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CHEMICAL REFINEMENT PROCEDURES IN THE ELECTROMAGNETIC SEPARATION OF ISOTOPES

Boyd Weaver

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August 8, 1955

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Isotope Chemistry Department

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ABSTRACT

Procedures used in the chemical refinement of electromagnetically separated isotopes of 47 elements are given in outline form.

CHEMICAL REFINEMENT PROCEDURES IN THE ELECTROMAGNETIC SEPARATION OF ISOTOPES

Boyd Weaver

In the large-scale electromagnetic separation of isotopes the products are obtained mixed with a large number of other elements. Some of these are derived from the materials of the isotope collectors, which may be made of copper, aluminum, stainless steel, or some other metal. Even when the material is graphite, the small amounts of varied impurities may be very significant when compared with the amount of isotope collected. The separators, large articles of equipment constructed of various metals and ceramic materials, are subjected to high temperatures and large electrical discharges. Consequently surprising quantities of their constituents are deposited with the isotopes. The highly energetic atoms of the separated isotopes usually cause sputtering of considerable quantities of the collector materials and are then redeposited as mixtures.

The function of isotope refinement chemists is to make these chemically impure isotopes useful to scientists. Much important physical research has been done with separated isotopes as deposits on targets; but whenever isotopic homogeneity is essential, nuclear reactions are to be measured quantitatively, or the effects of other elements must be eliminated, it is necessary to convert the separated isotopes to stable, pure materials of definite composition. In the process of refining nearly all of the naturally occurring isotopes, the Chemistry Department of the Stable Isotope Research and Production Division of the Oak Ridge National Laboratory has devised and developed procedures for nearly all of the isotopic elements.

The scope of chemistry has involved most of the anisotopic elements as well, since nearly all of these must be considered as possible contaminants. The principles and techniques are combinations obtained from extensive reviews of the literature of analytical chemistry and the chemists' experiences. Much published modern analytical chemistry, with its emphasis on instrumental methods, has had to be ignored, except where quantitative separations are discussed. Volumetric and electrometric methods have no value, since the final products must be weighable. The isotope chemist must even go beyond the usual gravimetric analysis, in which the final result is obtained by weighing a product. Frequently correct gravimetric determinations are only fortuitous combinations of losses and residual impurities. Since chemical purity is important in isotopes, the products are examined by spectro-chemistry. In some cases where the sum of the observed impurities is too small to be considered a large error in gravimetric analysis, it is still necessary to eliminate undesirable trace contaminants. In order to conserve precious material, spectrographic methods have been developed which give semiquantitative determinations of most of the common elements on one milligram of material, with limits of estimation amounting to only a few hundredths of one per cent. Persistent detection of some elements as impurities has led to doubts concerning the efficiency of some standard methods of separation and the revision or replacement of these methods. Spectrographic analyses also give the chemists a greater realization of the magnitude of coprecipitation and adsorption in chemical processes, as well as the importance of extreme care in performing chemical separations.

This report is intended as a brief compilation of refinement methods which may be useful to others engaged in the same functions or in chemical separations involving a large number of elements. The methods are given

in concise, skeletal form, meaningful only to those who can fill in the details. Exact quantities such as sizes of equipment and weights or volumes of reagents are usually omitted because of the large range of quantities of isotopes involved--from a few milligrams to many grams. The particular impurities removed by each step are not given. There is no indication of the frequent necessity to repeat steps and to process precipitates for the recovery of desired elements.

The procedures presented are those which are currently considered the best for the elements involved. Each of them is the result of the experience of one or more chemists and is influenced by personal preferences. In a few cases slight modifications have been made from applied procedures in order to provide greater consistency between elements with similar chemical behavior. Otherwise each has been tested by application to one or more isotopes.

No pretense is made that these are the final best procedures. Some of them lack experience in application. There is still considerable dissatisfaction with some, particularly that for antimony. Only a great amount of effort has removed ruthenium from an equally unsatisfactory status. Much further development in both chemical refinement and in spectrochemistry will be necessary whenever requirements of extreme purity occur. This demand has already been met successfully in the case of boron as a trace contaminant in the isotopes of several elements.

There is now in preparation a series of reports on chemistry in the electromagnetic separation of isotopes. Each report will treat a single element with respect to both the materials with which the separators are charged and the chemical refinement of the separated isotopes. It will give in some detail the background chemistry of each element, the experiences through which

procedures were developed, and results obtained by at least the latest procedure. This is a large undertaking, though most of the necessary information has been filed by chemists who performed the work. In the meantime the following brief procedures are offered as a contribution to the knowledge of chemical separation, which is the essence of analysis.

ACKNOWLEDGMENTS

The development and application of these procedures has been a cooperative achievement of all present and former members of the Chemistry Department. Those who are now engaged in this work are R. L. Bailey, W. C. Davis, F. A. Kappelmann, L. T. Royer, F. M. Scheitlin, C. W. Sheridan, and F. B. Thomas. The many suggestions of Dr. H. H. Willard, Consultant, have been very helpful. The Spectrochemical Laboratory, under the leadership of J. A. Norris, has made invaluable contributions to all of our progress.

I. Lithium

1. Dissolve Li from Cu pockets with dilute HCl, digest, and filter.
2. Make H_2S precipitation and filter.
3. Make alkaline with NH_4OH, introduce more H_2S, and filter.
4. Acidify filtrate with HCl, boil, and filter off S.
5. Destroy ammonium salts with aqua regia, then destroy nitrates by repeated treatments with boiling HCl and HCOOH. Remove HCOOH with HCl.
6. Dilute, boil, and precipitate sulfate with minimum of $BaCl_2$. Filter.
7. Evaporate filtrate to dryness and extract LiCl with a 1:1 mixture of pyridine and acetone or with 2-ethyl hexanol.
8. Filter through fritted glass and evaporate the volatile solvent. LiCl should be washed from 2-ethyl hexanol with water and dried.
9. Dissolve LiCl in H_2O, add excess H_2SO_4, and evaporate to dryness in Pt. Ignite carefully to 900°C.
10. Dissolve Li_2SO_4 in H_2O, filter, and evaporate to dryness.
11. Complete drying in oven at 150-200°C.

II. Boron

1. Scrape most of B from Cu (wet with H_2O).
2. Wash pocket with 1:1 HNO_3 to obtain remainder of B.
3. Transfer solids and solutions to flask with reflux condenser and add HNO_3 to complete solution.
4. Transfer to beaker, make alkaline with NaOH, and filter through paper. Evaporate to crystals.
5. Transfer to distilling flask, add CH_3OH, and acidify slightly with CH_3COOH.
6. Heat slowly and distill methyl borate in a stream of air at 65°C, collecting in a flask containing 8 N HCl and protected by a reflux condenser.
7. Heat to reflux and hydrolyze methyl borate.
8. Cool and transfer to a large beaker with cover.
9. Dry on steam bath to H_3BO_3.
10. Dissolve in H_2O and shake with decolorizing charcoal. Filter and dry on steam bath.

III. Carbon

Carbon isotopes have been processed only by washing repeatedly with HNO_3 and drying. Complete purification and preparation of homogeneous material can be obtained only by carrying the carbon through a chemical cycle such as that used in the Libby C^{14} dating technique. It is not quantitative.

IV. Magnesium

1. Dissolve Mg from Cu pockets with dilute HNO_3 and evaporate to near dryness.
2. Dissolve and filter.
3. Remove Cu from dilute solution by electrolysis with Pt or Cu electrodes.
4. Destroy nitrate by repeated additions of HCl and evaporation.
5. Make sulfide precipitation from dilute HCl and then from ammoniacal solution and filter.
6. Acidify with HCl, evaporate to near dryness, dilute, and filter through paper.
7. Make strongly basic with NH_4OH.
8. Add alcoholic 8-hydroxyquinoline until reddish color appears. Heat to $60^{\circ}C$ and let settle for 30 minutes.
9. Filter on fritted glass, wash with hot dilute NH_4OH, and dry on filter.
10. Transfer to Pt dish, cover with $H_2C_2O_4$, and heat to melting and resolidification.
11. Heat in furnace slowly to $800^{\circ}C$ to give MgO.

V. Silicon

1. Loosen Si from Cu pockets with HNO_3 and concentrate.
2. Add HCl, boil, dilute, and filter.
3. Add $HClO_4$ to filtrate, evaporate to fumes, dilute, and filter.
4. Combine solids and ignite at 1000°C.
5. Fuse SiO_2 with Na_2CO_3 in Pt.
6. Dissolve in H_2O and filter through paper in plastic funnel into plastic beaker.
7. Add $HClO_4$, transfer to glass beaker, heat to fumes of $HClO_4$, dilute, filter and ignite.
8. Repeat fusion, solution, and $HClO_4$ dehydration of SiO_2.
9. Dilute, filter, and ignite in Pt at 800°C.

VI. Sulfur

1. Reduce CuS with H_2 in silica tube at 900°C, collecting H_2S in series of traps containing NH_4OH and $CdCl_2$.
2. Combine all CdS precipitates and wash with H_2O in centrifuge.
3. Add excess $FeCl_3$ and acidify to 3 N HCl. Seal with sulfur-free stopper.
4. Shake until all CdS is oxidized to S.
5. Filter S on hard paper and wash with H_2O, then sparingly with ethanol.
6. Dissolve S with CS_2 into evaporating dish.
7. Evaporate CS_2 over warm H_2O and dry S in oven at 100°C.

VII. Chlorine

Recovery from collection on Mg in Cu pockets

1. Leach Mg dust and turnings with cold H_2O, filter.
2. Make just alkaline with Na_2CO_3, reduce volume to boiling
3. Filter, evaporate to near dryness, and transfer to still.

Recovery from collection on Ba in Cu pockets

1. Dissolve $BaCl_2$ and Ba in H_2O.
2. Filter and reduce volume to half by boiling.
3. Cool, filter out $Ba(OH)_2$ crystals, and reduce volume to half. Redissolve $Ba(OH)_2$, concentrate, and filter.
4. Combine filtrates and precipitate $BaCO_3$ with Na_2CO_3.
5. Filter, evaporate to near dryness, and transfer to still.

Purification

1. Add H_2SO_4 to still, heat, and collect HCl in air stream in flask of cold water connected to a test tube containing dilute NaOH.
2. Titrate HCl very carefully with NaOH to exact neutrality.
3. Dry NaCl by evaporation, transfer to Pt dish, and fuse.
4. Cool NaCl, dissolve in H_2O, filter through paper into silica ware, evaporate carefully, and dry at 300-400°C.

VII. Chlorine (Alternate Method)

1. Recover Cl_2 from metal collectors as salt in H_2O (as described above).
2. Acidify slightly with HNO_3.
3. Add sufficient $AgNO_3$ to precipitate all chloride.
4. Centrifuge and wash with H_2O.
5. Dissolve AgCl with NH_4OH, filter, and reprecipitate by neutralizing with HNO_3 and adding $AgNO_3$. Centrifuge and wash.
6. Dissolve AgCl with NH_4OH.
7. Prepare a Dowex 50 cation exchange column in the NH_4+ form and free of halides.
8. Prepare a Dowex 50 cation exchange column in the Na+ form and free of halides.
9. Pour the NH_4OH solution of AgCl through the first column, wash thoroughly with H_2O, and collect the effluent NH_4Cl solution.
10. Pour the NH_4Cl solution through the second column, wash thoroughly with water, and collect the effluent NaCl solution.
11. Evaporate to dryness, fuse in silica ware, dissolve in H_2O, filter, and dry at 300-400°C.

VIII. Potassium

1. Dissolve K from Cu pockets with H_2O followed by dilute HNO_3.
2. Remove Cu by electroplating on Pt or Cu electrodes.
3. Decompose HNO_3 by repeated evaporations with HCl and finally with HCOOH. Dilute and filter.
4. Make H_2S precipitation from dilute HCl solution. Filter.
5. Add freshly prepared ammonium sulfide and filter.
6. Acidify with HCl, boil, filter off S.
7. Avaporate filtrate to dryness and destroy ammonium salts with aqua regia.
8. Add excess $HClO_4$, evaporate to near dryness, dissolve in H_2O, and filter.
9. Add minimum amount of $BaCl_2$ to precipitate sulfate and filter.
10. Add $HClO_4$ and evaporate to dryness. Repeat with evaporation only to strong fumes of $HClO_4$. Dilute with equal volume of H_2O.
11. Cool solution to 0^oC and add equal volume of cold C_2H_5OH. Let stand for 15 minutes and filter on cold fritted glass. Wash with cold C_2H_5OH containing 0.2% $HClO_4$.
12. Wash $KClO_4$ through filter with hot H_2O into silica ware, evaporate to dryness and heat slowly to above 650^oC until conversion to KCl is complete.
13. Dissolve KCl in minimum H_2O, evaporate, and dry at 200^oC.

IX. Calcium

1. Dissolve Ca from Cu pockets with dilute HNO_3 and evaporate to near dryness.
2. Dissolve in H_2O and filter.
3. Remove Cu from dilute solution by electroysis with Pt or Cu electrodes.
4. Destroy nitrate by repeated additions of HCl, evaporation, and final treatment with HCOOH.
5. Make sulfide precipitation from very dilute HCl and then from ammoniacal solutions, filter, acidify filtrate with HCl, and boil off H_2S.
6. Precipitate Ca with NH_4OH and $(NH_4)_2C_2O_4$ at pH 6, filter, and ignite.
7. Redissolve in HCl, reprecipitate, filter, and ignite.
8. Redissolve in HCl, evaporate to dryness, dissolve in very dilute HCl, filter off SiO_2. Repeat.
9. Precipitate CaC_2O_4 from homogeneous solution by hydrolysis of methyl oxalate at 80-100°C.
10. Filter and ignite in porcelain to $CaCO_3$ carefully at no higher than 525°C.

X. Titanium

1. Ignite carbon pockets to 800°C.
2. Dissolve ash in 18 N H_2SO_4 and HF and dilute.
3. Filter through paper in plastic funnel into plastic beaker.
4. Precipitate $Ti(OH)_4$ with NH_4OH, wash in centrifuge.
5. Dissolve in saturated tartaric acid, make alkaline with NH_4OH, and saturate with H_2S.
6. Heat to coagulate sulfide, filter, wash with H_2S in H_2O.
7. Acidify filtrate with dilute H_2SO_4, boil, and filter.
8. Adjust to 1-2 N H_2SO_4, cool to 0°C, and add saturated cupferron in excess.
9. Filter on paper and wash with 1 N HCl and then with H_2O.
10. Dry, heat slowly, and ignite in porcelain at 700-800°C to TiO_2.

XI. Vanadium

Small quantities (V^{50})

1. Ignite carbon pockets at 600°C (V_2O_5 melts at 695°)
2. Dissolve ash in HCl and dilute.
3. Make sulfide precipitation, boil, and filter.
4. Concentrate filtrate and add to boiling 10% NaOH in excess. Filter.
5. Acidify filtrate with HCl, heat, and filter.
6. Cool filtrate in ice water and add cold 6% cupferron with stirring. Let stand 1 hour and filter. Wash with cold 1% HCl containing cupferron.
7. Ignite in porcelain at 500°C to give V_2O_5.

Large quantities (V^{51})

1. Ignite carbons at 600°C.
2. Dissolve ash in HCl, dilute and filter.
3. Make alkaline with NH_4OH, cool, and add H_2O_2.
4. Saturate with NH_4Cl and digest on steam bath over night. Filter NH_4VO_3 on paper.
5. Ignite in porcelain at 500°C to V_2O_5.

XII. Chromium

1. Ignite carbon pockets.
2. Dissolve and oxidize ash in boiling $HClO_4$.
3. Cool, filter CrO_3 on glass, dissolve in H_2O.
4. Make NH_4OH precipitation, filter on paper.
5. Acidify filtrate with H_2SO_4, reduce Cr(VI) with SO_2.
6. Precipitate $Cr(OH)_3$ with NH_4OH, filter on paper.
7. Ignite in porcelain to Cr_2O_3 at 1000°C.

XIII. Iron

1. Dissolve Fe from Cu pockets with HNO_3. Ignite carbon pockets and dissolve ash in HCl.
2. Dilute and filter.
3. Make repeated precipitations with NH_4OH, filtrations, and solutions with HCl until ammoniacal filtrate is free of Cu color.
4. Make H_2S precipitation from 6 N HCl. Filter.
5. Add tartaric acid to filtrate and make alkaline with NH_4OH. Saturate with H_2S, heat to coagulate, filter, and wash with dilute ammonium tartrate, then with hot H_2O.
6. Dissolve precipitate in 6 N HCl, add H_2O_2, and boil.
7. Cool, add H_2SO_4, and evaporate to dryness.
8. Dissolve in H_2O and filter.
9. Cool filtrate to 0^oC and add cold 6% cupferron solution. Filter and wash with ice-cold H_2O and then with cold 1:1 NH_4OH.
10. Ignite in silica ware at low heat and finally at 700^oC to give Fe_2O_3.

XIV. Nickel

A. Quantities less than 1 gram.

1. Ignite carbon pockets at 650°C in O_2.
2. Dissolve ash with HCl and H_2O_2, dilute, and filter.
3. Make alkaline with NH_4OH, digest, and filter.
4. Acidify filtrate with CH_3COOH.
5. Precipitate Ni with ethanol solution of dimethylglyoxime and filter.
6. Dissolve precipitate with 6 N HNO_3.
7. Dilute and electrolyze with Pt electrodes at 1 ampere.
8. Add H_2SO_4 and evaporate to dryness.
9. Dissolve in H_2O, filter, and evaporate to dryness.
10. Ignite in silica at 900°C.

B. Quantities greater than 1 gram.

1. Ignite carbon pockets at 650°C in O_2.
2. Dissolve ash with HCl and H_2O_2, dilute, and filter.
3. Make alkaline with NH_4OH, digest, and filter.
4. Acidify filtrate with H_2SO_4.
5. Saturate with H_2S, digest, and filter.
6. Evaporate filtrate to dryness, dissolve in H_2O and filter.
7. Evaporate filtrate to dryness and ignite in silica ware at 900°C.
8. Digest with boiling H_2O, filter, dry, and ignite to NiO in silica at 900°C.

XV. Copper

1. Ignite carbon pockets at 650°C in silica ware.
2. Dissolve ash in HNO_3, dilute, and filter.
3. Electrodeposit Cu on Pt at 1 ampere.
4. Dissolve in 6 N HNO_3 and filter.
5. Evaporate to dryness in a beaker and gradually heat to 350°C. to give CuO.

XVI. Zinc

1. Remove Zn from Cu pockets by vacuum sublimation at 450-500° in Pyrex tube. Condense Zn in cool part of tube.
2. Dissolve Zn from tube with HNO_3 and convert to sulfate.
3. Dilute sulfate solution to 3 N H_2SO_4 and precipitate Cu and Cd with H_2S. Dilute to 1 N H_2SO_4 and precipitate remaining Cd with H_2S.
4. Dilute and buffer to pH 3.5 with citric acid and NH_4OH. Precipitate Zn with H_2S.
5. Filter ZnS, dissolve from filter with 2 N H_2SO_4, and reprecipitate from ammonium citrate at pH 3.5. Filter.
6. Dissolve with HCl and evaporate to dryness.
7. Dissolve in H_2O and make NH_4OH precipitation.
8. Filter, adjust pH of filtrate to 3.5 with H_2SO_4, and precipitate ZnS again. Dissolve in HCl and dry.
9. Dissolve in little H_2O and add $H_2C_2O_4$ in C_2H_5OH. Digest cold and filter.
10. Heat precipitate slowly to 400°C in Pt and ignite at 1100°C to ZnO.

XVII. Gallium

1. Ignite carbon pockets in O_2 at 650°C.
2. Dissolve ash in HI and filter.
3. Decompose iodide with HNO_3 and dilute with H_2O.
4. Add NaOH in polyethylene to pH 11.5 and filter on paper.
5. Adjust filtrate to pH 7.5 with HNO_3, filter on paper, and wash thoroughly with H_2O.
6. Ignite in porcelain to Ga_2O_3 at 650°C.

XVIII. Germanium

1. Dissolve Ge from carbon pockets with 3% H_2O_2.
2. Obtain remaining Ge by ignition of carbon at 850°C.
3. Dissolve ash in much hot H_2O.
4. Combine solutions, filter through paper, and boil.
5. Add 2-5 g of $(NH_4)_2SO_4$ and enough 10% tannic acid to precipitate Ge.
6. Cool, centrifuge, and wash with 5% NH_4NO_3 solution.
7. Filter on paper by suction.
8. Ignite carefully in porcelain--keep temperature below 400°C until completely charred, then raise to 1000°C to give GeO_2.

XIX. Selenium

1. Dissolve Se from Cu pockets with HNO_3.
2. Remove HNO_3 by evaporation with HCl on steam bath. Dilute and filter.
3. Adjust to 6 N HCl and add $NH_2OH \cdot HCl$ and SO_2.
4. Digest on steam bath until reddish precipitate becomes gray and coagulates.
5. Centrifuge and wash with 6 N HCl, then with H_2O, and finally with C_2H_5OH.
6. Dry in centrifuge tube at 110°C.

XX. Bromine (See VII. Chlorine)

Method for quantitative removal of chloride impurity in NaBr has not been developed.

XXI. Rubidium

1. Dissolve Rb from Cu pockets with 1:1 HCl.
2. Evaporate to dryness, dissolve in very dilute HCl, and filter.
3. Electrolyze filtrate using carbon sheet electrodes, filter.
4. Make alkaline with NH_4OH and introduce H_2S. Filter.
5. Acidify slightly with HCl, boil, precipitate with $BaCl_2$, and filter.
6. Evaporate filtrate to dryness and transfer to silica dish.
7. Fuse RbCl.
8. Dissolve in H_2O, evaporate to dryness, redissolve, and filter.
9. Remove Ca by NH_4OH and $(NH_4)_2CO_3$ precipitation.
10. Acidify with HCl and evaporate to dry RbCl.
11. Remove Na and K, if present.
    (a) charge on 3 ft. column of amberlite I R-100 and elute with 0.1 N HCl, or
    (b) charge on 3 ft. column of Dowex-50 and elute with 0.3 N HCl.

    Ion exchange separation of these elements is only fractional and requires repetition.

XXII. Strontium

1. Dissolve Sr from Cu pockets by dilute HNO_3 and evaporate to near dryness.
2. Dissolve in H_2O and filter.
3. Remove Cu from dilute solution by electrolysis with Pt or Cu cathode.
4. Destroy nitrate by repeated additions of HCl and evaporation.
5. Make sulfide precipitation from dilute HCl and then from ammoniacal solution. Filter.
6. Acidify filtrate with HCl and evaporate to dryness.
7. Dissolve in H_2O and filter.
8. Make alkaline with NH_4OH, precipitate with $(NH_4)_2CO_3$, filter, and wash with $(NH_4)_2CO_3$ solution.
9. Ignite in porcelain at 800-900°C and weigh as $SrCO_3$.

XXIII. Zirconium

1. Strip Zr from Cu pockets with 1:1 HNO_3, digest, dilute, and filter.
2. Treat filtrate as follows:
   a. Add excess NH_4OH and filter.
   b. Dissolve precipitate with 1:1 HNO_3 and dilute.
   c. Remove Cu by electroplating at 1 ampere and filter.

This may be applied to filtrate from (1) if Cu is moderate.

3. Treat undissolved Zr metal as follows:
   a. Dissolve metal by repeated digestions with HNO_3 - H_2SO_4, dilute and filter.
   b. If Cu is high, electroplate at 1 ampere and filter.
4. Combine filtrates from 2(c) and 3(a) or 3(b), precipitate $Zr(OH)_4$ with NH_4OH, and filter, washing with dilute NH_4OH.
5. Dissolve $Zr(OH)_4$ with 6 N HCl and dilute to 3 N.
6. Precipitate Zr with excess 16% dl-mandelic (phenylglycolic) acid solution (at least 150 ml per gram of ZrO_2).
7. Digest at 85°C for 20 minutes and filter.
8. Ignite mandelate to ZrO_2 by gradual heating in porcelain to 1000°C.

XXIV. Molybdenum

1. Recover Mo from carbon pockets by ignition in a stream of O_2 in a silica tube at 800-850°C, collecting MoO_3 in cool part of tube.
2. Dissolve MoO_3 with NaOH solution, acidify with H_2SO_4, and filter.
3. Dilute filtrate, add H_2SO_3, and boil to remove excess SO_2.
4. Cool to 0°C and precipitate Mo with α-benzoin oxime. Filter on paper.
5. Dry precipitate and ignite at 500°C.
6. Dissolve MoO_3 in NH_4OH, filter, acidify with H_2SO_4, and precipitate with α-benzoin oxime.
7. Dry precipitate and ignite in porcelain at 500°C to give MoO_3.

XXV. Ruthenium

1. Ignite carbon pockets in silica tube with O_2 at no more than 650°C and flush tube with N_2.
2. Reduce Ru oxides to Ru with H_2 at 800°C.
3. Digest solids in beaker with hot 6 N HNO_3 and filter on paper.
4. Ignite paper and contents at 600°C.
5. Solubilize ash by repeated fusions of 5:1 KOH-KNO_3 mixture in Ag dish. Dissolve in H_2O.
6. Acidify solution with HCl and filter.
7. Saturate filtrate with H_2S, boil, let settle 24 hours, and filter on paper.
8. Ignite slowly to 650°C in silica dish.
9. Digest with hot concentrated HNO_3, dilute, and filter on paper.
10. Ignite paper and contents at 600°C.
11. Reduce to Ru with H_2 in silica tube at 800°C.

If other platinum group metals are present, the Ru may be distilled from them as RuO_4 by the procedure of Gilchrist (J. Am. Chem. Soc. 57, 2565 (1935))

XXVI. Palladium

1. Ignite carbon pockets in silica at 650°C.
2. Dissolve ash in aqua regia, dilute, and filter.
3. Precipitate Pd from filtrate with dimethylglyoxime in ethanol.
4. Ignite carefully in silica ware to PdO at 800°C.
5. Reduce PdO with HCOOH and dry at 110°C.

XXVII. Silver

1. Dissolve Ag from Cu pockets with HNO_3. Dilute with H_2O and filter.
2. Precipitate AgCl with HCl and centrifuge.
3. Dissolve AgCl with NH_4OH.
4. Reprecipitate AgCl by acidifying with HNO_3, centrifuge, and wash with H_2O.
5. Dissolve AgCl in NH_4OH, add hydroquinone, and warm to precipitate Ag.
6. Centrifuge Ag and wash with C_2H_5OH.
7. Dry Ag at 150°C.

XXIX. Indium

1. Ignite carbon pockets in O_2 at 650°C.
2. Dissolve ash in dilute HNO_3-H_2SO_4 and filter.
3. Precipitate $In(OH)_3$ with NH_4OH, digest on steam bath, and filter on paper.
4. Dissolve precipitate with dilute HNO_3, reprecipitate with NH_4OH, and centrifuge.
5. Dissolve $IN(OH)_3$ in hot 16% dl-mandelic (phenylglycolic) acid, let cool, and filter on paper.
6. Ignite carefully in porcelain to In_2O_3 at 700°C.

XXVIII. Cadmium

1. Remove Cd from Cu pockets by vacuum sublimation at 500°C in Pyrex tube. Condense Cd in cool part of tube.
2. Dissolve Cd from tube with HNO_3 and convert to sulfate.
3. Make sulfide precipitation from 9 N H_2SO_4 and filter through paper.
4. Precipitate CdS from 2 N H_2SO_4 and filter.
5. Dissolve CdS in HCl and evaporate to dryness.
6. Dissolve in minimum H_2O and dilute with C_2H_5OH.
7. Precipitate cadmium oxalate with $H_2C_2O_4$ in C_2H_5OH.
8. Filter and ignite carefully to 850°C in Pt to give CdO.

XXX. Tin

1. Ignite carbon pockets.
2. Reduce SnO_2 with H_2 for 24 hours at 550°C. Sweep with argon.
3. Chlorinate first at room temperature and then at 200°C, collecting gases in H_2SO_4 - HCl solution.
4. Precipitate SnO_2 with NH_4OH.
5. Centrifuge and wash with NH_4NO_3.
6. Dissolve in HCl, add tartaric acid and NH_4OH. Saturate with H_2S, heat to boiling, and filter on paper.
7. Acidify filtrate with HCl, precipitating SnS_2.
8. Heat to boiling, filter, and wash with NH_4NO_3.
9. Ignite SnS_2 in porcelain to SnO_2 at 900°C.

XXXI. Antimony

1. Dissolve Sb from stainless steel pockets with aqua regia.
2. Boil to complete solution, dilute, and filter.
3. Destroy HNO_3 by repeated boiling with HCl.
4. Precipitate Sb_2S_3 with H_2S and filter.
5. Dissolve Sb_2S_3 with HCl in reflux flask.
6. Add 100 g citric acid and neutralize with NH_4OH.
7. Add 100 g KCN and 100 g sodium hydrosulfite, $Na_2S_2O_4 \cdot 2H_2O$, and digest 2 hours on steam bath. Centrifuge.
8. Treat solution with more reductant until no more precipitate is obtained.
9. Wash Sb repeatedly with H_2O, then with ethanol, and dry at 110°C. Further purification, including specific procedures for removal of Sn and As, may be necessary.

XXXII. Tellurium

1. Dissolve Te from Al pockets with HNO_3 and aqua regia.
2. Evaporate to dryness on a steam bath.
3. Add HCl and evaporate to strong fumes.
4. Dilute to 3 N HCl, add hydrazine hydrochloride, and heat.
5. Introduce SO_2until Te precipitates. Filter and add more SO_2 to filtrate.
6. Add about 1 g of $Fe_2(SO_4)_3$, make alkaline with NaOH, and filter $Fe(OH)_3$ with residual Te.
7. Dissolve precipitate with HCl and reduce again with hydrazine and SO_2.
8. Combine Te fractions, dissolve in 1:1 HNO_3, convert to chloride solution, and repeat reduction.
9. Wash Te in centrifuge successively with warm H_2O, diethyl ether, and ethanol.
10. Dry at 110°C.

XXXIII. Barium

1. Dissolve Ba from Cu pockets with dilute HNO_3 and evaporate to near dryness.
2. Dissolve in H_2O and filter.
3. Remove Cu by electrolysis with Pt or Cu cathode.
4. Destroy nitrate by repeated additions of HCl, evaporation, and final treatment with HCOOH.
5. Make sulfide precipitation from very dilute HCl and then from ammoniacal solution. Filter. Acidify filtrate with HCl and boil off H_2S.
6. Precipitate $BaCO_3$ from filtrate with NH_4OH and $(NH_4)_2CO_3$ and filter or centriguge, washing with H_2O.
7. Dissolve $BaCO_3$ with CH_3COOH, filter, repeat precipitation, centrifuge, and wash with H_2O and acetone.
8. Dry at 250°C and analyze.
9. If Ca and Sr are present, dissolve $BaCO_3$ in CH_3COOH, add $(NH_4)_2CrO_4$ and digest on steam bath. Centrifuge and wash.
10. Dissolve in HCl and H_2SO_4 and wash $BaSO_4$ in centrifuge tube with H_2O and acetone.
11. Dry $BaSO_4$ and fuse with Na_2CO_3 in Pt, soak with hot H_2O and wash $BaCO_3$ in centrifuge.
12. Dissolve $BaCO_3$ in CH_3COOH and filter into NH_4OH and $(NH_4)_2CO_3$. Digest on steam bath, cool, and wash with very dilute $(NH_4)_2CO_3$.
13. Ignite in Pt to 800°C.

XXXIV. Lanthanum

1. Ignite carbon pockets at 700°C in O_2.
2. Dissolve ash in HCl and filter.
3. Precipitate $La(OH)_3$ with NH_4OH and filter.
4. Dissolve in hot citric acid solution.
5. Make H_2S precipitation and filter.
6. Make filtrate ammoniacal, add H_2S, and filter.
7. Make filtrate 0.5 N in HNO_3, boil, and filter.
8. Precipitate $La_2(C_2O_4)_3$ from filtrate with $H_2C_2O_4$ and filter.
9. Ignite in porcelain to La_2O_3 at 900°C. Protect La_2O_3 from atmospheric H_2O and CO_2.

XXXV. Cerium

1. Ignite carbon pockets at 700°C in O_2.
2. Dissolve CeO_2 with HNO_3 and H_2O_2.
3. Precipitate $Ce(OH)_4$ with NH_4OH, adding excess H_2O_2 to oxidize Ce completely.
4. Boil off all excess H_2O_2 and filter.
5. Dissolve $Ce(OH)_4$ with 3 N HNO_3 and extract Ce with 4 equal volumes of diethyl ether. Reprocess aqueous solution through oxidation, precipitation, solution, and extraction. Protect from light as much as possible through all operations.
6. Wash Ce from ether with H_2O.
7. Precipitate $Ce(OH)_4$ with NH_4OH and centrifuge.
8. Dissolve $Ce(OH)_4$ in hot citric acid solution.
9. Make H_2S precipitation and filter.
10. Make filtrate ammoniacal, add H_2S, and filter.
11. Make filtrate 0.5 N in HNO_3, boil, and filter.
12. Precipitate $Ce_2(C_2O_4)_3$ from filtrate with $H_2C_2O_4$ and filter.
13. Ignite in porcelain to CeO_2 at 900°C.

XXXVI. Neodymium

1. Ignite carbon pockets at 700°C in O_2.
2. Dissolve ash in HCl and filter.
3. Precipitate $Nd(OH)_3$ with NH_4OH and filter.
4. Dissolve precipitate in CH_3COOH, dilute, and make H_2S precipitation. Filter.
5. Precipitate $Nd_2(C_2O_4)_3$ with $H_2C_2O_4$. Filter on paper.
6. Ignite to Nd_2O_3 (may contain other rare earths).
7. Dissolve Nd_2O_3 in HCl and place on column of fine Dowex 50 cation exchanger. Elute with 5% citric acid buffered to pH 3.1. Collect fractions and reprocess as needed.
8. Precipitate $Nd_2(C_2O_4)_3$ and ignite in porcelain at 900°C. Protect Nd_2O_3 from atmospheric CO_2 and H_2O.

XXXVII. Samarium

1. Ignite carbon pockets at 700°C in O_2.
2. Dissolve ash in HCl and filter.
3. Precipitate $Sm(OH)_3$ with NH_4OH and filter.
4. Dissolve precipitate in CH_3COOH, dilute, and make H_2S precipitation. Filter. Precipitate $Sm_2(C_2O_4)_3$ with $H_2C_2O_4$. Filter on paper.
5. Ignite to Sm_2O_3.
6. Dissolve in CH_3COOH.
7. Shake with sufficient 0.25 N sodium amalgam to reduce all Sm and Eu to amalgams. Discard aqueous.
8. Wash amalgam sparsely with 1:1 CH_3COOH to remove Eu. Some Sm may be washed out.
9. Wash samarium from amalgam with dilute HNO_3.
10. Precipitate oxalate and ignite in porcelain at 900°C to Sm_2O_3.

XXXVIII. Gadolinium

1. Ignite carbon pockets at 700°C in O_2.
2. Dissolve ash in HCl.
3. Precipitate $Gd(OH)_3$ with NH_4OH and filter.
4. Dissolve precipitate in CH_3COOH, dilute, and make H_2S precipitation. Filter.
5. Precipitate $Gd_2(C_2O_4)_3$ with $H_2C_2O_4$. Filter on paper.
6. Ignite to Gd_2O_3. (May contain other rare earths).
7. Dissolve Gd_2O_3 in CH_3COOH.
8. Shake with sufficient 0.25 N sodium amalgam to reduce all Sm and Eu to amalgams. Separate phases.
9. Precipitate $Gd_2(C_2O_4)_3$, filter, and ignite.
10. Dissolve Gd_2O_3 in HCl and place on column of fine Dowex 50 cation exchanger. Elute with 5% citric acid buffered to pH 3.1. Collect fractions and reprocess according to purity.
11. Precipitate $Gd_2(C_2O_4)_3$, filter, and ignite in porcelain at 900°C to Gd_2O_3.

XXXIX. Hafnium (See XXIII. Zirconium)

XL. Tantalum

1. Recover Ta from carbon pockets by scraping with a steel scraper attached to a vacuum system, by which all dust is drawn into a fritted glass funnel.
2. Ignite dust at 600°C in Pt.
3. Dissolve ash in mixture of HNO_3 and HF, dilute with H_2O, and filter on plastic funnel into another Pt dish.
4. Precipitate $Ta_2O_5 \cdot xH_2O$ with NH_4OH, filter, and redissolve with dilute HF. Repeat to removal of Cu.
5. Add equal volume of $HClO_4$, boil to strong fumes of $HClO_4$ and cool.
6. Decant $HClO_4$, wash several times by decantation with concentrated HNO_3, then with dilute HNO_3.
7. Filter on paper and wash with dilute HNO_3.
8. Ignite in porcelain at 600° to Ta_2O_5.

XLI. Tungsten

1. Remove W from Cu pockets by scraping and leaching with aqua regia. Boil to oxidize W to WO_3.
2. Dilute with H_2O and filter on paper.
3. Heat filtrate and add cinchonine solution to precipitate traces of WO_3.
4. Dissolve WO_3 through paper with NH_4OH.
5. Adjust pH to 8 with HCl, saturate with H_2S, dilute, boil, and let cool. Filter through paper.
6. Acidify with HCl, boil, add aqua regia, concentrate, dilute, boil, and add cinchonine solution. Boil 30 minutes and let cool over night.
7. Filter on paper and wash with cinchonine solution.
8. Dry, char, and ignite carefully to 700°C in silica ware.
9. Transfer to Pt, heat with HF and H_2SO_4, and ignite to WO_3.

XLII. Rhenium

1. Recover Re from carbon pockets by ignition in a stream of O_2 in a silica tube at 900°C, collecting Re_2O_7 in NH_4OH.
2. Evaporate slowly to near dryness, dissolve in dilute NH_4OH, and filter.
3. Evaporate filtrate until part of NH_4ReO_4 crystallizes, decant, and wash crystals with cold, dilute NH_4OH.
4. Continue fractional crystallization by redissolving crystals and evaporating solutions. Complete drying of crystals in vacuum desiccator.
5. Remove Re from final dried mother liquor by volatilization with O_2 at 400°C, collecting Re_2O_7 in NH_4OH and dry ice traps. Dry carefully.
6. Combine all fractions and reduce NH_4ReO_4 to Re with H_2 at increasing temperatures from 150° to 900°C.
7. Wash Re repeatedly with H_2O in centrifuge and dry in vacuum desiccator.

XLIII. Platinum

1. Ignite graphite pockets in O_2 at 650°C.
2. Dissolve ash in aqua regia.
3. Evaporate to crystals with excess HCl and destroy residual HNO_3 with HCl.
4. Dissolve in 1 M HCl, heat, and filter.
5. Cool, add excess solid NH_4Cl and equal volume of ethanol.
6. Let stand 24 hours, filter, and wash with 20% NH_4Cl.
7. Dry and ignite in silica at 800°C.
8. Reduce to Pt with H_2 in silica ware at 800°C.

XLIV. Iridium

1. Ignite carbon pockets in O_2 at 650°C.
2. Treat ash successively with HCl and HNO_3.
3. Filter and ignite.
4. Fuse metal with NaCl in Cl_2 at 850°C.
5. Dissolve in H_2O and filter.
6. Precipitate hydrated oxide with NaOH at pH 6 and filter.
7. Decompose to metal by heating and leach out salts with H_2O.
8. Complete reduction with H_2 in silica tube at 800°C.

XLV. Mercury

1. Distill Hg from silver pockets at 500°C in vacuo, collecting in cold trap.
2. Dissolve Hg in HNO_3 and dilute.
3. Electroplate Hg on Au cathode.
4. Repeat distillation, solution, and plating; weigh on Au.
5. Dissolve Hg in HNO_3 and dilute to definite volume in flask.

XLVI. Thallium

1. Dissolve Tl from Cu pockets with HNO_3, dilute, and filter.
2. Add excess $(NH_4)_2S_2O_8$ and NH_4OH and boil off excess NH_4OH. Cool, add slight excess NH_4OH, and filter.
3. Dissolve precipitate in HCl, add $N_2H_4 \cdot 2HCl$ solution and heat to boiling. Make slightly alkaline with NaOH or KOH, boil 5 minutes, and filter.
4. Add H_2O_2 to filtrate and boil off excess.
5. Add excess of $(NH_4)_2S_2O_8$ and NH_4OH and boil off excess NH_4OH. Cool and add very slight excess of NH_4OH.
6. Transfer to plastic centrifuge tube or bottle and wash repeatedly with very dilute NH_4OH until ammonium salts are absent. Dry at 110°C.
7. Transfer to Pt dish and ignite to Tl_2O_3 at 400°C.

XLVII. Lead

1. Dissolve Pb from Cu pockets with dilute HNO_3, heat, and filter.
2. Neutralize with NH_4OH, acidify weakly with CH_3COOH.
3. Precipitate $PbCrO_4$ by adding solution of $K_2Cr_2O_7$ and wash out all excess Cr with H_2O.
4. Dissolve in dilute HCl and convert to sulfate by heating to dense fumes of H_2SO_4.
5. Dilute with H_2O and let stand to precipitate $PbSO_4$.
6. Filter and wash with H_2O and C_2H_5OH to remove chromate.
7. Add saturated solution of $(NH_4)_2CO_3$ to $PbSO_4$ and digest over night at 40°C with constant stirring. Let settle and decant. Wash in centrifuge with $(NH_4)_2CO_3$ solution, then with H_2O to absence of sulfate.
8. Dry in oven, transfer to procelain crucible and heat slowly to 650°C. Ignite 3-4 hours to obtain yellow PbO.