used for the determination of lead either by the electrolytic method given under Silica Method or by the sulfate method under Analysis of Barium Sulfate - Lead Sulfate Precipitate.

Determination of Lead The samples should be taken from the fresh hot solution as discussed in the introduction. Pipette two ml. of 50 % NaOH into a 25 ml. volumetric flask; then add from a pipette not more than one ml. of the sample. Add sufficient water to make the volume of the sample plus water equal one ml; then add one ml. of 0.1M NaCl and mix. Now fill to near the graduation mark with 1M NaOH, and thoroughly mix. Place the flask in the thermostatic bath, preferably at 30°C to facilitate keeping lead in solution.

The standard and blank may be prepared at the same time. The blank contains all of the reagents except that one ml. of water is used instead of the sample plus water. These are placed in the constant temperature bath. At the end of one-half hour, equilibrium temperature should have been reached. Fill each flask to the graduation mark with 1M NaOH, and mix thoroughly. Pour the entire contents of the flask into a 30 ml. beaker, and set it in the constant-temperature bath. Insert the dropping mercury electrode and the silver chloride electrode. (For the preparation of the silver chloride electrode, see the polarographic determination by the incremental method, taking readings at 0.60 and 1.15 volts and at the instrument sensitivity which gives nearly a full-scale reading. Determine like readings for the standard solution and the blank solution.

Calculation:

$$\mu a \text{ for sample} = \mu a \text{ for sample} - \mu a \text{ for blank}$$

$$\mu a \text{ per mg Pb} = \frac{\mu a \text{ for standard} - \mu a \text{ for blank}}{\text{mg Pb in standard}}$$

$$\text{milligrams lead sample} = \frac{(\mu a \text{ for sample}) (\mu a \text{ per mg Pb})}{\text{volume of sample}}$$

ANALYSIS OF SODIUM HYDROXIDE-SODIUM CARBONATE FILTRATE AND SODIUM CARBONATE FILTRATE

Silica, lead, and sulfate are the determinations to be made on these solutions. The fresh, hot solutions should be sampled at once, and aliquots taken for the determinations before cooling and precipitation occurs. If a

precipitate forms, it is practically impossible to dissolve it. Sample by agitating thoroughly to distribute the fine precipitate evenly, and pipette while the solution is in motion.

Determination of Sulfate The filtrate from the silica determination is used. Remove the heavy metals before precipitating the sulfate as BaSO_4 . Adjust the acidity with HCl to 0.2 normal by spot testing with methyl violet to a blue-green color. Heat to near boiling, and bubble in H_2S until the precipitate coagulates. Filter on a Gooch crucible with suction, and wash six times with hot, 0.1N HCl saturated with H_2S . Immediately make the filtrate alkaline with NH_4OH to a distinct odor and, while holding at near the boiling point, treat with H_2S gas for ten minutes. Test with alkacid paper, and, if the solution is not at pH8 or higher, add more NH_4OH and continue the addition of H_2S for five minutes more. Filter on Whatman No. 1 paper. If the filtrate is colored, boil the solution briefly to coagulate residual precipitate and then refilter. The filtrate is then boiled gently to remove $(\text{NH}_4)_2\text{S}$. Acidify with HCl , and continue boiling to remove H_2S . If the filtrate is allowed to stand, oxidation of some of the sulfur to sulfate may occur.

After removal of H_2S , the hot filtrate is adjusted to 0.1 molar in HCl and ten ml. of 0.25M BaCl_2 is added drop by drop from a burette while the solution is vigorously stirred. Set on the steam bath for a minimum of one hour; then allow to cool. Filter on Whatman No. 42 paper; wash with water until the washings are chloride free. Place the paper in a previously prepared porcelain crucible, and dry at 110°C . Char the paper over a low flame, and then allow the char to glow off. Ignite at 700° to 800°C to constant weight.

ANALYSIS OF BARIUM SULFATE-LEAD SULFATE PRECIPITATE

A 0.5 g. sample is mixed with six g. Na_2CO_3 (or four g. Na_2CO_3 and two g. K_2CO_3) in a platinum crucible. The crucible is placed on a silica triangle and gradually brought to fusion temperature with a Meker burner. The final fusion is best accomplished at 950°C in the electric muffle furnace. The crucible is cooled, and placed with the cover in a 250 ml. beaker for water extraction.

When ready to proceed without interruption, add hot water to the beaker, boil on a hot plate for a few minutes, and decant the solution through a paper filter. Add more hot water to the beaker and boil. Lift the crucible and lid out, rinse and scrub (use a rubber policeman and repeat rinsings). If lumps remain, they must be disintegrated by longer boiling and by triturating with a glass rod. Use a minimum of water in the above treatments (50 ml.). If more liquid is needed, use 0.01M Na_2CO_3 . Wash out the beaker with hot Na_2CO_3 wash solution. Add the wash solution to the filter, and wash the precipitate on the filter with four portions of hot water.

Pour hot 1N HCl through the filter paper, catching the filtrate in a 250 ml. beaker. Wash the paper thoroughly with this acid and then six times with

water. In this procedure the funnel must be covered at first to prevent spattering losses due to evolution of CO_2 .

Dry the paper, ignite, and weigh the ash to determine the insoluble residue. Use a platinum crucible. The insoluble residue may be silica and/or barium sulfate. If the ash is weighable, it must be treated with $\text{HF-H}_2\text{SO}_4$, ignited, and reweighed. A weighable residue at this point must be brought into solution by repeating the fusion and the resulting solutions combined.

The HCl solution of the carbonates is boiled to expel CO_2 . Now neutralize with $6\text{N NH}_4\text{OH}$ (litmus). Acidify with six normal acetic acid (to pH of two using alkacid paper). Precipitate the lead as PbS by passing in H_2S until coagulation is evident. Filter off the PbS , and wash the precipitate thoroughly (ten times) using 0.1 normal acetic acid saturated with H_2S . Keep the beaker of filtrate covered. The filtrate should be clear and colorless, denoting absence of lead. Pass H_2S into the filtrate again for 15 minutes to determine if precipitation is complete.

The precipitate is reserved for determination of lead electrolytically or as lead sulfate.

Determination of Barium Since air oxidation would cause BaSO_4 precipitation, the filtrate is immediately made alkaline with $6\text{N NH}_4\text{OH}$ (pH eight to nine), and H_2S passed in for ten minutes to precipitate any ammonium sulfide-group elements. After ten washings with $0.03\text{M (NH}_4)_2\text{S}$ wash solution, the precipitate is discarded unless needed for other determinations.

The filtrate and washings are now boiled for five to ten minutes to remove $(\text{NH}_4)_2\text{S}$. Remove the beaker from the heat, acidify to pH of one (as indicated by alkacid paper) with 6N HCl . Continue boiling until H_2S is completely removed.

Remove the beaker from the heater, and add ten ml. of $2\text{M H}_2\text{SO}_4$ dropwise from a burette with constant stirring to precipitate BaSO_4 . Return the beaker to the heater or steam bath, and hold at near the boiling point for one hour. Let stand for one hour or overnight at room temperature.

The precipitate of BaSO_4 is filtered on a No. 42 paper and washed eight times with hot water. Place the moist paper in a tared porcelain crucible, and dry in the oven or over a low flame. Char the paper over a low Bunsen flame, and when the paper is completely charred, ignite strongly to red heat for one-half hour. Cool in a desiccator, and weigh. Repeat the ignition, cooling, and weighing to constant weight.

Calculation:

$$\text{Per cent barium sulfate} = \frac{\text{wt. of precipitate}}{\text{wt. of sample}} \times 0.5885 \times 100$$

Determination of Lead, as Lead Sulfate The H_2S precipitate and paper or the Gooch crucible from the preliminary separation is placed in a 150 ml. beaker, treated with ten ml. conc. HNO_3 and ten ml. of $18\text{N H}_2\text{SO}_4$ and digested to

dissolve the sulfide and oxidize the paper. The H_2SO_4 is omitted if the Gooch filter was used. The solution is evaporated to SO_3 fumes. Cool, add ten ml. more HNO_3 , and evaporate to SO_3 fumes. Use more H_2SO_4 if needed to keep the residue in solution, and maintain a volume of ten ml. of H_2SO_4 . Repeat until all evidence of carbon is gone. Cool, and carefully wash down the sides of the beaker with water. Evaporate again to appreciable SO_3 fumes. Repeat the washings and fuming once more.

Now cool, dilute to 25 ml. with water, and heat to assist in the solution of impurities. Now add 50 ml. water with stirring. Let stand for one hour or overnight. Filter on a previously tared Gooch crucible ignited at 500° to 600°C . Wash the precipitate with cold 1:20 H_2SO_4 eight times. Dry in the oven, and then ignite for one hour at 500° to 600°C and weigh. Wash the precipitate with cold, 1:20 H_2SO_4 eight times. Dry in the oven and ignite again for one hour at 500° to 600°C . A muffle furnace is preferred to a burner. If ignited with a burner, the crucible should be placed inside an empty crucible over the burner. Cool in a desiccator, and weigh. Repeat to constant weight.

Calculation:

$$\text{Per cent lead} = \frac{\text{wt. of precipitate} \times 0.6832 \times 100}{\text{wt. of sample}}$$

Determination of Lead, Polarographically About 30 to 40 mg. BaSO_4 is soluble in 50 % NaOH near its boiling point. The procedure is identical with that for the determination of lead in the residue (see Analyses Made Directly on Residue Samples). If the lead content is too low to give a suitable polarographic wave on a 30 mg. sample, a larger sample, (50 to 70 mg.) may be used, and the digestion with two ml. of 50 % NaOH continued for seven to ten minutes before making up the solution.

Determination of Lead, Electrolytically Lead can be electrolytically deposited from NaOH solution on a smooth platinum electrode. Gauze electrodes tend to retain electrolyte tenaciously, even on very thorough washing, and therefore are not recommended. A controlled cathode potential plating unit is preferred for this work. A sample containing not more than 20 mg. of lead is digested with five ml. of hot 50 % NaOH with trituration. A five ml. glass stirring rod and a 50 ml. beaker are used. After the digestion is continued for five minutes at the boiling point, the beaker is removed from the hot plate, cooled to below 100°C , and diluted with warm, 1M NaOH . BaSO_4 will precipitate. The electrolysis is carried out at about 50°C . A platinum wire anode and a rectangular platinum cathode about 8 by 20 ml. with platinum lead wire are used. At the start of the electrolysis, the cathode potential can then be increased to 1.5 volts, and the electrolysis continued for another half-hour, by which time all lead should be deposited.

After lowering the electrolytic beaker, briefly rinse the electrodes and calomel control half-cell tip with a stream of water from the wash bottle. Place the beaker of water under the electrodes, and immerse the electrodes

allowing them to rinse for five minutes with stirring. Now lower the beaker, remove the cathode, shake off the adhering drop of water, dip the cathode in alcohol and in ether. The cathode is ready for immediate weighing. It is advisable to return the cathode to the electrolytic apparatus, continue the electrolysis for another half-hour, rewash, and reweigh. A drop of the electrolytic solution may be tested with H_2S .

The increase in weight of the cathode is the weight of lead in the sample.

ANALYSIS OF THE NITRIC ACID FROM THE CHROMATE-TO-NITRATE CONVERSION

The HNO_3 filtrate from the conversion of barium-radium chromate to the nitrate is a slightly diluted 70% HNO_3 . It contains all the chromium from the conversion as dissolved chromic acid. If not cleanly filtered, it may contain a little barium-radium nitrate, which settles on standing. The analytical determinations on this material are (1) the nitric acid concentration, (2) the chromic anhydride concentration, and (3) the barium content.

Determination of the Nitric Acid Concentration The HNO_3 concentration can be determined fairly closely by either making a density measurement with a hydrometer or pycnometer and checking the result in a conversion table, or by titrating a weighed sample with standard NaOH . The presence of chromic acid will cause errors in either result.

It is best to distill the sample to dryness. Since the chromium does not distill, the distillate can then be thoroughly mixed and be analyzed more accurately by the methods just mentioned.

Determination of Chromium A 300-ml. sample is distilled down to a small liquid residue with care since the chromic anhydride will decompose if it is too strongly heated. The residue is now diluted to 250 ml. with water in a volumetric flask, and aliquots of ten ml. removed for assay. After further dilution to a convenient volume, an aliquot is titrated with standardized 0.1N $\text{Na}_2\text{S}_2\text{O}_3$ solution. Since one ml. of standard 0.1 normal reagent is equivalent to 1.734 mg. of hexavalent chromium, the chromium content of the original acid is easily calculated as follows:

Grams chromium per ml. = ml. reagent X $\underline{N}$ X 0.01734 X 0.08333

Determination of Barium Distill a minimum of 300 ml. of the HNO_3 , dissolve the residue, and dilute to 250 ml. as described in the preceding paragraph. Treat the solution while hot with ten ml. of 1M H_2SO_4 and set aside overnight. Only a trace of precipitate can be expected. This is filtered on as small a filter as possible and weighed. Usually the barium precipitate is entirely absent or can be reported only as an unweighable trace.

VIII. REFERENCES

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