MERCURY

Hg, at.wt. 200.61; sp.gr. 13.595; \(^1\) m.p. — 38.9\(^0\) C; \(^1\) b.p. 357.33\(^0\) C; \(^1\) oxides, HgO, HgO.

DETECTION

Metallic mercury is recognized by its physical properties. It is the only metal which is a liquid at ordinary temperatures. The element forms a convex surface when placed on glass.

Mercury in the mercurous form is precipitated by hydrochloric acid as white mercurous chloride, HgCl. This compound is changed by ammonium hydroxide to the black precipitate of metallic mercury and nitrogen dihydrogen mercuric chloride.

Mercury in the mercuric form is not precipitated by hydrochloric acid. The sulphide of the element is thrown out from an acid solution as black HgS. The precipitate first appears white, changing to orange-yellow, then brown and finally to black, as the H₂S gas is passed into the solution. The element is distinguished from the other members of the group by the insolubility of its sulphide in yellow ammonium sulphide and in dilute nitric acid.

If the mercury sulphide is dissolved in aqua regia, the nitric acid expelled by taking to dryness, then adding hydrochloric acid and evaporating again to dryness, the residue taken up with a little hydrochloric acid, diluted with water, and treated with a solution of stannous chloride, a white precipitate of mercurous chloride is first formed, which is further reduced to metallic mercury by an excess of the reagent.

ESTIMATION

The metal is found free in the upper portions of cinnabar deposits. As an amalgam with silver it occurs in horn silver. Cinnabar, HgS, is the only ore of mercury of commercial importance. The element has been found in quartz, sandstone, schists, iron pyrites, bituminous substances, eruptive and sedimentary rocks of all ages. It occurs in sulphide ores of other metals—especially in zinc ores.

Preparation and Solution of the Sample

It will be recalled that nitric acid is the best solvent for the metal and its amalgams. The oxides are insoluble in alkalis. Mercureic oxide is dissolved by acids. Hydrochloric acid forms mercurous chloride with the lower oxide, insoluble in dilute hydrochloric acid.

\(^1\)Van Nostrand’s Chem. Annual—Olsen.
\(^*\)Circular 35 (2d Ed.) U. S. Bureau of Standards.

Chapter contributed by Wilfred W. Scott.

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MERCURY

Ores. If mercury is to be determined by the dry procedure, the finely ground sample may be mixed directly with the flux and determined as directed later.

For opening up the ore for the volumetric method by Seamon see method at close of the chapter, page 312.

For decomposition of ores see also thiocyanate method, page 312a.

SEPARATIONS

Separation of Mercury from the Iron and Zinc Groups, or from the Alkaline Earths and the Alkalies. Mercury is precipitated as a sulphide from an acid solution of the mercuric salt by hydrogen sulphide, together with the members of the hydrogen sulphide group. Sufficient acid should be present to prevent the precipitation of zinc sulphide. Iron, aluminum, chromium, manganese, cobalt, nickel, zinc, the alkaline earths and the alkalies remain in solution.

Separation of Mercury from Arsenic, Antimony, and Tin. The sulphides obtained by passing hydrogen sulphide into an acid solution, preferably of the chlorides, are digested with yellow ammonium sulphide solution. Arsenic, antimony and tin dissolve, whereas mercury sulphide remains insoluble. Sulphides of the fixed alkalies dissolve mercury as well as arsenic, antimony and tin, so cannot be used in effecting a separation.

Separation from Lead, Bismuth, Copper and Cadmium. These elements remain with mercury upon removal of arsenic, antimony and tin as their sulphides are insoluble in ammonium sulphide. (CuS slightly soluble.) The precipitated sulphides are transferred to a porcelain dish and boiled with dilute nitric acid, sp.gr. 1.2 to 1.3. After diluting slightly with water the solution is filtered and the residue of mercuric sulphide washed with dilute nitric acid and finally with water. If much lead is present in the solution it is apt to contaminate the residue by a portion being oxidized to lead sulphate and remaining insoluble. In this case the residue is treated with aqua regia, the solution diluted and mercury chloride filtered from PbSO₄ and free sulphur. Mercury is best determined as HgS by the ammonium sulphide method described later. Traces of lead do not interfere, as lead is completely removed by remaining insoluble in potassium hydroxide, whereas mercury sulphide dissolves. See method.

Separation from Selenium and Tellurium. The mercury selenide or telluride is dissolved in aqua regia, chlorine water added and the solution diluted to 600 to 800 cc., phosphorous acid is added and the solution allowed to stand for some time; mercurous chloride is precipitated, selenium and tellurium remaining in solution. Selenium and tellurium will precipitate in hot concentrated solutions when treated with phosphorous acid, but not in dilute hydrochloric acid solutions.

Mercury in Organic Substances. The material is decomposed by heating in a closed tube with concentrated nitric acid, or by heating with 10% H₂SO₄ and sufficient (NH₄)₂S₂O₈, added in small portions until the organic matter is decomposed.
GRAVIMETRIC METHODS

Determination of Mercury by Precipitation with Ammonium Sulphide

The following method, suggested by Volhard, is generally applicable for determination of mercury. The element is precipitated by ammonium sulphide as HgS. The precipitate dissolved in caustic is again thrown out by addition of ammonium nitrate to the sulpho salt solution of mercury.

\[ \text{Hg}(\text{SNa})_2 + 2\text{NH}_4\text{NO}_3 = 2\text{NaNO}_3 + (\text{NH}_4)_2\text{S} + \text{HgS}. \]

Procedure. The acid solution of the mercuric salt is nearly neutralized by sodium carbonate, and is then heated with a slight excess of ammonium sulphide reagent, freshly prepared. Sodium hydroxide solution is added until the dark-colored liquid begins to lighten. The solution is now heated to boiling and more sodium hydroxide added until the liquid is clear. If lead is present it will remain undissolved and should be filtered off. Ammonium nitrate is now added to the solution in excess and the mixture boiled until the greater part of the ammonia has been expelled. The clear liquid is decanted from the precipitate through a weighed Gooch crucible and the precipitate washed by decantation with hot water and finally transferred to the crucible and washed two or three times more. The mercuric sulphide is dried at 110° C. and weighed as HgS.

\[ \text{HgS} \times 0.8622 = \text{Hg} \quad \text{or} \quad \times 0.9307 = \text{HgO}. \]

Notes. Alumina and silica are apt to be present in caustic.

Free sulphur may be removed, if present, by boiling with sodium sulphite, \( \text{Na}_2\text{SO}_3 + \text{S} = \text{Na}_2\text{S}_2\text{O}_3 \). The sulphur may be extracted with carbon disulphide. The Gooch crucible is placed upon a glass tripod in a beaker, containing carbon disulphide, and a round-bottomed flask filled with cold water is placed over the mouth of the beaker to serve as a condenser, Fig. 47. By gently heating over a water bath for an hour the sulphur is completely extracted from the sulphide. Carbon disulphide is removed from the precipitate by washing once with alcohol followed by ether. The residue is now dried and weighed.

Determination of Mercury by Electrolysis

Mercury is readily deposited as a metal from slightly acid solutions of its salts.

Procedure. The neutral or slightly acid solution of mercuric or mercurous salt is diluted in a beaker to 150 cc. with water and 2 to 3 cc. of nitric acid added. The solution is electrolyzed with a current of 0.5 to 0.1 ampere, and an E.M.F. of 3.5 to 5 volts. A gauze cathode is recommended, or a platinum dish with dulled inner surface may be used. One gram of mercury may be deposited in about fifteen hours (or overnight). The time may be shortened to about three hours by increasing the current to 0.6 to 1 ampere.
The metal is washed with water without interrupting the current and then with alcohol. After removing the adhering alcohol with a filter paper, the cathode is placed in a desiccator containing fused potash and a small dish of mercury. The object of this mercury is to prevent loss of the deposit by vaporization.

The increased weight of the cathode is due to metallic mercury.

Notes. In the electrolysis of mercuric chloride turbidity may be caused by formation of mercurous chloride by reduction, but this does no harm, as the reduction to metallic mercury follows. Mercury may be electrolyzed from its sulphide solutions, obtained by dissolving its sulphide in concentrated sodium sulphide.

**Determination of Mercury by the Holloway-Eschka Process Modified**

When mercury sulphide is heated with iron filings metallic mercury is volatilized, iron sulphide being formed. The mercury vapor is condensed on a silver or gold plate. The use of iron for this reduction was suggested by Eshcka and his method modified by Holloway. In ores containing arsenic the addition of zinc oxide is recommended. Erdmann and Marchand use lime for decomposing the mercury compound. The reactions may be represented as follows:

\[ \text{HgS} + \text{Fe} = \text{FeS} + \text{Hg} \text{ or } \text{HgX} + \text{CaO} = \text{CaX} + \text{Hg} + \text{O}. \]

**Apparatus.** This consists of a deep glazed porcelain crucible, the size depending upon the charge of the sample to be taken. Generally a 30-cc. crucible is used for a 2-gram sample with 4 grams of flux. The crucible is covered by a silver or gold plate that lies perfectly flat and fits snugly around the edges of the crucible. It may be necessary to grind the top of the receptacle on emery paper to obtain a perfectly level edge.

The crucible is suspended in a hole through an asbestos board or quartz plate, to prevent the flame heating the upper portion of the vessel.

The lid of the crucible is kept cool by a cylindrical condenser of metal through which a stream of water passes. A small Erlenmeyer flask may be used, with a tube passing to the bottom of the flask through a rubber stopper, and a second tube just passing through the stopper.

Holloway has a weight placed on the metal condenser to hold the lid firmly against the crucible. The illustration (Fig. 48) shows the form of the apparatus set up for the run.

**Procedure.** The sample containing not over 0.1 gram of mercury is placed in the crucible with 5 to 10 grams of fine iron filings and intimately mixed. Additional filings are put over the charge. Sulphide ores containing arsenic are best mixed with about twice the weight of a flux of zinc oxide and sodium carbonate in the proportion 4 to 1, and about five times the weight of iron filings added.
The weighed silver cover is placed on the crucible and the apparatus set up as shown in the illustration, Fig. 48.

The bottom of the crucible is gradually heated with a small Méker flame until it glows slightly. Overheating should be avoided. The upper portion of the crucible should never become hot and the lid should remain cold. After heating for about thirty minutes the system is allowed to cool without disconnecting the condenser. The disk is now removed, dipped in alcohol and dried in a desiccator over fused potash or soda. The increase of weight of the dried disk is due to metallic mercury.

Notes. If the sample contains less than 1% mercury, take 2 grams; if 1 to 2% mercury, take 1 gram; if the sample contains 2 to 5%, take 0.5-gram sample. If high in mercury, grind sample with sand and take an aliquot portion.

It is advisable to repeat the test with a clean foil to be sure that all the mercury has been driven out of the sample. The foil may be freed from mercury by heating.

VOLUMETRIC DETERMINATION OF MERCURY

Seamon's Volumetric Method

Seamon's Volumetric Method. Weigh 0.5 gram of the finely ground ore into an Erlenmeyer flask of 125 cc. capacity. Add 5 cc. of strong hydrochloric acid and allow it to act for about ten minutes at a temperature of about 40°C., then add 3 cc. of strong nitric acid and allow the action to continue for about ten minutes longer. The mercury should now all be in solution. Now if lead be present, add 5 cc. of strong sulphuric acid; it may be omitted otherwise. Dilute with 15 cc. of water and then add ammonia cautiously until the liquid is slightly alkaline. Bismuth, if present, will be precipitated. Acidify faintly with nitric acid, filter, receiving the filtrate in a beaker, and wash thoroughly.

Add to the filtrate 1 cc. of strong nitric acid that has been made brownish in color by exposure to the light, and titrate with a standard solution of potassium iodide until a drop of the liquid brought into contact with a drop of starch liquor, on a spot-plate, shows a faint bluish tinge. It is a good plan to set aside about one-third of the mercury solution and add it in portions until the endpoint is successively passed, finally rinsing in the last portion and titrating to the end-point very carefully.

Deduct 0.5 cc. from the burette reading and multiply the remaining cc. used by the percentage value of 1 cc in mercury to obtain the percentage in the ore.

The standard potassium iodide solution should contain 8.3 grams of the salt per liter. Standardize against pure mercuric chloride. Dissolve a weighed amount of the salt in water, add 2 cc. of the discolored nitric acid and titrate as above. One cc. of standard solution will be found equivalent to about 0.005 gram of mercury, or about 1% on the basis of 0.5 gram of ore taken for assay.

The precipitate of red mercuric iodide which forms during the titration may not appear if the amount of mercury present is very small, but this failure to precipitate does not appear to affect the result.

Iron, copper, bismuth, antimony, and arsenic, when added separately to the ore, did not influence the results in Seamon's tests. Silver interferes. Duplicate results should check within 0.1 to 0.2 of 1%.

1 "Manual for Assayers and Chemists," p. 112.
Volumetric Thiocyanate Method for Mercury

A sample containing 0.1 to 0.5 g. Hg placed in a flask is decomposed by adding 10 cc. dilute H₂SO₄ (1 : 1) and about 0.5 g. KMnO₄ crystals. The mixture is agitated and heated to fumes. The solution cooled is diluted to 50 cc. with cold water, then boiled and the MnO₂ dissolved by adding a few crystals of oxalic acid (small portions at a time).

The solution is filtered, and any residue washed with dilute (1 : 10) H₂SO₄. The sulphide group are now precipitated with H₂S and filtered off. The precipitate, transferred to a casserole, is digested for some time with dilute HNO₃ (2 : 1), the solution then diluted with hot water and filtered and the HgS washed with dilute HNO₃ (1 : 1).

The HgS is transferred to a flask with a few cc. of hot water and then 5 cc. of strong H₂SO₄ and 0.5 g. KMnO₄ are added and the mixture heated to fumes. Oxalic acid crystals are added until the MnO₂ dissolves and the mixture again heated to fumes to destroy the excess of oxalic acid. The solution, cooled, is diluted to 100 cc. (It should now be clear.)

About 5 cc. of a saturated solution of ferric ammonium sulphate solution (acidified with HNO₃) are added and the solution titrated with 0.1 N thiocyanate solution.

1 cc. 0.1 N thiocyanate = 0.01003 g. Hg.

Solutions. Ferric Indicator. Make a saturated solution of ferric ammonium sulphate or ferric sulphate. Add sufficient nitric acid (freed from nitrous acid by heating) to clear the solution and produce a pale yellow color. 5 cc. of this solution (the Editor prefers less) is used in the test. Ferric nitrate may be used if the sulphate is not available.

Thiocyanate Reagent. A tenth normal solution may be made by dissolving 7.4 grams of NH₄CNS or 9.2 grams of KCNS in water and diluting to a liter. The solution may be standardized against a standard silver solution, containing 0.01079 grams silver per cc.

40 cc. of the silver solution is measured into a beaker or Erlenmeyer flask and diluted to about 100 cc. The ferric indicator is added and the solution is titrated with the thiocyanate solution. Each addition of the thiocyanate will produce a temporary red color, which fades out as long as there is silver uncombined with thiocyanate. A drop in excess of the thiocyanate produces a permanent faint red color.

1 By A. H. Low (Chemist-Analyzer, 1919, 29, 13).
MERCURY

Mercury in Organic Matter. The compound is decomposed by the method of Carius by heating in a closed tube (see page 145) with strong nitric acid (d. 1.42). The acid solution is neutralized by addition of sodium hydroxide and sufficient excess of the alkali added to insure a slight excess. Pure potassium cyanide is now added in quantity sufficient to dissolve the mercuric oxide precipitate, and the solution saturated with \( \text{H}_2\text{S} \) gas. Ammonium acetate is added and the solution boiled until nearly all the \( \text{NH}_3 \) has been expelled. The precipitate is allowed to settle and then filtered off and washed with hot water, and then with hot dilute HCl and again with water. The precipitate is dried at 110° C. and weighed as mercuric sulphide \( \text{HgS} \).

Note. Should free sulphur be present its removal is accomplished by extraction with pure \( \text{CS}_2 \), see page 310.
MOLYBDENUM

Mo, at. wt. 96.0; sp.gr. 8.6–9.01; m.p. 2500° C; oxides, MoO₃, MoO₂, MoO₄.

DETECTION

Molybdenum appears in the hydrogen sulphide group, being precipitated by H₂S in acid solution as the sulphide. It passes into solution by digestion with ammonium sulphide or sodium sulphide along with arsenic, antimony, tin, gold and platinum. By addition of metallic zinc, antimony, together with tin, gold and platinum are precipitated as metals while molybdenum remains in solution. Arsenic, that has not volatilized as arsine, is expelled by evaporation. Nitric acid is now added and the solution taken to dryness. Molybdenum is extracted from the residue with ammonium hydroxide.

A dilute solution of ammonium molybdate treated with a soluble sulphide gives a blue solution.

Sodium thiosulphate added to a slightly acid solution of ammonium molybdate produces a blue precipitate with a supernatant blue solution. With more acid a brown precipitate is formed.

Sulphur dioxide produces a bluish-green precipitate if sufficient molybdenum is present, or a colored solution with small amounts. The reducing agents, stannous chloride, or zinc in acid solution, produce a play of colors when they react with molybdenum solutions, due to the formation of the lower oxides. The solution becomes blue, changing to green, brown and yellow.

Molybdenum present as molybdate is precipitated by disodium phosphate as yellow ammonium phosphomolybate from a nitric acid solution. The precipitate is soluble in ammonium hydroxide.

A pinch of powdered mineral on a porcelain lid, moistened with a few drops of strong sulphuric acid, stirred and heated to fumes, then cooled, will produce a blue color when breathed upon. The color disappears on heating, but reappears on cooling. Water destroys the color.

Molybdenite is very similar to graphite in appearance. It is distinguished from it by the fact that nitric acid reacts with molybdenite, MoS₂, leaving a white residue, but has no action upon graphite. The blowpipe gives SO₂ with molybdenite and CO₂ with graphite.

ESTIMATION

The determination is required in the ores—molybdenite, MoS₂ (60% Mo); molybdite, MoO₃ (straw yellow); wulfenite, PbMoO₄ (yellow, bright red, olive green or colorless); Ilsenmannite, MoO₃+MoO₂; powellite, CaMoO₄; pattersite, CoMoO₄; belonites, MgMoO₄; eosite, lead-vanado-molybdate; achromatite,

Chapter contributed by Wilfred W. Scott, A. M. Smoot and J. A. Holladay.

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lead molybdate and arsenate with tin oxide and lead chloride. Some iron and copper ores also contain molybdenum.

The metal is determined in certain self-hardening steels and alloys.

The reagents ammonium molybdate and the oxide-molybdic acid, $\text{MoO}_3$, are valuable for analytical purposes. Tests of their purity may be required.

### Preparation and Solution of the Sample

In dissolving the substance the following facts should be kept in mind: The metal is easily soluble in aqua regia; soluble in hot concentrated sulphuric acid, soluble in dilute nitric acid, oxidized by excess to $\text{MoO}_3$. It is dissolved by fusion with sodium carbonate and potassium nitrate mixture. It is insoluble in hydrochloric, hydrofluoric and dilute sulphuric acids.

The oxide $\text{MoO}_3$ is but slightly soluble in acids and alkalies; $\text{MoO}_3$ is insoluble in hydrochloric and hydrofluoric acids. $\text{MoO}_3$ as ordinarily precipitated, is soluble in inorganic acids and in alkalies. The oxide sublimed is difficultly soluble.

Molybdates of the heavy metals are insoluble in water, the alkali molybdates are soluble.

**Ores.** Molybdenum ores are decomposed by fusion with a mixture of sodium carbonate and potassium nitrate, or with sodium peroxide, in an iron crucible, 0.5 gram of the sample being taken and 10 times its weight of fusion mixture. The melt is disintegrated with about 150 cc. of water, the alkali partly neutralized with $(\text{NH}_4)_2\text{CO}_3$ and filtered. The molybdenum is in the filtrate, the iron remains in the residue.

It is advisable to dissolve the residue in a little dilute HCl, pour this solution a hot solution of an excess of NaOH and again filter off the iron hydroxide, adding the filtrate to the first lot.

The combined filtrates and washings are treated with about 5 cc. of a 50% tartaric acid solution or its equivalent in crystals. (This prevents W and V from separating out) and the solution saturated with $\text{H}_2\text{S}_2$. The thiomolybdate solution is made slightly acid with $\text{H}_2\text{SO}_4 (1:2)$ $\text{MoS}_2$ precipitates. Further details are the same as those given on page 323.

For Acid Decomposition see procedure on page 322.

**Steel and Iron.** One to 2 grams of the drillings are dissolved, a mixture of 25 cc. HCl and 2 cc. HNO$_3$, additional HNO$_3$ (1:1) being added to oxidize the iron, if necessary. (KClO$_3$ crystals may be used.) A large excess of the oxidizing agent is to be avoided. The solution is evaporated to near dryness and the pasty residue taken up with about 25 cc. water and 10 cc. HCl, and gently heated. A yellow residue is due to $\text{WO}_3$. This is removed by filtration and washed. The filtrate contains the molybdenum. This is now treated according to the procedure given under "Separations" for removal of iron.

### Separations

**Separation of Molybdenum from Iron.** The solution containing the molybdennum is treated very cautiously with 2 N NaOH solution to neutralize the greater part of the free acid, but not with such an amount that would color the solution red. The yellow solution is heated to boiling.

In a separate vessel is placed 2 N NaOH in sufficient quantity to combine with all the iron of the sample and about 50% excess (1 cc. of 2 N NaOH = 0.1 g. Fe) 30 cc. should be sufficient. This solution is heated to boiling
and to it is added the hot solution containing the molybdenum. The sample should be added very slowly, preferably through a special funnel with capillary tube, stirring the solution vigorously during the addition. With care a complete separation of iron, free from molybdenum, may be effected, the molybdenum remaining in solution. The mixture is transferred to a 500 cc. volumetric flask.

The volume is made up to exactly 500 cc. and the precipitate allowed to settle. A portion is now filtered off, the first 5–10 cc. being rejected and the following 250 cc. of filtrate is retained for analysis of molybdenum.

Separation from the Alkaline Earths. Fusion of the substance with sodium carbonate and extraction of the melt with water gives a solution of molybdenum, whereas the carbonates of barium, calcium and strontium remain undissolved.

Separation from Lead, Copper, Cadmium and Bismuth. The sulphides of the elements are treated with sodium hydroxide and sodium sulphide solution and are digested by gently heating in a pressure flask. Molybdenum dissolves, whereas lead, copper, cadmium and bismuth remain insoluble. If the solution of the above elements is taken, made strongly alkaline, and treated with H₂S, the sulphides of the latter elements are precipitated and molybdenum remains in solution. The precipitates are filtered off and the filtrate containing molybdenum is placed in the pressure flask, the solution made slightly acid with sulphuric acid and the mixture heated under pressure, until the liquid appears colorless, MoS₂ is precipitated and may be converted into the oxide as described later.

Separation from Vanadium is effected by a molybdenum sulphide precipitation in acid solution.

Separation from Arsenic. Arsenic, present in the higher state of oxidation, is precipitated by magnesia mixture, added to a slightly acid solution (5 cc. of concentrated hydrochloric acid per 100 cc. of solution for each 0.1 gram arsenic). The solution is neutralized with ammonia (methyl orange), and the arsenic salt filtered off. MoS₂ is now precipitated with H₂S in presence of free sulphuric acid in the pressure flask.

Separation from Phosphoric Acid. Phosphoric acid is precipitated from an ammoniacal solution as magnesium ammonium phosphate. Molybdenum may then be precipitated as the sulphide from the filtrate.

Separation from Titanium. The metals of the ammonium sulphide group are precipitated by adding ammonium hydroxide and ammonium sulphide. Molybdenum remains in solution and passes into the filtrate. H₂S is passed into the solution until it appears red; sulphuric acid is then added until the solution is acid, when molybdenum sulphide precipitates.

Separation from Tungsten. Molybdenum may be precipitated by H₂S as MoS₂ in presence of tartaric acid. Tungsten does not precipitate.

Ether Extraction Method. Ether extracts not only iron but also molybdenum (see p. 248). The ether is evaporated off on a steam bath (avoid a free flame, as ether is inflammable) and the solution taken to near dryness. 10 cc. of sulphuric acid are added and hydrochloric acid expelled by concentration to fumes. After cooling, 100 cc. of water are added and 2–3 grams of ammonium bisulphite, to reduce the iron. The solution is boiled to expel the excess of SO₃ and molybdenum is precipitated by H₂S in a pressure flask. After cooling slowly, the sulphide, MoS₂, is filtered off, washed and ignited and weighed as MoO₂.
GRAVIMETRIC METHODS FOR THE DETERMINATION
OF MOLYBDENUM

Precipitation as Lead Molybdate

Preliminary Remarks. This method, suggested by Chatard, has been pronounced by Breatly and Jbottson to be "one of the most stable processes found in analytical chemistry." "It is not interfered with by the presence of large amounts of acetic acid, lead acetate, or alkali salts (except sulphates). The paper need not be ignited separately and prolonged ignition at a much higher temperature than is necessary to destroy the paper does no harm. From faintly acid solution lead molybdate may be precipitated free from impurities in the presence of copper, cobalt, nickel, manganese, zinc, magnesium and mercury salts." It may be readily separated from iron and chromium. Barium, strontium, uranium, arsenic, cadmium and aluminum do not interfere if an excess of hydrochloric acid has been added to the solution followed by lead acetate and sufficient ammonium acetate to destroy the free mineral acid.

The method is not adapted to use with molybdeneite, MoS₂, because of the sulphate that forms on oxidation.

Vanadium and tungsten, if present, must be removed.

Special Reagents. Lead Acetate. A 4% solution is made by dissolving 20 grams of the salt in 500 cc. of warm water. A few cc. of acetic acid are added to clear the solution.

Precipitation of Lead Molybdate. The solution acidified with acetic acid (5 cc. per 200 cc.) and free from iron, is heated to near boiling and the lead acetate reagent added slowly until no further precipitation occurs and then about 5% excess. (1 cc. of the 4% lead acetate reagent will precipitate about 0.01 gram of molybdenum.) The precipitate is allowed to settle a few minutes and filtered hot into a weighed Gooch crucible or into a filter paper. (Refiltering first portion if cloudy.)¹ The precipitate is washed with hot water until free of chlorides and the excess of the lead acetate.

The precipitate dried and ignited in a porcelain crucible at red heat for about twenty minutes is weighed as PbMoO₄.

\[
PbMoO₄ \times 0.2815 = Mo. \quad PbMoO₄ \times 0.3923 = MoO₃.
\]

\[
Mo \times 3.8241 = PbMoO₄. \quad MoO₃ \times 2.5491 = PbMoO₄.
\]

Determination of Molybdenum as the Oxide, MoO₃

Especially applicable where fusion with an alkali carbonate has been required.

Decomposition of Ore. One gram of the ore is fused with 4 grams of fusion mixture, (Na₂CO₃ + K₂CO₃ + KNO₃), and the cooled melt extracted with hot water.

If manganese is present, indicated by a colored solution, it may be removed by reduction with alcohol, the manganese precipitate filtered off and washed with hot water, the solution evaporated to near dryness and taken up with water, upon addition of nitric acid as stated below.

The solution containing the alkaline molybdate is nearly neutralized by adding HNO₃, the amount necessary being determined by a blank, and to the cold, slightly alkaline solution, a faintly acid solution of mercuric nitrate is added.

¹ Note. Addition of ammonium nitrate to the solution tends to prevent formation of colloidal PbMoO₄. Paper pulp (ashless) may be added to assist rapid filtration.
MOLYBDENUM

added until no further precipitation occurs. The precipitate consists of mer-
curious molybdate and carbonate (chromium, vanadium, tungsten, arsenic and
phosphorus will also be precipitated if present). The solution containing the
precipitate is boiled and allowed to stand ten to fifteen minutes to settle, the black
precipitate is filtered off and washed with a dilute solution of mercurous nitrate.
The precipitate is dried, and as much as possible transferred to a watch-glass.
The residue on the filter is dissolved with hot dilute nitric acid, and the solution
received in a large weighed porcelain crucible. The solution is evaporated to
dryness on the water bath and the main portion of the precipitate added to this
residue, and the product heated cautiously over a low flame until the mercury
has completely volatilized. The cooled residue is weighed as MoO₃.

\[ \text{MoO}_3 \times 0.6667 = \text{Mo}. \]

**Note.** If Cr, V, W, As or P are present a separation must be effected. Molyb-
denum should be precipitated in an H₂SO₄ solution in a pressure flask as the sulphide
by H₂S as given in the following method, and arsenic if present removed by magnesia
mixture as indicated in the procedure for separation of arsenic from molybdenum.
If these impurities are present the molybdenum oxide may be fused with a very little
Na₂CO₃, and leached with hot water and the filtrate treated with H₂S as directed.

Precipitation of Molybdenum as the Sulphide by H₂S

**A. Precipitation from Acid Solution.** By this procedure molybdenum
is precipitated along with members of the hydrogen sulphide group, if present,
but free from elements of the following groups.

The cold molybdenum solution slightly acid with sulphuric acid (in presence
of Ba, Sr or Ca an HCl solution is necessary) is placed in a small pressure
flask and saturated with H₂S, the flask closed and heated on the water bath until
the precipitate has settled. The solution is cooled and filtered through a weighed
Gooch crucible.

**B. Precipitation from an Ammoniacal Solution.** By this procedure molyb-
denum is precipitated with antimony, arsenic, tin if present, but is free from
mercury, lead, bismuth, copper and cadmium.

Hydrogen sulphide is passed into the cold ammoniacal solution of molyb-
denum (in presence of tungsten or vanadium add tartaric acid) until it assumes
a bright red color, it is now acidified with dilute sulphuric acid, the precipitate
allowed to settle and the solution filtered through a weighed Gooch crucible.

*In either case A or B* the precipitate is washed into the Gooch crucible
with very dilute sulphuric acid followed by several washings with the acid and
then with alcohol until free from acid. The Gooch is placed within a larger
nickel crucible and covered with a porcelain lid. After drying at 100° C. it is
placed over a small flame and carefully heated until the odor of SO₂ can no longer
be detected. The cover is now removed and the open crucible heated to constant
weight. The residue consists of MoO₃.

\[ \text{MoO}_3 \times 0.6667 = \text{Mo}. \]

**Note.** Arsenic will contaminate the residue if present. The method for its
removal has been given.

¹ The oxide, MoO₃, sublimes at bright red heat. The volumetric method is more
reliable. See page 319.
VOLUMETRIC METHODS FOR THE DETERMINATION OF MOLYBDENUM OR MOLYBDIC ACID

The Iodometric Reduction Method

Principle. When a mixture of molybdic acid and potassium iodide in presence of hydrochloric acid is boiled, the volume having defined limits, free iodine is liberated and expelled and the molybdic acid reduced to a definite lower oxide; by titrating with a standard oxidizing agent the molybdic acid is determined.

Reaction. 2MoO₃ + 4KI + 4HCl = 2MoO₂⁺ + I₂ + 4KCl + 2H₂O.

Reagents. N/10 solutions of iodine, sodium arsenite, potassium permanganate, sodium thiosulphate.

Analytical Procedure. Reduction. The soluble molybdate in amount not exceeding an equivalent of 0.5 gram MoO₃ is placed in a 150-cc. Erlenmeyer flask, 20 to 25 cc. of hydrochloric acid (sp.gr. 1.2) added together with 0.2 to 0.6 gram potassium iodide. A shortstemmed-funnel is placed in the neck of the flask to prevent mechanical loss during the boiling. The volume of the solution should be about 60 cc. The solution is boiled until the volume is reduced to exactly 25 cc. as determined by a mark on the flask. The residue is diluted immediately to a volume of 125 cc. and cooled. Either process A or B may now be followed.

A. Reoxidation by Standard Iodine. A solution of tartaric acid, equivalent to 1 gram of the solid, is now added, and the free acid nearly neutralized with sodium hydroxide solution (litmus or methyl orange indicator) and finally neutralized with sodium acid carbonate, NaHCO₃, added in excess. A measured amount of N/10 iodine is now run in. The solution is set aside in a dark closet for two hours, in order to cause complete oxidation, as the reaction is slow. The excess iodine is now titrated with N/10 sodium arsenite.

One cc. N/10 iodine = .0144 gram MoO₃ = .0096 gram Mo.

On long standing a small amount of iodate is apt to form. This is determined by making acid with dilute HCl and titrating with N/10 sodium thiosulphate.

B. Reoxidation of the Residue by Standard Permanganate. To the reduced solution about 0.5 gram of manganese sulphate in solution is added, followed by a measured amount of N/10 permanganate solution, added from a burette until the characteristic pink color appears. A measured amount of standard N/10 sodium arsenite, equivalent to the permanganato is then run in and about 3 grams of tartaric acid added. The acid is neutralized by acid sodium or potassium carbonate, the stopper and the sides of the flask rinsed into the main solution. The residual arsenite is now titrated by N/10 iodine, using starch indicator.

Notes. Tartaric acid prevents precipitation during the subsequent neutralization with NaHCO₃. A and B.

The addition of manganese salt in B is to prevent the liberation of free chlorine by the action of KMnO₄ on HCl.

In addition to the oxidation of the lower oxides to molybdic acid, potassium permanganate added in B liberates free iodine from H₂I, it produces iodic acid, and forms the higher oxides of manganese. The standard arsenite, on the other hand, converts free iodine and the iodate to HI and reduces the higher oxides of manganese.

Estimation by Reduction with Jones Reductor and Oxidation by Standard Permanganate Solution

**Principle.** The procedure depends upon the reduction of molybdcic acid to Mo\(_2\)O\(_5\) by passing its solution through a column of amalgamated zinc into a solution of ferric alum, and subsequent oxidation to MoO\(_3\) by standard potassium permanganate solution.

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

\[5\text{MoO}_3 + 6\text{KMnO}_4 + 9\text{H}_2\text{SO}_4 = 10\text{MoO}_4 + 3\text{K}_2\text{SO}_4 + 6\text{MnSO}_4 + 9\text{H}_2\text{O}.\]

**Reagents.** Potassium permanganate approximately N/10 standardized against a standard molybdic acid solution.

10% solution of ferric alum.

2.5% solution of sulphuric acid.

**Apparatus.** Jones Reductor.

\(R\) = reductor tube 50 cm. long, 2 cm. inside diameter. Smaller tube prolongation length 20 cm., inside diameter 0.5 cm.

\(Zn\) = column of zinc 40 cm. long. \(Zn\) shot 8 mesh to sq. cm.;

\(F\) = receiving flask;

\(P\) = pressure regulator with gauge, set to give pressure in receiving flask of less than 20 cm. water;

\(G\) = platinum cone or gauze with mat of fine glass wool 2 cm. thick;

The zinc in reductor should be protected from the air by covering with water, stop-cock \(S\) being closed when not in use.

**Procedure.** The receiving flask of the Jones reductor, Fig. 49, is charged with about 30 cc. of 10% ferric alum and 4 cc. of phosphoric acid. Through the 40-cm. column of amalgamated zinc in the reductor are passed in succession 100 cc. of dilute sulphuric acid (2.5% sol.), the molybdic acid in the form of ammonium molybdate dissolved in 10 cc. of water and acidified with 100 cc. of dilute sulphuric acid followed by 200 cc. more of the dilute sulphuric acid and 100 cc. of water. The reduced green molybdcic acid upon coming in contact with the ferric alum solution produces a bright red color.

The solution is titrated with N/10 KMnO\(_4\) solution.

One cc. of N/10 KMnO\(_4\) = \(\frac{0.0144}{3}\) gram MoO\(_3\) = \(\frac{0.0096}{3}\) gram molybdenum.

\(^1\) W. A. Noyes and Frohman, Jr. Am. Chem. Soc., 35, 919. After a thorough examination of the various methods for determining molybdenum, Messrs. Smoot, Lundell and Holladay pronounce this method to be superior to any other.
Notes on Reductor Technique

Use of the following greatly simplified and correspondingly more rapid reductor technique is recommended by J. A. Holladay.

1. The reductor should contain a column of 20 x 30 mesh amalgamated zinc \( \frac{3}{4}'' \) in diameter and 10 inches long. If the molybdenum solution is given a preliminary reduction by heating with 2 grams of 20 mesh zinc for the purpose of precipitating copper (which is subsequently removed by filtration on asbestos), the length of the zinc column may safely and advantageously be reduced to 8''. The lengths specified apply only to a column \( \frac{3}{4}'' \) in diameter; the lengths for tubes of different diameters would have to be determined experimentally. The zinc should be as free from iron and as low in other impurities as possible.

2. If the reductor has been standing idle for longer than one day it is cleaned by passage of 50 cc. of 6% sulphuric acid, and 50 cc. of water, both at room temperature, a small amount of the water being left in the funnel which forms the reductor inlet. The acid and water are discarded after having been passed through the reductor. These operations are only necessary when the reductor has been standing idle for some time.

3. The required amount of ferric phosphate solution and sufficient water (about 50 cc.) to cause the tip of the reductor outlet tube to dip beneath the surface of the liquid are added to the flask.

4. The molybdenum solution (volume 50 to 100 cc., acidity 6% \( \text{H}_2\text{SO}_4 \)) which may be at room temperature or slightly warm, is passed through the reductor rapidly. The total time required for the passage of the molybdenum solution and the liquids which follow it need not exceed from 1 to 3 minutes. No advantage results from having the solution hot—on the contrary, the greater action of the hot acid solution on the zinc is a disadvantage. No increase in accuracy is obtained by passing the solution through the reductor at a slower rate than that specified.

5. When the funnel which forms the inlet of the reductor is nearly but not entirely empty, 150 cc. of water at room temperature are passed through the reductor. In the case of samples containing relatively small amounts of molybdenum, 100 cc. of water is sufficient. In no case is the funnel permitted to become entirely empty and the stopcock is closed while some of the wash water remains above the surface of the zinc.

Norr. It is unnecessary to have this solution hot as is sometimes recommended. This statement is confirmed by recent work of G. E. F. Lundell and H. B. Knowles, U. S. Bureau of Standards, Ind. Eng. Chem.
MOLYBDENUM

Method for Determining Molybdenum and Vanadium in a Mixture of their Acids

Principle of the Method. The procedure depends upon the fact that vanadic acid alone is reduced by SO$_2$ in a sulphuric acid solution, whereas both vanadic and molybdic acids are reduced by amalgamated zinc, in each case the reducing agents forming definite lower oxides which are readily oxidized to definite higher oxides by KMnO$_4$.

**Reactions.**

SO$_2$ Reduction:
1. $V_2O_5 + SO_2 = V_2O_4 + SO_3$ (No action on MoO$_3$)

Zn Reduction:
2. $V_2O_5 + 3Zn = V_2O_3 + 3ZnO$
3. $2MoO_3 + 3Zn = Mo_2O_7 + 3ZnO$

KMnO$_4$ Oxidation:
4. $5V_2O_5 + 2KMnO_4 + 3H_2SO_4 = 5V_2O_3 + K_2SO_4 + MnSO_4 + 3H_2O$
5. $5V_2O_4 + 6KMnO_4 + 9H_2SO_4 = 5V_2O_5 + 3K_2SO_4 + 6MnSO_4 + 9H_2O$
6. $5MoO_3 + 6KMnO_4 + 9H_2SO_4 = 10MoO_5 + 3K_2SO_4 + 6MnSO_4 + 9H_2O$

From the reactions "4" and "5" it is seen that three times the amount of KMnO$_4$ is required to oxidize $V_2O_5$ to $V_2O_4$, as is required in the case of $V_2O_4$, hence—total cc. KMnO$_4$ required in oxidation of the zinc-reduced oxides minus three times the cc. KMnO$_4$ required in oxidizing the tetroxide of vanadium formed by the sulphur dioxide reduction = cc. KMnO$_4$ required to oxidize MoO$_3$ to MoO$_5$. From these data molybdenum and vanadium may readily be calculated.

**Method of Procedure. A. Vanadic Acid.** The solution containing the vanadic and molybdic acids in a 250- to 300-cc. Erlenmeyer flask, is diluted to 75 cc. acidified with 2 to 3 cc. of strong sulphuric acid, heated to boiling and the vanadic acid reduced by a current of SO$_2$ passed into the solution until the clear blue color indicates the complete reduction of the vanadic acid to $V_2O_4$. The cooling is now continued and CO$_2$ passed into the flask to expel the last trace of SO$_2$.

Standard N/10 KMnO$_4$ is now run into the reduced solution to the characteristic faint pink. From reaction "4," vanadic acid may be calculated.

One cc. N/10 KMnO$_4$ = .0182 gram $V_2O_5$ = .0051 gram vanadium.

**B. Molybdic Acid.** The reduction by Jones' reductor, and titration of the combined acids reduced by amalgamated zinc with N/10 potassium permanganate solution, is carried out exactly as described in the determination of molybdic acid alone. In this case 50 cc. of 10% ferric alum and 8 cc. of the phosphoric acid is placed in the receiving flask.

**Calculation.** Total permanganate titration in B minus three times the titration in A gives the permanganate required to oxidize MoO$_3$ to MoO$_5$. From equation i the molybdc acid may now be calculated.

One cc. N/10 KMnO$_4$ = $\frac{.0144}{3}$ gram MoO$_3$ = $\frac{.0096}{3}$ gram molybdenum.

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1 Reduction of vanadium by SO$_2$ in presence of molybdenum, Graham Edgar, J. Am. Chem. Soc., (4) 25, 332. No reduction of MoO$_3$ when 0.4 gram is present with 5 cc. H$_2$SO$_4$ in 25 cc. volume.

For theoretical considerations and data on accuracy of method see "Methods of Chemical Analysis," F. A. Gooch.

27
DETERMINATION OF MOLYBDENUM IN ORES

The commercial ores of molybdenum are molybdenite, the native sulphide (MoS₂), and wulfenite, lead molybdate. Occasionally molybdenum ochre (the trioxide) may be met with, but this mainly occurs in very small proportion associated with molybdenite as an oxidation product of the sulphide.

Molybdenite is sold either as high grade selected mineral or as concentrates which are usually the product of flotation processes. The important determinations in molybdenite are molybdenum, arsenic, copper and phosphorus; sometimes bismuth is present and occasionally lead.

Owing to the complex nature of wulfenite the determination of molybdenum is more difficult and the number of impurities which may be sought for is much greater.

The following methods for the determination of molybdenum in commercial ores and concentrates are the result of co-operative work between the laboratories of the Electro Metallurgical Company and Ledoux & Company. It is believed that all important sources of error have been considered and eliminated so far as the usual commercial ores are concerned.

Determination of Molybdenum in Wulfenite or Molybdenite

One gram of the finely ground ore is dissolved by treatment with 15 cc. of nitric acid (sp.gr. 1.42) and 7 cc. of sulphuric acid (sp.gr. 1.84) at a temperature just short of boiling in a 150 cc. covered beaker. When practically complete decomposition has been effected, the liquid is evaporated until fumes of sulphur trioxide are freely expelled. After cooling addition is made of about 40 cc. of water, the solution is boiled to dissolve the molybdenum, cooled to room temperature and filtered into a 250 cc. beaker. The residue, consisting of lead sulphate, silica, etc., is washed with very dilute H₂SO₄. The residue rarely, if ever, contains Mo, nevertheless it should be examined to make sure that decomposition is complete. To this end it is digested with 15 cc. to 25 cc. of ammonium acetate solution (prepared by mixing 8 cc. of (NH₄)OH (0.90) with 10 cc. H₂O and adding 7 cc. of 99% C₂H₂O₂) to remove all lead sulphate. The filter paper is washed with hot dilute acetic acid and with water. It is then ignited in a platinum crucible and the silica is removed by treatment with a drop of sulphuric acid and several cc. of hydrofluoric acid and evaporating to the expulsion of sulphuric acid. If an appreciable residue remains after this treatment, it is fused with potassium pyrosulphate and tested for molybdenum by means of tartaric acid and ammonium sulphide as described later.

To the solution containing all of the molybdenum there is added sufficient ferric sulphate to provide ten times as much iron as there is arsenic present: from 0.2 to 0.3 gram of iron is usually ample. The acid solution is then nearly neutralized with ammonia (addition of a sufficient amount to impart a red tint to the clear yellow solution is to be avoided), heated nearly to boiling and poured very slowly and with vigorous stirring into 75 cc. of warm ammonia solution (15 cc. (NH₄)OH 1.90 sp.gr. 60 cc. H₂O) contained in a 250 cc. beaker. When it has settled the ferric hydroxide (which will carry down quantitatively all arsenic in the ore) is filtered and washed thoroughly with hot water; it is then dissolved in a slight excess of hot dilute (1 to 4) sulphuric acid and the resulting solution is again heated to boiling and poured into 75 cc. of warm

1 By James A. Holladay and A. M. Smoot.
ammonia solution as before; the iron hydrate is again washed. The two filtrates, which will contain all the molybdenum, are collected in a 600 cc. beaker. It is essential that arsenic, which is usually present in these ores, be eliminated, and the method described furnishes a simple and effective way for accomplishing this. The addition of ferric sulphate would be omitted only in case arsenic is known to be absent or when the ore itself carries sufficient iron to take care of the arsenic.

To the combined ammoniacal filtrates there are added 2 grams of tartaric acid and when the acid has dissolved the liquid is saturated with hydrogen sulphide. The presence of tartaric acid is necessary to prevent precipitation of vanadium and tungsten along with the molybdenum. Both of these elements are ordinary constituents of wulfenite concentrates. Under these conditions the molybdenum remains in the solution as ammonium thiomolybdate, \((\text{NH}_4)_2\text{MoS}_4\), which imparts a deep red color to the solution. If a small precipitate of insoluble sulphides separates out, it is filtered off and washed with dilute ammonium sulphide solution; if the solution remains clear this step is omitted. Copper in the amounts usually present remains entirely in solution at this point and is reprecipitated with molybdenum when the solution is subsequently acidified. The thiomolybdate solution is then made slightly acid with sulphuric acid (1 to 2). Molybdenum is thus precipitated as trisulphide.

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

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

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

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

All the molybdenum in the solution is then reduced from the sesquivalent to the trivalent condition by passage through the zinc reductor into a solution of ferric sulphate containing phosphoric acid—the solution is then titrated with N/10 permanganate. The details of the reductor and the method of preparing it are given on page 319 and 320.

It is essential to run a blank determination, using the same quantity of zinc that was used to separate copper and the same volumes of water and acid—passing the solution through the reductor under the same conditions. With good zinc the correction may be about 0.2 cc.

**Method for Molybdenum in Pure Molybdenite Concentrates**

Molybdenum may be determined in the same way as in wulfenite, but owing to the higher Mo content of the material only 0.5 gram may be taken for the determination.

In case of very pure and high-grade molybdenite, which rarely contains any interfering element except traces of arsenic, the method may be simplified. It suffices to treat 0.5 gram of the pulp with 10 cc. of strong HNO₃ and 7 cc. of H₂SO₄ and evaporate to fumes. A single treatment usually results in complete decomposition, but if the solution shows any particle of decomposed material a further addition of 5 cc. of HNO₃ and a second evaporation to fumes may be necessary. In order to remove all HNO₃, the H₂SO₄ solution is diluted by washing down the sides of the beaker with 5 cc. of water and the evaporation to fumes is repeated.

After cooling, 35 cc. of water and ferric sulphate equivalent to about 0.1 gram of metallic iron are added. The solution is poured into an ammonia solution, the same as in the longer method, the iron hydrate carrying any arsenic is filtered off, dissolved in H₂SO₄ and reprecipitated. The united filtrates contain all the molybdenum; they are concentrated by evaporation to a volume of 150 cc. which also serves to expel the excess of ammonia. The solution is acidulated with H₂SO₄, reduced and titrated as in the longer method.

This method, of course, is not applicable in the presence of vanadium, tungsten or other impurities which might be reduced and reoxidized in the final operations, but it serves very well for the analysis of high grade molybdenite.
MOLYBDENUM

Determination of Commonly Occurring Substances in Molybdenum Ores

Determination of Arsenic

Two grams of the 100-mesh sample are treated with 20 cc. of nitric acid (sp.gr. 1.42) and 7 cc. of sulphuric acid (sp.gr. 1.84) in a 150 cc. beaker. The liquid is heated for a short time at a temperature just below the boiling point and is then evaporated until fumes of sulphuric anhydride are freely evolved. The residue is taken up with 40 cc. of water and boiled for a few minutes. Approximately one gram of cuprous chloride and five grams of ferrous ammonium sulphate are added, and transfer is made of the solution to the distillation flask of the apparatus shown on page 39, arsenic chapter, the beaker being rinsed with 40 cc. of hydrochloric acid (sp.gr. 1.20). It is important that the amount of water used be kept to a minimum so as to insure presence of sufficiently concentrated hydrochloric acid in the distillation flask to rapidly and completely volatilize the arsenic.

For distillation of the arsenic, the Knorr Arsenic and Antimony Distillation Apparatus (mentioned above see page 39) is very satisfactory. The rate at which arsenic distills over is greatly influenced by the size and form of apparatus employed; by use of the Knorr apparatus it is rapidly and completely volatilized. After having attached the flask, the inlet funnel is filled about half full of hydrochloric acid (sp.gr. 1.20). The outlet of the condenser tube is caused to dip just beneath the surface of 100 cc. of distilled water in a 350 cc. beaker containing a lump of ice. The solution in the distillation flask is heated to boiling; concentrated hydrochloric acid is introduced through the funnel tube drop by drop at a rate sufficient to replace the evaporation, or in other words, in amount sufficient to keep the level of liquid in the flask constant. It is necessary to keep a steady flame under the flask; if the solution in the beaker starts to be sucked back into the condenser tube, the apparatus is quickly raised so as to lift the lower end of the condenser out of the distillate. All of the arsenic will usually distill over in 30 or 35 minutes; at the end of this time the beaker holding the condensate is replaced by another one containing about 100 cc. of water and a lump of ice, and the distillation is continued for another 15 minutes. The second distillate is tested separately to determine whether it contains any arsenic.

By the above described procedure the arsenic is separated from any other elements likely to be present by volatilization as arsenious chloride, AsCl₂; it may be determined in the resulting solution by either gravimetric or volumetric methods. Where only occasional determinations have to be made, the gravimetric method is perhaps the more convenient. The hydrochloric acid distillate is warmed and saturated with hydrogen sulphide by passage of a rapid stream of gas. Filtration is made of the arsenious sulphide, As₂S₃, and it is washed with hydrogen sulphide water. The yellow precipitate is dissolved in the least necessary amount of ammonia (1 to 1) and the paper washed with hot water; the volume is kept as low as possible, the filtrate being received in a 150 cc. beaker. To the filtrate there are added 6-10 cc. of “perhydrol” (30% H₂O₂) for every 0.1 gram of arsenic supposed to be present; if “perhydrol” is not available, there are used instead 60-100 cc. of 3% hydrogen peroxide (free from phosphorus), but use of the former is preferable since it permits keeping the volume small. It is essential that enough hydrogen peroxide be used to oxidize the arsenic completely to the arsenic condition. Some commercial brands of hydrogen peroxide contain considerable amounts of phosphorus, making it always necessary to determine it and make a correction for the weight of magnesium pyrophosphate formed from it which would otherwise be counted as arsenic. The resulting solution is evaporated on a hot plate for some time, boiled for ten minutes with the cover glass on, and cooled in ice water. Ten cc. of “magnesia mixture” are added, followed by ammonia (sp.gr. 0.90) to the extent of one-third the volume of the solution, and the liquid is stirred vigorously for some time and then allowed to stand in a cool place for at least 15 hours. The magnesium ammonium arsenate is filtered on a weighed Gooch crucible and washed 10-15 times with small amounts of cold 2.5% ammonia water. It is then drained as completely as possible by suction, dried at 105° C., and heated gradually in an electric muffle furnace to a temperature of 400°-500° C. until no more ammonia is evolved. The temperature is then increased to 800°-900° C. and kept there for about 10 minutes. After having cooled the crucible in a desiccator and weighed it, the amount of arsenic is calculated from the weight of magnesium pyrosilicate, Mg₂As₂O₇, which contains 48.27% arsenic. A “blank” must be run on the reagents used and any arsenic found be deducted.
When more than occasional analyses have to be made, the following volumetric method can be used to advantage; the only superiority of the gravimetric process is that visual evidence of the presence of arsenic is furnished by the yellow arsenious sulphide. The distillate containing the arsenic in the form of arsenious chloride, As₄Cl₅, is made slightly ammonical, litmus paper being used as indicator, and the solution being kept cool. Sufficient sulphuric acid (1 to 1) to render the liquid slightly acid is next added. To the cold, slightly acid solution there is added 8–10 grams of sodium bicarbonate, 0.3 gram of potassium iodide and several cc. of starch solution (a water solution of Kahlbaum's "Lödiche Starke" or soluble starch is used) and the solution is titrated with a standard iodine solution each cc. of which is equal to 0.001 gram of arsenic. The titration is based on the reaction:

\[ \text{KH}_2\text{AsO}_4 + \text{I}_2 + 2\text{NaHCO}_3 = \text{KHAso}_4 + 2\text{NaI} + 2\text{CO}_2 + \text{H}_2\text{O} \]

The reaction between arsenic and iodine is shown by the equation:

\[ \text{As}_2\text{O}_3 + 2\text{I}_2 + 4\text{H}_2\text{O} = 2\text{H}_3\text{AsO}_4 + 4\text{I}^- \]

A "blank" must be run and deducted.

The iodine solution is prepared by dissolving 3.5 grams of pure resublimed iodine with 7 grams of potassium iodide and a very small amount of water. When the iodine has completely dissolved, the solution is diluted to 1 liter and mixed thoroughly; it is standardized against pure As₂O₃. This is accomplished by carefully weighing 0.0000 gram of pure resublimed As₂O₃ and transferring it to a 250 cc. beaker. Eight to ten grams of sodium bicarbonate and sufficient hot water to dissolve it are added and the solution is heated until the As₂O₃ has completely dissolved. The solution is then diluted to 250 cc., cooled, 0.3 gram of potassium iodide and 2–3 cc. of starch solution are added and the liquid is titrated with the iodine solution to the usual blue end point. The weight of As₂O₃ used (0.0000 gram) contains exactly 0.04545 grams of arsenic so the number of cc. used in the titration, divided into 0.04545, gives the arsenic value of one cc. of the iodine.

Determination of Copper

(a) In Molybdenite. Four grams of finely ground sample are treated with 35 cc. of nitric acid (sp.gr. 1.42) and 10 cc. of sulphuric acid (sp.gr. 1.84) in a 250 cc. beaker provided with a clock-glass cover. The solution is digested at a temperature somewhat below the boiling point until most of the molybdenite has dissolved. Subsequently the liquid is boiled until strong fumes of sulphur trioxide are expelled. After having allowed the beaker and its contents to cool, 50 cc. of water are added and the solution is boiled briskly for a few minutes and filtered on a 0 cc. paper into a 250 cc. beaker. The residue is washed thoroughly with hot water and discarded.

An excess of sodium hydroxide solution is added to the filtrate and the solution is boiled for several minutes and filtered on a 0 cc. paper. The precipitate of ferric hydroxide, etc., is washed with hot water to remove the molybdenum. Solution is then made of this precipitate, which will contain all of the copper, in 30 cc. of hot dilute (1 to 3) sulphuric acid, the paper being washed with about 50 cc. of hot water and the filtrate and washings being collected in a 150 cc. beaker. The copper in the solution obtained as above described is completely precipitated in the metallic condition by placing a sheet of pure aluminum (conveniently bent into the form of a triangle 1 inch in height which stands on its edge in the beaker) in the beaker and boiling for about ten minutes. Complete precipitation is not obtained until the iron has been reduced, when the aluminum should appear clean and the precipitated copper be detached or only loosely adherent. After removal from the source of heat, the clock glass and sides of the beaker are rinsed with a jet of hydrogen sulphide water. The aluminum, the copper content of which should be accurately determined, is weighed before and after use and a correction is applied for the copper introduced from it.

Filtration is made of the solution on a very small filter paper, the copper being transferred to the paper and the aluminum being left as clean as possible in the beaker. The precipitate is washed with hot water and the filtrate and washings are discarded. Solution is then made of the copper in 5 cc. of hot nitric acid (1 to 1), this being accomplished by first dropping the acid over the aluminum and then pouring it on the copper. The aluminum and filter paper are both washed with hot water, the filtrate and washings being collected in a 100 cc. lipless beaker. After boiling the solution to expel oxides of nitrogen, 2 cc. of sulphuric acid (sp.gr. 1.84) are added and determination is made of the copper by electrolysis, a platinum gauze cathode and spiral anode being employed.
Determination of Copper

(b) In Wulfenite. Four (4.0000) grams of the 100-mesh sample are treated with approximately 30 cc. of 10% sodium hydroxide solution in a 250 cc. beaker provided with a clock-glass cover. The solution is boiled briskly for 10 minutes, which is usually sufficient to insure practically complete decomposition of the wulfenite. Addition is then made of about 70 cc. of hot water and the precipitate of iron oxide, etc., which will contain all of the copper, is allowed to settle. The supernatant liquid is decanted through a 9 cm. filter paper and the precipitate is then transferred to the paper and washed well with hot water. The filtrate and washings are discarded. As a result of these operations separation of the copper from practically all of the molybdenum and from the greater part of the lead is accomplished.

The paper containing the residue is returned to the original 250 cc. beaker and treated with 6 cc. of sulphuric acid (sp.gr. 1.84) and 10 cc. of nitric acid (sp.gr. 1.42). The contents of the beaker are cautiously heated until frothing is nearly over, and then boiled briskly until fumes of sulphuric anhydride are evolved. After having permitted the liquid to partly cool, 10 cc. of nitric acid (sp.gr. 1.42) are added and the evaporation to fumes is repeated. The cover glass and sides of the beaker are cleaned with a few cc. of water and the solution is once more evaporated to fumes in order to insure destruction of all carbonaceous matter from the filter paper and complete expulsion of nitric acid. In practice the total time consumed in making these evaporations is small.

Having allowed the beaker and its contents to cool somewhat, addition is made of 50 cc. of water and the solution is boiled for a short while, cooled, and filtered on a 9 cm. paper into a 150 cc. beaker. The precipitate of lead sulphate, etc., is washed with cold 10% sulphuric acid and discarded, the copper passing completely into the filtrate and washings, which should have a total volume of not more than 100 cc.

The copper in the solution obtained as above described is completely precipitated in the metallic condition by placing a sheet of pure aluminum (conveniently bent into the form of a triangle 1 inch in height which stands on its edge in the beaker) in the beaker and boiling for about ten minutes. Complete precipitation is not obtained until the iron has been reduced, when the aluminum should appear clean and the precipitated copper be detached or only loosely adherent. After removal from the source of heat, the clock-glass and sides of the beaker are rinsed with a jet of hydrogen sulphide water. The aluminum, the copper content of which must be accurately determined, is weighed before and after use and a correction is applied for the copper introduced into the solution from it.

Filtration is made of the solution on a very small filter paper, the copper being transferred to the paper and the aluminum being left as clean as possible in the beaker. The precipitate is washed with hot water and the filtrate and washings are discarded. Solution is then made of the copper in 5 cc. of hot nitric acid (1 to 1), this being accomplished by first dropping the acid over the aluminum and then pouring it on the copper. The aluminum and filter paper are both washed with hot water, the filtrate and washings being collected in a 100 cc. lipless beaker. After boiling the solution to expel oxides of nitrogen, 2 cc. of sulphuric acid (sp.gr. 1.84) are added and determination is made of the copper by electrolysis, a platinum gauze cathode and spiral anode being employed.

Determination of Phosphorus

(a) Molybdenite. Four grams of the finely ground sample are treated with 35 cc. of nitric acid (sp.gr. 1.42) and 10 cc. of sulphuric acid (sp.gr. 1.84) in a 250 cc. beaker provided with a cover glass. The liquid is heated at a temperature somewhat below the boiling point until decomposition of the mineral appears to have been secured, when it is boiled until strong fumes of sulphuric anhydride are given off. When the residue has cooled, 40 cc. of water are added and the solution is boiled for several minutes and filtered on a 9 cm. paper into a 300 cc. Erlenmeyer flask. The residue is washed well with hot water, ignited in a porcelain crucible and transferred to a platinum crucible and evaporated with 2 or 3 drops of sulphuric acid (sp.gr. 1.84) and several cc. of hydrofluoric acid. After completely expelling the sulphuric acid, any small residue remaining is fused with a pinch of potassium pyrosulphate and dissolved in water and added to the main solution.

A few drops of strong permanganate solution (25 grams per liter) are added to the solution obtained as previously described, and it is boiled to insure complete oxidation of the phosphorus to the tribasic condition. Just sufficient sulphuric acid to decompose the excess of permanganate or separated manganese oxide is then added and the
boiling is continued for a few minutes longer. A slight excess of ammonia is added and the ferric hydroxide, etc., which will carry down practically all of the phosphorus, is filtered and washed thoroughly with hot water. Solution is made of the precipitate in hot dilute (sp.gr. 1.135) nitric acid and the phosphorus is precipitated with "molybdate solution" and determined as described for wulfenite.

(b) Wulfenite. Two (2,000) grams of the agate ground sample of wulfenite are treated with 20 cc. of nitric acid (sp.gr. 1.42) and 10 cc. of sulphuric acid (sp.gr. 1.84) in a 150 cc. beaker. The liquid is heated for a short while at a temperature just below the boiling point and then boiled until fumes of sulphuric anhydride are freely evolved. The residue is taken up with 40 cc. of water, boiled a few minutes, cooled, filtered into a 300 cc. Erlenmeyer flask, and the lead sulphate, silica, etc., are washed with cold 10% sulphuric acid and discarded.

A few drops of strong permanganate solution (25 grams per liter) are added to the filtrate from the lead sulphate and it is boiled to insure complete oxidation of the phosphorus to the tribasic condition. Just sufficient sulphurous acid is added to decompose the excess of permanganate or separated manganese oxide and the boiling is continued for a minute or two longer.

The acid solution is nearly neutralized with ammonia, partly cooled, and to it there are added one gram of tartaric acid and then a slight excess of ammonia. If less than 2 grams of sample should be employed, as in case of very high phosphorus ores, correspondingly less tartaric is to be used, since an excess tends to prevent complete precipitation of the phosphorus.

Twenty cc. of "magnesia mixture" and 4 or 5 glass beads (6 mm. diameter) are added to the warm solution and it is thoroughly chilled by immersion in a mixture of crushed ice and salt. The contents of the flask are then vigorously shaken (an efficient shaking machine can be used to advantage) for about 15 minutes, the solution being chilled several times during the shaking. The glass beads aid in starting the precipitation of the magnesium ammonium phosphate. Fifteen cc. of ammonia (sp.gr. 0.90) are next introduced and the contents of the flask are again thoroughly chilled and shaken briskly for 10-15 minutes longer. The flask is then packed in ice in a refrigerator and allowed to stand for 15 hours.

The magnesia precipitate, which may contain small amounts of basic magnesia compounds, iron, and possibly tartrates, is filtered on a 9 cm. paper and washed thoroughly with cold 10% ammonia water. The glass beads are transferred to the filter but no attempt is made to remove all of the precipitate from the flask. Under the conditions described, molybdenum, tungsten, and vanadium should all pass completely into the filtrate.

Solution is made of the magnesium ammonium phosphate in the least necessary amount of hot dilute hydrochloric acid and the paper is washed with hot water. The filtrate and washings are caught in the same 300 cc. Erlenmeyer flask and evaporated down to a volume of approximately 5 cc. After cooling, addition is made of 10 cc. of a saturated solution of sulphurous acid, the flask and its contents are permitted to stand in a warm place for 5 or 10 minutes, 20 cc. of hydrochloric acid (sp.gr. 1.20) are added and the solution is evaporated to a bulk of about 5 cc. to expel completely arsenic. Twenty cc. of nitric acid (sp.gr. 1.42) are added and the solution is again boiled down to a volume of about 10 cc. in order to eliminate practically all of the hydrochloric acid. After having been diluted with 50 cc. of water, the solution is oxidized by boiling with an excess of strong permanganate solution (25 grams per liter) and then cleared by the addition of a few cc. of sulphurous acid. The liquid is boiled for a minute or two to expel nitrous fumes, and then cooled. A piece of litmus paper is dropped into the solution and a slight excess of ammonia (sp.gr. 0.90) is added. This is followed by addition of an excess of 1 or 2 cc. of colorless nitric acid (sp.gr. 1.42). The temperature of the solution is brought to 40° C. and the phosphorus is precipitated by addition of 40 cc. of "molybdate solution" and five minutes' vigorous shaking. Determination is made of the precipitate as in the ammonium phosphomolybdate by either the Alkalimetric or the Molybdenum Reduction (Emerson) Method.

The "magnesia mixture" is prepared in the following manner: Fifty-five grams of crystallized magnesium chloride, MgCl₂·6H₂O, or twenty-five grams of the anhydrous salt, are dissolved in water and filtered. Fourteen grams of ammonium chloride are dissolved in water, a little bromine water and a slight excess of ammonia are added and the solution is filtered. The two solutions are mixed, sufficient ammonia is added to give a decided odor, and enough water is added to bring the volume up to one liter. The solution is allowed to stand for several days with occasional vigorous shaking and is filtered into one or more cereon bottles. Ten cc. of the reagent will precipitate about 0.085 gram of phosphorus.
NICKEL

Ni, at. wt. 58.69; sp. gr. 8.6–8.9; m. p. 1452° C.; oxides, NiO, Ni₂O₃, Ni₃O₄.

DETECTION

After bringing the sample into solution by one of the methods described under Preparation and Solution of the Sample, silica is removed, if present, in the usual manner, by evaporating the solution to dryness in the presence of an excess of hydrochloric acid, dissolving the residue and boiling with hydrochloric acid and filtering off the silica.

*Hydrogen sulphide* is then passed through the solution to remove the elements precipitated by this reagent. The filtrate from this precipitation is then boiled to expel the excess of hydrogen sulphide and a little nitric acid added to oxidize any ferrous iron to the ferric state. (See page 331, Separations.) Ammonium hydroxide is then added to precipitate iron, aluminum and chromium. Cobalt, nickel, manganese and zinc are precipitated from the filtrate by adding a solution of colorless ammonium sulphide or by passing hydrogen sulphide through the ammoniacal solution. Manganese and zinc are separated from the precipitate by washing with cold hydrochloric acid of about 1.035 sp.gr. A small quantity of the precipitate is fused with borax in the loop of a clean platinum wire. A green color in the cool bead indicates nickel. Fairly small quantities of cobalt interfere with this test, so if the bead is colored blue it will be necessary to make further tests for nickel.

*Dimethylglyoxime* will precipitate nickel as oxime from an acetic acid solution containing sodium acetate and in this manner separate it from cobalt, manganese and zinc. After precipitating iron, aluminum and chromium and filtering them off, the solution is slightly acidified with hydrochloric acid, then is neutralized with sodium hydroxide, and acidified with acetic acid. A solution of dimethylglyoxime is added, when nickel, if present, will be precipitated as a flocculent red precipitate.

Nickel may be detected in the presence of cobalt by adding a solution of sodium hydroxide to the solution of cobalt and nickel until a slight precipitate is formed, then somewhat more potassium cyanide then is necessary to redissolve the precipitate and finally two volumes of bromine water. Warm gently and allow to stand for some time. If a precipitate of nickel hydroxides separates, filter, wash and test with the borax bead.

Nickel may also be detected in the presence of cobalt by precipitating the cobalt as nitrite, as described in the chapter on cobalt, and then precipitating the nickel as hydroxide with sodium hydroxide and bromine water and testing the precipitate with the borax bead.

*Alpha benzildoxime* added to an ammoniacal solution of nickel precipitates an intensely red salt having the composition C₅H₁₂N₃O₃Ni. This precipitate is very voluminous. Silver, magnesium, chromium, manganese and zinc do not interfere with this reaction.

Chapter by W. L. Savell, Paul D. Mercia and Thos. Fudge.

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ESTIMATION

The determination of nickel is required, principally, in the analysis of ores, metallic nickel and its alloys, but is also required in the analysis of metallic cobalt and cobalt products as well as in a host of miscellaneous materials.

In the majority of cases the results of a nickel determination are calculated in terms of metallic nickel. Even in the determination of nickel in nickel-plating solution the results are calculated in terms of metallic nickel since this is the factor by which the solutions are controlled.

Preparation and Solution of the Sample

The materials in which nickel occurs ordinarily, may, in general, be brought into solution by treatment with acids, but in the case of some refractory ores and alloys, a fusion is required first to make the acid treatment effective. When treating ores containing sulphides or arsenides a strong oxidizing treatment is necessary to break up these compounds. Metallic nickel may be dissolved easily in nitric acid, more slowly in hydrochloric acid and still more slowly by sulphuric. Nickel alloys may be dissolved in a mixture of hydrochloric acid and nitric acid.

General Procedure for Ores. One gram of the finely powdered ore is weighed into a porcelain dish and mixed intimately with 3 grams of powdered potassium chlorate. The dish is covered with a watch-glass and 40 cc. concentrated nitric acid added slowly. The dish is allowed to stand in a cool place for a few minutes, then placed on a water bath and digested until the sample is completely decomposed, stirring the mixture frequently with a glass stirring rod, and adding a little potassium chlorate from time to time until the decomposition is complete. The watch-glass is then removed and any particles that may have spattered on it are washed back into the dish and the evaporation continued to dryness. This evaporation to dryness is repeated with the addition of 10 cc. of concentrated hydrochloric acid, and the silica dehydrated by heating for an hour or more in an air oven at 110° C. The dry residue is moistened with concentrated hydrochloric acid and the sides of the dish washed down with hot water, the mixture heated to boiling and allowed to boil for a few minutes, then withdrawn from the heat and filtered, hot, after the insoluble matter has settled.

Treat the filtrate for the removal of interfering elements as directed under Separations.

Fusion Method. The above method is used where it is desired to determine insoluble matter or “gangue.” As a method of bringing the nickel in the sample into solution it is quite satisfactory and when the insoluble matter burns to a pure white ash the ignited residue may be weighed as silica, but in some cases this method does not give sufficient information regarding the composition of the gangue.

If it is necessary to make a complete analysis it is usually better to fuse the sample with the sodium and potassium carbonate mixture containing a little potassium nitrate and then treat in the usual manner to determine silica.

Potassium Bisulphate Fusion. In the treatment of nickel and cobalt oxides these are ground to a fine powder and a representative sample of 1 gram is fused with 10 grams of potassium bisulphate. This may be done in a porcelain or silica crucible or dish. The melt is extracted with water and the silica filtered off. A small casserole has been found to be very useful for this fusion.
Solution of Metallic Nickel and Its Alloys. From 1 to 5 grams of the well-
mixed drillings are treated with a minimum quantity of nitric acid and 20 cc. 
1:1 sulphuric acid added and the solution evaporated to fumes of sulphur tri-
oxide. Allow the fuming to continue for ten minutes. Dilute carefully with a 
little water and filter off the insoluble. Continue as directed in the following 
detailed analyses.

It may be necessary to use a mixture of nitric and hydrochloric acids to bring 
certain alloys into solution, after which the procedure is the same as above.

SEPARATIONS

Separation of the Ammonium Sulphide Group, Containing Nickel from 
the Hydrogen Sulphide Group. Mercury, Lead, Bismuth, Copper, Cadmium, 
Arsenic, Antimony, Tin, Gold, Molybdenum, etc.

The hydrogen sulphide group elements are precipitated from an acid solution 
(HCl) by H₂S, and removed by filtration, nickel, etc., passing into the filtrate.

Separation of the Ammonium Sulphide Group from the Alkaline Earths 
and Alkalies. Nickel is precipitated with other members of the group by 
passing H₂S into its ammoniacal solution, or by adding (NH₄)₂S solution. The 
alkaline earths and alkalies are not precipitated.

Separation of Nickel from Cobalt. This procedure can be carried out in 
exactly the same manner as the method given for the determination of nickel 
by precipitation of nickel with dimethylglyoxime, since cobalt is soluble as oxime. 
In case more cobalt is present than nickel a larger excess of the reagent must 
be used. The excess of acid is best neutralized with ammonium hydroxide. If 
both metals are to be determined, cobalt may be determined electrolytically 
in the filtrate.

An alternate method is to determine the cobalt and nickel as oxides, or metal 
by electrolysis, together. The oxides, or plate, are dissolved in nitric acid and 
the nickel determined in the solution, cobalt being found by difference.

For other methods see Separation of Cobalt from Nickel, under Cobalt, page 188.

Separation of Nickel from Manganese. Nickel is precipitated by dimethyl-
glyoxime from an acetic acid solution containing sodium acetate, manganese 
being determined in the filtrate.

Separation of Nickel from Zinc. Zinc does not interfere in the dimethyl-
glyoxime precipitation of nickel when ammonium salts are present. It is advis-
able to precipitate the nickel in a dilute acetic acid solution, thus avoiding the 
addition of a large amount of ammonium salts as would be necessary if the pre-
cipitation took place in an ammoniacal solution. Zinc readily remains in solution, 
and may be determined in the filtrate from the nickel oxime precipitate. The 
following procedure is recommended:

The solution containing the two metals is neutralized with ammonium hydrox-
ide and then made just slightly acid with acetic acid and sodium acetate added. 
Dimethylglyoxime solution is now added to the solution, which is nearly boiling, 
and the procedure given for the determination of nickel by this reagent is followed.

Separation of Nickel from Iron. Nickel cannot be separated satisfactorily 
from iron by precipitating the latter with ammonium hydroxide, as some of the 
nickel is invariably cluded by the ferric hydroxide precipitate. Two modifi-
ctions of the oxime method may be used.

(1) The iron, if present as a ferric salt, is converted into a complex salt by
adding from 1 to 2 grams of tartaric acid, and the solution diluted to 200 or 300 cc., boiled and the nickel precipitated as the oxime in an ammoniacal solution by the prescribed method. Iron forms no oxime under these conditions.

The iron may be precipitated from this filtrate by colorless ammonium sulphide and the sulphide converted to ferric oxide (Fe₂O₃) by ignition.

(2) Ferric iron is reduced to the ferrous condition by warming with sulphurous acid, in a nearly neutral solution. If the original solution has an excess of acid, it is treated with a solution of sodium hydroxide until a permanent precipitate is formed. This is dissolved with a few drops of hydrochloric acid and the iron reduced by adding from 5 to 10 cc. of a saturated solution of sulphur dioxide or by passing dioxide through the solution. The solution is diluted to 200 or 300 cc. and the solution of dimethylglyoxime added in slight excess, followed by sodium acetate until a permanent precipitate of nickel oxime is formed. After adding 2 grams more of sodium acetate the solution is filtered immediately. The iron is precipitated from the filtrate by oxidizing with bromine water and adding ammonium hydroxide to precipitate the basic acetate of iron.

Procedure (1) is suitable for the determination of nickel in iron and steel.

Separation of Nickel from Aluminum. This method is the same as procedure (1) given above.

Separation of Nickel from Chromium. This separation cannot be carried out in an acetic acid solution. From 1 to 2 grams of tartaric acid are added and from 5 to 10 cc. of a 10% ammonium chloride solution, subsequently. The solution is made ammoniacal, but no precipitate should form. If the solution becomes cloudy, it is acidified with hydrochloric acid and additional ammonium chloride added and again made ammoniacal and the nickel precipitated as oxime according to directions given from this precipitation.

GRAVIMETRIC METHODS FOR THE DETERMINATION OF NICKEL

Precipitation of Nickel by Alpha Benzildioxime

The alcoholic solution of alpha benzildioxime gives an intensely red precipitate of C₆H₃N₂O₂Ni, when added to ammoniacal solutions containing nickel. The reaction is more characteristic for nickel than is that with dimethylglyoxime and is more delicate. In a volume of 5 cc. (according to F. H. Atack), 1 part of nickel in 2,000,000 parts of water may be detected. In the presence of 100 times as much as cobalt only a faint yellow color is produced by the cobalt. One part of nickel per million of water will cause precipitation with the compound, whereas no precipitate is formed with dimethylglyoxime under the same conditions. With glyoxime iron produces a pink color, with alpha benzildioxime ferrous salts give a faint violet color, hence do not interfere in the detection of nickel. Silver, magnesium, chromium, manganese, and zinc do not interfere. Since the nickel precipitate with this reagent is exceedingly voluminous it is advisable to have not more than 0.025 gram of nickel in the solution in which the nickel is being determined. The method is adapted to the detection and determination of minute traces of the element up to small amounts of less than 10% nickel.
Reagent, Alpha Benzdioxime. This may be prepared by boiling 10 grams of benzil (not necessarily pure) with 8 to 10 grams of hydroxylamine hydrochloride in methyl alcohol solution. After boiling for three hours the precipitate is filtered off and dried, washed with hot water and then with a small amount of 50% alcohol, and dried. This dried precipitate consists of pure benzdioxime (m.p. 237° C.). A further yield may be obtained by boiling the filtrate with hydroxylamine hydrochloride. The reagent is prepared by dissolving 0.2 gram of the salt per liter of alcohol to which is added ammonium hydroxide to make 5% solution, sp.gr. 0.96 (50 cc. per liter).

Procedure. A slight excess of the warmed solution of the above reagent is stirred into the ammoniacal solution containing nickel and the whole heated on the water bath for a few moments to coagulate the precipitate. Quantitative precipitation is complete after one minute. The liquid is filtered through a Gooch crucible, with suction, or onto a filter paper, for which a counterpoise has been selected. The counterpoise paper is treated in exactly the same manner as the one containing the precipitate. The precipitate is washed with 50% alcohol, followed by hot water, and is then dried at 110° C. In weighing the precipitate the counterpoise filter is placed in the weight pan of the balance. The precipitate contains 10.93% nickel. Weight of $C_{34}H_{27}N_7O_3Ni\times0.1093 = Ni$.

Notes. Acetone may be used instead of alcohol as a solvent of the reagent. The compound is more soluble in acetone than in alcohol.

The precipitate does not pass through the filter as does the compound with dimethylglyoxime.

The method is affected by the presence of nitrates, hence these must be removed by evaporation of the solution with sulphuric acid to fumes, before the addition of the reagent to the nickel solution.

In the presence of cobalt an excess of the reagent must be used, as in the case of the dimethylglyoxime precipitation.

In the presence of iron and chromium Rochelle salt, sodium citrate or tartaric acid are added to prevent precipitation of the hydroxides of these metals upon making the solution alkaline.

In the presence of manganese a fairly large excess of the reagent is required, the solution being slightly acid with acetic acid.

Zinc and magnesium are kept in solution by addition of ammonium chloride.

Large amounts of copper must be removed by precipitating with hydrogen sulphide before addition of the reagent.

The nickel salt with the reagent forms an extremely voluminous precipitate so that a concentration of 0.09 gram of nickel per 250 cc. is as high as is desirable. The process is applicable to the determination of nickel in the filtrate obtained in the separation of zinc after the removal of the hydrogen sulphide, formic acid, etc.


Precipitation of Nickel by Dimethyl-glyoxime

Preliminary Considerations. This method has been demonstrated by O. Brunck to be the most accurate and expeditious procedure known for nickel.¹ By this method 1 part of nickel may be detected when mixed with 5000 parts of cobalt or 1 part of nickel may be detected in 400,000 parts of water. The nickel precipitate with this reagent is almost completely insoluble in water and is only very slightly soluble in acetic acid, but is easily decomposed by strongly dissociated acids, so that the precipitation is incomplete in neutral solutions of nickel chloride, sulphate or nitrate. If, however, the free acid formed is neutral-

ized with sodium, potassium or ammonium hydroxides or by addition of the acetate salts of these bases, nickel will be completely precipitated, not even a trace being found in the filtrate.

"The quantitative determination of nickel in the presence of other metals is a simple operation. The nickel should be in the form of a convenient salt.

"The concentration of the solution does not matter; the precipitation can take place either in a solution of the greatest concentration, or in a very dilute solution. The reaction is not hindered by the presence of ammonium salts."

Iron, aluminum, chromium, cobalt, manganese and zinc do not interfere. Theoretically 4 parts of dimethylglyoxime, added as a 1% alcoholic solution, are necessary; a certain excess does no harm provided the alcohol volume does not exceed more than half that of the water solution containing the nickel salt, as alcohol has a solvent action on the oxime. The compound is very stable and volatilizes undecomposed at 250° C.

An excess of ammonium hydroxide is also to be avoided in the solution in which the precipitation takes place.

It has been observed that the precipitate of nickel with dimethylglyoxime may be safely ignited to the oxide NiO without loss, if the filter is first carefully charred without allowing it to take fire, then gradually heated to redness.

Procedure. Such an amount of the sample should be taken that the nickel be not over 0.1 gram, as glyoxime of nickel is very voluminous and a larger amount would be difficult to filter. If cobalt is present it should not exceed 0.1 gram in the sample taken.¹

If hydrogen sulphide has been used to precipitate members of the second group, it is expelled by boiling the acid solution and the volume brought to 250 cc.

One or 2 grams of tartaric acid are added to prevent the precipitation of the hydroxides of iron, aluminum and chromium by ammonium hydroxide (this treatment is omitted if these are absent), and 5 to 10 cc. of a 10% solution of ammonium chloride added to keep zinc and manganese in solution, should they be present. Ammonium hydroxide is now added until the solution is slightly alkaline. If a precipitate forms, ammonium chloride is added to clear the solution, followed by ammonium hydroxide to neutralize the acid. The solution should remain clear after this treatment, otherwise the ammonium chloride is added in solution or as salt until the solution of the sample will remain clear. It is then heated to nearly boiling and the alcoholic solution of dimethylglyoxime added until the reagent is approximately seven times, by weight, the weight of nickel present. Ammonium hydroxide is now added until the solution has a distinct odor of this reagent. The precipitation of the scarlet red nickel salt is hastened by stirring. It is advisable to place the mixture on the steam bath for fifteen to twenty minutes to allow the reaction to go to completion before filtering. The precipitate is filtered off, into a platinum sponge Gooch crucible, sometimes known as a Neubauer Gooch crucible. (Other forms of Gooch crucible are used for this purpose, but the Neubauer crucible has been found to be most satisfactory.) The precipitate is dried for about two hours at 110 to 120° C. and weighed as C₄H₄N₂O₂Ni, which contains 20.32% Ni.

Weight of precipitate multiplied by 0.2032 = weight of nickel.

¹If the sample contains more than 0.1 gram of cobalt, a large excess of ammonium hydroxide and dimethylglyoxime is necessary to prevent its precipitation, hence it is advisable to take such weights of samples that the cobalt content will be less than this weight.
In place of a C-seal crucible a tared filter paper may be used. It must be remembered, however, that a blank filter paper of the same kind as used for the precipitate must be used as a counterbalance, after treating in exactly the same manner as the one containing the precipitate. This is necessary because it has been found that filter paper loses weight during washing and drying.

Precipitation of Nickel by Electrolysis ¹

This precipitation is conducted in exactly the same manner as the one described under Cobalt for the Precipitation of Cobalt by Electrolysis, and requires that the same precautions be exercised in the practice of the method.

In the presence of cobalt the two elements may be determined together by electrolysis as described below and the deposited metal redissolved and the two elements separated by one of the methods given under Cobalt or Nickel.

Procedure. After the sample has been brought into solution by one of the methods outlined under Preparation and Solution of the Sample, the solution is evaporated with 20 cc. of 1 : 1 sulphuric acid for every gram of metal in the sample. The evaporation is continued until the solution has fumed strongly for ten minutes. Cool carefully and dilute with 20 cc. of water. Heat the solution to nearly boiling and pass hydrogen sulphide for one hour to precipitate members of the second group. This long treatment is necessary to insure complete precipitation of arsenic. Filter and boil to expel hydrogen sulphide. Add 5 cc. nitric acid to insure oxidation of iron compounds to the ferric state and add ammonium hydroxide until just slightly alkaline. Filter off the ferric hydroxide and wash with water containing a small quantity of ammonium hydroxide. To recover occluded nickel dissolve the precipitate in hydrochloric acid and reprecipitate the iron with addition of a little hydrogen peroxide. Combine the filtrates. Evaporate to about 250 cc. and add 50 cc. of strong ammonium hydroxide and electrolyze as described under Cobalt, page 170.

The increase in weight of the electrode is the weight of cobalt and nickel in the sample. The percentage of cobalt and nickel in the sample is found by multiplying the increase in weight of the electrode by 100 and dividing by the weight of the sample.

Note. The deposition of cobalt and nickel by the above method has been found to be the most accurate of the electrolytic methods. In the solutions containing the organic acids there is always more or less carbide deposited on the cathode with the metal. This causes high results.

Nickel in Metallic Nickel

This determination may be made in the manner described under Precipitation of Nickel by Electrolysis, separating cobalt before or after the electrolysis or by the method described under Precipitation of Nickel by Dimethylglyoxime. The latter method is recommended.

Nickel in Cobalt and Cobalt Oxide

The dimethylglyoxime precipitation is used in combination with the electrolytic precipitation. See chapter on Cobalt.

VOLUMETRIC DETERMINATION OF NICKEL

Determination of Nickel in Alloys

This method, as described by S. W. Parr and J. M. Lindgren,\(^1\) consists of a modification of the dimethylglyoxime method. The precipitation takes place in the usual manner and the precipitate is dissolved in sulphuric acid and the excess titrated with a standard solution of potassium hydroxide.

Procedure. The alloy is dissolved in nitric or hydrochloric acids and if iron, aluminum or chromium are present twice their weight of tartaric acid is added to prevent their precipitation. If chromium is present ammonium chloride is also added. If manganese or zinc is present hydrochloric acid should be used and most of the free acid evaporated. Add a few cc. of hydrogen peroxide to oxidize any ferrous iron to the ferric state. Dilute to 300 or 400 cc. and neutralize the free acid by sodium acetate. Heat the solution to nearly boiling and add five times as much dimethylglyoxime, in 1% alcoholic solution, as the nickel present. Then completely neutralize with ammonium hydroxide, using a very slight excess (or the solution may be neutralized with sodium acetate). Heat until all the nickel is precipitated. Filter and wash. Place the precipitate and filter in a beaker, add an excess of 0.05N sulphuric acid, dilute to 200 cc., heat until solution is complete and titrate back with 0.1N potassium hydroxide solution, taking the first faint yellowish tinge as the end-point. The solutions are standardized against pure nickel.

Note. Cobalt should not exceed 0.1 gram per 100 cc. and an excess should be used of the dimethylglyoxime.

Nickel in Nickel-plating Solutions

In most cases it is quite unnecessary to separate the cobalt from the nickel in making this determination and, as the principal impurity is usually iron, the best practice is to follow the method given under Precipitation of Cobalt by Electrolysis, page 170.

If chlorides or organic matter are present in the solution the preparation of the solution for electrolysis is accomplished in the following manner:

From the well-stirred solution in the plating tank, withdraw about 200 cc. and place in a small beaker. Prepare a 100-cc. burette by thoroughly cleaning it with the sulphuric acid and potassium bichromate mixture and distilled water. Wash finally with a few cc. of the nickel solution and fill the burette with the solution from the plating tank.

Run 66.7 cc. into an evaporating dish and add 2 cc. 1:1 sulphuric acid. Evaporate to fumes of sulphur trioxide and allow to fume strongly for ten minutes. Dissolve in a little water. Dilute to 200 cc. carefully, neutralize with a solution of ammonium hydroxide and add 50 cc. of strong ammonium hydroxide and electrolyze. (See Precipitation of Cobalt by Electrolysis.)

The increase in weight of the cathode in grams multiplied by 2 gives the weight in ounces of nickel in one United States gallon of the plating solution.

NICKEL

Potassium Cyanide Method for Nickel

The method is rapid and accurate and is especially adapted for determining nickel in steel. Iron, manganese, chromium, zinc, vanadium, molybdenum and tungsten do not interfere. Copper, however, should be removed if present. The method depends upon the selective action of potassium cyanide for nickel in preference to silver iodide, used as an indicator, the reactions taking place as indicated, the solution being slightly alkaline with ammonia—

\[
\text{(a)} \quad \text{Ni}(\text{NH}_3)_2\text{SO}_4 + 4\text{KCN} = \text{K}_2\text{Ni}((\text{CN})_4 + \text{K}_2\text{SO}_4 + 6\text{NH}_3
\]

\[
\text{(N.B. 4KCN} \approx \text{Ni)}
\]

\[
\text{(b)} \quad \text{AgI} + 2\text{KCN} = \text{KAg(CN)}_2 + \text{KI}
\]

\[
\text{(N.B. 2KCN} \approx \text{Ag)}
\]

Reagents.

\text{N/10 Silver Nitrate}.—10.788 grams of pure silver are dissolved in nitric acid and made to 1000 cc. or 16.99 g. of the silver nitrate salt. (See Index for reagent.) 1 cc. = 0.01302 g. KCN.

If preferred the reagent may be made to be equivalent to about 0.001 gram Ni per cc. by dissolving 5.85 grams of AgNO₃ per liter.

\text{Potassium Iodide}.—25% solution.

\text{N/10 Potassium Cyanide}.—13.5 grams of pure KCN are dissolved in water, 5 grams of KOH added and the solution made to 1000 cc.

The cyanide solution is standardized against the silver nitrate solution.

If it is desired to have a solution equivalent to 0.001 g. Ni, 5 grams of KCN per liter is the approximate strength required.

\text{Standardization of the Cyanide}.—Fifty cc. of the KCN solution are diluted to about 150 cc., 5 cc. of the KI reagent added and the solution titrated with the standard AgNO₃ reagent until a faint permanent opalescence is obtained. A drop of the KCN solution should be sufficient to clear this. Note the number of cc. required and calculate the normality factor of the cyanide in terms of the silver nitrate reagent.

\text{Example}.—Suppose 49 cc. of the silver nitrate reagent were required for the 50 cc. of the cyanide solution, then the normality would be 49 \div 50 \times N/10 or 0.98 N/10.

1 cc. N/10 solution is equivalent to 0.002934 gram nickel.

The reagent may be standardized against a nickel steel of the U. S. Bureau of Standards, following the procedure given below and calculating as follows:

\[
\text{Nickel factor} = \frac{\text{Gram Ni in standard taken}}{(\text{cc. KCN required}) - (\text{cc. KCN equivalent to 5 cc. AgNO}_3)}
\]

\text{Citric Solution}.—200 grams of (NH₄)₂SO₄, 150 cc. concentrated NH₄OH and 120 grams of citric acid per 1000 cc.
Procedure.1

One gram of the steel drillings or such an amount of material as contains not over 0.1 g. Ni, is dissolved in a beaker with 20 cc. of hydrochloric acid (1:1). When action ceases 10 cc. of nitric acid (1:1) are added and the solution boiled until the red nitrous acid fumes are driven off.

About 100 cc. of the citrate solution are added. If 2 per cent. or more of chromium is present the amount of citrate solution is doubled. The solution is now diluted to about 250 cc.

Exactly 5 cc. of the standard silver nitrate solution are now added from a pipette or burette, and then ammonium hydroxide, drop by drop, until the cloudiness caused by the silver chloride just disappears. Two cc. of the potassium iodide solution are now added.

The solution is titrated with the standard potassium cyanide solution with constant stirring until the turbidity just disappears. The end point is reached when there is no longer a distinction in clearness of the drop of the reagent and its surrounding liquid to which it is added.1

If the end point is passed, a measured amount of silver nitrate (5–10 cc.) is added and the cyanide titration repeated.

Calculation.—Deduct the cc. KCN equivalent of the total silver nitrate solution used from the total cc. of the KCN solution required in the titration. The remainder is the potassium cyanide required by the nickel.

The cc. KCN required by Ni multiplied by the factor for Ni = gram nickel in the sample.

1. A large excess of ammonia is to be avoided as the AgI is soluble in a large excess.
2. The presence of sulphates increases the sensibility of the end point.
3. The silver nitrate solution should not be stronger than that indicated in the method as there is danger of the iodide of silver settling out as a curdy precipitate in stronger solutions.
4. A white film is apt to form on the surface of the liquid if exposed to the air for some time. This produces no error.

Carnot’s1 Gravimetric Oxide Method for Nickel

Sodium carbonate is added to the nickel solution, in slight excess until alkaline. Nickel is now precipitated with ammonia or ammonium carbonate from a boiling solution. The precipitate is filtered, washed and ignited to oxide, NiO, and so weighed.

Determination of Nickel in Nickel Steel—Ether Extraction Cyanide Titration Method

The following procedure is recommended by the A. S. T. M.

Reagents Required

Hydrochloric Acid.—600 cc. HCl (d. 1.2) dil. with 400 cc. water.
Nitric Acid.—1000 cc. HNO₃ (d. 1.42) and 1200 cc. water.
Potassium Iodide.—20 grams per liter.
Silver Nitrate.—0.5 cc. per liter.
Potassium Cyanide.—4.589 grams KCN per liter. The reagent is stand-

1 A. Carnot, Jour. Chem. Soc., 1918, 11, 133.
ardized against nickel steel of known nickel content as determined by the gravimetric dimethylglyoxime method.

Procedure. A sample of 1 gram of steel is dissolved by addition of 20 cc. of the dilute hydrochloric acid and then the iron oxidized by addition of 2 cc. of strong nitric acid (d. 1.42) and the solution boiled to expel the brown nitrogen fumes. After cooling the solution is transferred to an 8-oz. separatory funnel, hydrochloric acid being used to rinse out the containing beaker into the funnel. The solution is shaken with 50 cc. of ether for about 5 minutes, then allowed to settle for 1 minute and the lower clear layer drawn into a second separatory funnel (8-oz.). To the first ether solution are added 10 cc. of strong HCl (d. 1.2), cooling, and then shaking as before. After settling 1 minute the lower layer is drawn into the second separatory funnel. 50 cc. of ether are added to the second separatory funnel, the solution shaken for 5 minutes, then settled 1 minute, and the lower clear layer drawn into a 150-cc. beaker. The ether is expelled by gentle heat. 0.2 gram of potassium chlorate is added, the solution boiled to decompose the chlorate, then diluted to 100 cc. with hot water, and made faintly ammoniacal and boiled for 5 minutes. The manganese dioxide is filtered off and washed with hot water. To the filtrate are added 10 cc. of strong hydrochloric acid, the solution heated just short of boiling and copper precipitated with H₂S, and filtered off and washed with hot water. The filtrate is boiled to expel H₂S, and the boiling continued until the volume is reduced to about 100 cc. The solution is cooled, made distinctly ammoniacal, 10 cc. each of silver nitrate and potassium iodide solutions added and the solution titrated with standard potassium cyanide to a clear solution.

Determination of Bismuth in Metallic Nickel

Dissolve 20 grams of nickel drillings in 200 cc. 1 to 1 nitric acid in an 800-cc. beaker. Add 5 grams of potassium chlorate, boil for ten minutes. Cool and add 75 cc. of sulphuric acid. Evaporate until fuming strongly, cool. Add 600 cc. of water, boil gently to insure solution all the bismuth sulphate. Cool again, filter and wash with 1 to 10 sulphuric acid. Do not allow to stand too long before filtering, some basic bismuth sulphate may separate. Pass a current of hydrogen sulphide gas through for one half hour. Bismuth, copper, arsenic, antimony, etc., are precipitated as sulphides. Filter, washing with hot water. Rinse the precipitate as completely as possible into a beaker, add 3 or 4 grams of pure potassium cyanide, warm gently for some time. Bismuth sulphide will remain undissolved. Filter through same filter as before, in order to act upon traces of sulphides that could not be washed into the beaker, and wash with hot water. Place the filter and precipitate into a 100-cc. lid beaker and heat with 10 cc. of 1 to 1 nitric acid until the separated sulphur is clean and the filter well disintegrated. Dilute a little and then filter and wash thoroughly with 1 to 1 nitric acid. Partially neutralize the filtrate with ammonium, but without producing any permanent precipitate, and then add a solution of ammonium carbonate in very slight excess. Heat nearly to boiling for some time until the bismuth carbonate has settled well, and then filter and wash with hot water. Dry the precipitate and transfer it to a small weighed porcelain crucible, removing it from the paper as completely as possible. Burn the latter carefully and add the ash to the precipitate in the crucible. Ignite the whole at a low red heat, cool and weigh as Bi₂O₃, which contains 89.68 per cent of bismuth.
Determination of Lead in Metallic Nickel

Dissolve 20 grams of nickel drillings in 200 cc. of 1 to 1 nitric acid in a 1200-cc. beaker. Evaporate to 100 cc. Add 100 cc. sulphuric acid and evaporate to heavy fumes.

Cool and add 800 cc. water. Boil gently to insure solution of sulphates, cool and add 200 cc. of 95 per cent alcohol, stir and allow to stand over night.

Filter off the lead sulphate and wash two or three times with 2 per cent sulphuric acid and once with cold water. Place filter paper, containing the lead sulphate, in a beaker and add 10 grams of slightly ammoniacal ammonium acetate and 50 cc. of water. Boil a few minutes. Filter and wash with hot water.

Filtrate, containing all the lead in solution as the acetate, is acidified slightly with acetic acid and heated to boiling. Precipitate lead by adding 20 cc. of a 5 per cent solution of potassium dichromate. Boil until precipitate changes to orange or red. Allow precipitate to settle over night.

Filter the lead chromate on a weighed Gooch crucible. Wash with water and finally with alcohol. Dry at 110° C., and weigh as PbCrO₄, which contains 64.10 per cent of lead.

Determination of Aluminum in Metallic Nickel

Dissolve 10 grams of nickel drillings in 100 cc. dilute nitric acid (one part water, two parts nitric acid) in a 600-cc. covered beaker, add 1 or 2 grams potassium chlorate, boil for one hour, add about 100 cc. cold water and about 5 grams ammonium chloride, make slightly alkaline with ammonia. Transfer to a 500-cc. platinum dish. Boil a few minutes, filter off iron and aluminum hydrates and wash with hot water two or three times.

The precipitate is again transferred to 500-cc. platinum dish by redissolving in 1 to 3 hydrochloric acid, add a few grams of ammonium chloride, make slightly alkaline with ammonia. Boil a few minutes, filter off iron and aluminum hydrates and wash with hot water two or three times. Repeat re-dissolving and ammonia precipitation with addition of a few grams of ammonium chloride. After final re-precipitation transfer the precipitate to 100-cc. platinum dish by washing and dissolving the precipitate in 1 to 3 hydrochloric acid. Evaporate to dryness on a steam bath. Add 2 grams pure sodium hydrate and about 2 cc. of water. Fuse at low temperature for ten minutes. Cool and add about 50 cc. of water. Place on steam bath for a few minutes. Transfer to a 500-cc. platinum dish, add 300 cc. of water. Filter into a 500-cc. casserole containing 30 cc. of hydrochloric acid. Evaporate the filtrate to dryness on the hot plate. Add 50 cc. 1 to 3 hydrochloric acid, boil and filter into a 200-cc. platinum dish. Add a few grams of ammonium chloride to the filtrate and make it slightly alkaline with ammonia. Boil a few minutes, filter on ashless paper, wash with hot water. Ignite in a small platinum crucible and weigh as Al₂O₃ which contains 53.00 per cent of aluminum.

Notes. If the aluminum oxide should contain a small amount of chromium, it should be fused with sodium peroxide and the chromium determined by color. Deduct the weight of chromium oxide found from the weight of aluminum oxide.

Notes. Run a blank analysis; that is, add to it all the reagents, and subject the contents to the same operations as the samples of drillings and at the same time. Deduct any alumina contained from the result of the actual assay. If this blank amounts to .004 gram, the reagents are unfit for the above analysis and the determination should be repeated with other reagents.

This method is devised for Metallic Nickel as furnished by The International Nickel Company (Huntington Works).
Method of Determining Silicon, Tungsten and Chromium in Metallic Nickel

Dissolve 1 gram of drillings in 50 cc. of 1 to 1 hydrochloric acid in a 200-cc. lip beaker. Add a few drops of nitric acid at intervals until sample has decomposed. Add 5 cc. nitric acid, boil down to 10 cc. Add about 50 cc. of water and boil for five minutes and filter. Wash well with 5 per cent hot hydrochloric acid and finally with water. Evaporate filtrate to dryness, take up in 25 cc. of 1 to 1 hydrochloric acid, dilute to 50 cc., boil, filter and wash with hot water. Ignite the two precipitates in a weighed platinum crucible, being careful not to heat above a red heat. Cool and weigh.

Add 3 drops of sulphuric acid and 5 cc. hydrofluoric acid, evaporate and ignite at low red heat. Cool and weigh.

Loss equals SiO₂ × 0.4693 equals Silicon.

The residue is impure tungstic oxide. To purify it, fuse it with 5 grams sodium carbonate, dissolve and filter off residue. Wash with hot water, ignite, weigh and subtract from weight of impure tungstic oxide.

WO₃ × 0.793 equals Tungsten.

Add 25 cc. nitric acid, dilute to 200 cc., boil until salts are all dissolved. Oxidize by adding slowly 3 grams potassium permanganate dissolved in a small amount of water until a permanent color remains, showing an excess of permanganate. Decompose the excess of permanganate by boiling twenty minutes. A precipitate of manganese dioxide should remain. If none remains, add more potassium permanganate. Keep volume of solution approximately constant. Filter off manganese dioxide, cool to room temperature, dilute to 350 cc., add an excess of standard ferrous ammonium sulphate and titrate excess with standard potassium permanganate to a pink color which remains one minute.

Having found by titration the excess of ferrous ammonium sulphate and deducted this from the total amount of the salt used, the weight of the remainder multiplied by 0.0427 equals Chromium, or the iron value of the ferrous ammonium sulphate multiplied by 0.31 equals Chromium.

Method for Determining Arsenic, Antimony and Tin in Metallic Nickel

Dissolve 5 grams of the nickel drillings in 50 cc. of 1 to 1 nitric acid in a 145-cc. covered silica crucible. Cool and add 10 cc. sulphuric acid, evaporate until fumes of sulphuric acid are given off copiously, cool, then add 25 cc. water, evaporate until the fumes of sulphuric acid are almost all driven off, cool and add about 30 grams of potassium bisulphate (fused). Fuse and keep in a fused condition for one half hour. Cool and transfer the fusion after breaking it up in a porcelain mortar to 10-cc. distilling flask (as per drawing). Allow the outlet of the condenser to dip about one half inch into beaker half full of cold water, then add 5 grams anhydrous ferrous sulphate to the distilling flask, then add 150 cc. hydrochloric acid and distil to about 30 cc., then add 50 cc. more hydrochloric acid and distil again to about 30 cc., remove beaker containing water and distillate and place another beaker half full of cold water under the outlet of the condenser. Again add 50 cc. hydrochloric acid and distil to about 30 cc. Pass hydrogen sulphide gas through both distillates to precipitate the arsenic as arsenous sulphide. All the arsenic should be in the first distillate. The second distillate is made so as to see if all the arsenic has been distilled over. Filter the arsenous sulphide on weighed Gooch crucible, wash with hot water, then with alcohol, ether, and carbon bisulphide, dry at 100°C. and weigh as As₂S₃ which contains 50.93 per cent of arsenic.

Add the solution in the distilling flask, add 400 cc. hot water, then transfer to 800-cc. lip beaker, nearly neutralize with ammonia, then add 8 cc. hydrochloric acid, heat to boiling, pass stream of hydrogen sulphide gas through solution to saturation, then let stand for two or three hours, filter off antimony, tin and copper sulphides, wash precipitate quickly and thoroughly with hot water, then wash the precipitate into a 200-cc. lip beaker and wash filter with dilute sodium sulphide solution, add a few crystals of sodium sulphide to solution in the beaker. Let stand in warm place for an hour, then filter off the copper sulphide, wash with dilute sodium sulphide solution, the filtrate
contains all the antimony and tin. Evaporate the filtrate to about 20 cc., then pour in hot concentrated solution of oxalic acid. This will dissolve the tin sulphide and leave the antimonous sulphide undissolved. Pass hydrogen sulphide gas through the boiling solution for half an hour, filter off antimonous sulphide on weighed Gooch crucible, wash quickly and thoroughly with hot water, place Gooch crucible on steam plate and add fuming nitric acid, evaporate until dry, then heat to a dull red heat, cool and weigh as SnO₂, which contains 78.97 per cent of antimony.

Add to the filtrate from the antimonous sulphide 30 cc. of hydrochloric acid and 4 grams potassium chlorate, evaporate to about 25 cc., nearly neutralize with ammonia, dilute to 150 cc. with hot water, pass hydrogen sulphide gas through hot solution for half hour, filter on weighed Gooch crucible, wash quickly and thoroughly with hot water, place Gooch crucible on steam plate, add fuming nitric acid, evaporate until dry, then heat to a dull red heat, cool, and weigh as SnO₂, which contains 78.80 per cent of tin.

Note: Blank should be run on everything used in the above determinations and at the same time, if any arsenic, antimony or tin is found in the blank, it should be deducted.

Method for Determining Zinc in Nickel

Dissolve 5 grams of drillings in 75 cc. of 1:1 nitric acid in a 400-cc. beaker. Dilute to 350 cc. Cool and plate out the copper over night with .3 amper. After the copper is all plated, pour the solution and water used in washing off cathode into a 500-cc. beaker.

Add 30 cc. of hydrochloric acid and take to dryness on a steam bath. Add 10 cc. of hydrochloric acid and again take to dryness. Take up in 100 cc. of water and 3 cc. of hydrochloric acid. Boil and filter off any silica.

Add a concentrated solution of sodium carbonate to the filtrate until a distinct precipitate of nickel and zinc carbonates remain. Carefully dissolve this precipitate by adding 1 per cent sulphuric acid, stirring for at least two minutes after each addition of acid. (Great care should be taken in adding the 1 per cent sulphuric acid because if more than just enough to dissolve the carbonates is used, no zinc sulphide will precipitate.) Add 2 grams ammonium sulphate. Dilute to 400 cc. and cool.

Connect a tube to hydrogen sulphide gas and pass gas through solution using a tube which has been drawn to one millimeter diameter at the end. Pass the gas through for 40 minutes. Disconnect and allow to stand for three hours. Filter through a double ashless paper and wash two or three times with hot water, containing hydrogen sulphide.

To free the zinc sulphide of traces of nickel, dissolve in 50 cc. of 1:6 sulphuric acid. Dilute to 100 cc. and boil off the hydrogen sulphide gas. Cool and make slightly alkaline with ammonia.

Make acid with acetic acid. Add an equal volume of 50 per cent acetic acid.

Cool and precipitate the zinc sulphide as before. Allow to settle three hours. Filter through a double ashless paper. Wash with hot water containing hydrogen sulphide.

Place filter paper containing zinc sulphide into a small porcelain evaporating dish. Ignite and keep at a temperature of about 800° C. for one hour. Cool and weigh as zinc oxide, which contains 80.34 per cent zinc.

The procedures on pages 336c to 336f are methods of The International Nickel Company that have been contributed by Dr. Paul D. Mercia and Mr. Thos. Fudge.
NITROGEN

Element. N₂, at.wt. 14.01; D. (air) 0.9674; m.p. −210°; b.p. −195.5° C.; oxides, N₂O, N₂O₃, N₂O₅, N₂O₆, N₂O₅.
Ammonia. NH₃, m.w. 17.03; D. (air) 0.5971; sp.gr. liquid 0.8234; m.p. −77.3°; b.p. −38.5° C. Crit. temp. 130°; liquid at 0° with 4.2 atmospheres pressure. Commercial 28% NH₃, sp.gr. 0.90.
Nitric Acid. HNO₃, m.w. 63.02; sp.gr. 1.53; m.p. −41.3°; b.p. 85° C. Boiling-point of commercial 98% acid is a little above 85°, but gradually rises to 126° and the strength of acid falls to 68.9%, sp.gr. is then 1.42. The acid now remains constant, the distillate being of the same strength.

DETECTION

Element. Organic Nitrogen. Organic matter is decomposed by heating in a Kjeldahl flask with concentrated sulphuric acid as described under preparation and solution of the sample. Ammonia may now be liberated from the sulphate and so detected.
Nitrogen in Gas. Recognized by its inertness towards the reagents used in gas analysis. The element may be recognized by means of the spectroscope.
Ammonia. Free ammonia is readily recognized by its characteristic odor. A glass rod dipped in hydrochloric acid and held in fumes of ammonia produces a white cloud of ammonium chloride, NH₄Cl.
Moist red litmus paper is turned blue by ammonia. Upon heating the paper the red color is restored, upon volatilization of ammonia (distinction from fixed alkalies).

Nessler’s Test.¹ Nessler’s reagent added to a solution containing ammonia, combined or free, produces a brown precipitate, NH₂I·H₂O. If the ammoniacal solution is sufficiently dilute a yellow or reddish-brown color is produced, according to the amount of ammonia present. The reaction is used in determining ammonia in water.
Salts of ammonia are decomposed by heating their solutions with a strong base such as the hydroxides of the fixed alkalies or the alkaline earths. The odor of ammonia may now be detected.
Nitric Acid. Ferrous Sulphate Test. About 1 to 2 cc. of the concentrated solution of the substance is added to 15 to 20 cc. of strong sulphuric acid in a test-tube. After cooling the mixture, the test-tube is inclined and an equal volume of a saturated solution of ferrous sulphate is allowed to flow slowly down over the surface of the acid. The tube is now held upright and gently tapped. In the presence of nitric acid a brown ring forms at the junction of the two solutions.

¹The reagent is made by dissolving 20 grams of potassium iodide in 50 cc. of water, adding 32 grams of mercuric iodide and diluting to 200 cc. To this is added a solution of potassium hydroxide—134 grams KOH per 260 cc. H₂O.

Chapter contributed by Wilfred W. Scott.
The test for nitrate may be made according to the quantitative procedure given for determining of nitric acid (see later). It should be remembered that ferrous sulphate should be present in excess, otherwise the brown color is destroyed by the free nitric acid. Traces of nitric acid in sulphuric produce a pink color with the sulphuric acid solution of ferrous sulphate. (See Determination of Nitric Acid—Ferrous Sulphate Method.)

Ferro- and ferricyanides, chlorates, bromides and bromates, iodides and iodates, chromates and permanganates interfere.

**Diphenylamine Tests for Nitrates.** \((C_6H_5)_2NH\) dissolved in sulphuric acid is added to 2 or 3 cc. of the substance in solution on a watch-glass. Upon gently warming a blue color is produced in presence of nitrates. Nitric acid in sulphuric acid is detected by placing a crystal of diphenylamine in 3 or 4 cc. of the acid and gently warming. \(Cl^-, ClO^-, Br^-, I^-, Mn^{2+}\), \(Cr^{3+}\), \(Se^{4+}\), \(Fe^{3+}\) interfere.

**Copper** placed in a solution containing nitric acid liberates brown fumes.

**Phenolsulphonic Acid Test.** See chapter on Water Analysis.

**Detection of Nitrous Acid. Acetic Acid Test.** Acetic acid added to a nitrite in a test-tube (inclined as directed in the nitric acid test with ferrous sulphate), produces a brown ring. Nitrates do not give this. If potassium iodide is present in the solution, free iodine is liberated. The free iodine is absorbed by chloroform, carbon tetrachloride or disulphide, these reagents being colored pink. Starch solution is colored blue.

Nitrous acid reduces iodic acid to iodine. The iodine is then detected with starch, or by carbon disulphide, or carbon tetrachloride.

**Potassium Permanganate Test.** A solution of the reagent acidified with sulphuric acid is decolorized by nitrous acid or nitrite. The test serves to detect nitrous acid in nitric acid. Other reducing substances must be absent.

### ESTIMATION

**Occurrence. Element.** Free in air to extent of 78%+ by volume and 76% - by weight.

Air weight of 1 liter = 1.293 grams. With oxygen as 32, air = 28.95.

**Composition of Air. On the Basis of 1000 Liters of Atmosphere**

<table>
<thead>
<tr>
<th>Element</th>
<th>Liters per 1000 L</th>
<th>Weight per 1000 L grams</th>
<th>Percent by Vol</th>
<th>Percent by Wt</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrogen</td>
<td>780.3</td>
<td>975.80</td>
<td>78.1</td>
<td>75.47-</td>
</tr>
<tr>
<td>Oxygen</td>
<td>209.0</td>
<td>269.84</td>
<td>21.0</td>
<td>23.19-</td>
</tr>
<tr>
<td>Argon</td>
<td>9.4</td>
<td>16.76</td>
<td>0.9</td>
<td>1.286+</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>0.3</td>
<td>0.59</td>
<td>0.04</td>
<td>0.045</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>0.1</td>
<td>0.01</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Neon</td>
<td>0.015</td>
<td>0.01339</td>
<td></td>
<td></td>
</tr>
<tr>
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<td>Krypton</td>
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<td>0.00018</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Xenon</td>
<td>0.000006</td>
<td>0.00003</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Nitrogen is found combined in nature as potassium nitrate (salt peter), KNO₃; sodium nitrate (Chili salt peter), NaNO₃, and to a less extent as calcium nitrate,
Ca(NO₃)₂. It occurs in plants and in animals, in the substances proteids, blood, muscle, nerve substance, in fossil plants (coal), in guano, ammonia and ammonium salts.

**Free nitrogen** is estimated in the complete analysis of gas mixtures. In illuminating gas the other constituents are removed by combustion and absorption and the residual gas measured as nitrogen.

**Total nitrogen** in organic substances is best determined by decomposition of the materials with sulphuric acid as described later, and estimating the nitrogen from the ammonia formed.

**Combined nitrogen** in the form of ammonia and nitric acid specially concerns the analyst. In the evaluation of fertilizers, feedstuffs, hay, fodders, grain, etc., the nitrogen is estimated after conversion to ammonia. Ammonia, nitrates and nitrites may be required in an analysis of sewages, water, and soils. Nitric acid is determined in Chili saltpeter, in the evaluation of this material for the manufacture of nitric acid or a fertilizer, the nitrate being reduced to ammonia and thus estimated.

We will take up a few of the characteristic substances in which nitrogen estimations are required, e.g., in organic substances as proteids, in soils and fertilizers; in ammonium salts, nitrates, and nitrites, free ammonia in ammoniacal liquors, nitric acid in the evaluation of the commercial acid and in mixed acids.

In general nitrogen is more accurately and easily measured as ammonia, to which form it is converted by reduction methods. Large amounts are determined by titration, whereas small amounts are estimated colorimetrically. Nitric acid and nitrates may be determined by direct titration by the Ferrous Sulphate Method outlined later. The procedure is of value in estimation of nitrates in mixed acids. The nitrometer method for determining nitrates (including nitrites), and the free acid in mixed acids, is generally used by manufacturers of explosives.

**Preparation of the Sample**

It will be recalled that compounds of ammonia and of nitric acid are generally soluble in water. All nitrogen compounds, however, are not included. Among those which are not readily soluble the following deserve mention: compounds of nitrogen in many organic substances; nitrogen bromophosphide, NFBr; nitrogen selenide, NSe; nitrogen sulphide, N₂S; nitrogen pentasulphide, N₅S₅; ammonium antimonate, NH₄SbO₃·2H₂O; ammonium iodate, H₂NIO₃ (2.6 grams per 100 cc. H₂O); ammonium chloroplatinate, (NH₄)₂PtCl₆ (0.67 gram); ammonium chloriridate, (NH₄)₂IrCl₆ (0.7 gram); ammonium oxalate, (NH₄)C₂O₄·H₂O (4.2 grams); ammonium phosphomolybdate, (NH₄)₆PO₄·12MoO₃ (0.03 gram); nitron nitrate, C₂₀H₃N₄·HNO₃.

**Organic Substances**

By oxidation of nitrogenous organic substances with concentrated sulphuric acid, containing mercuric oxide, or potassium permanganate, the organic matter is destroyed and the nitrogen is changed to ammonia, which is held by the sulphuric acid as sulphate. Nitrates are reduced by addition of salicylic acid, zinc dust, etc., previous to the oxidation process. Practically all the procedures are based on the Kjeldahl method of acid digestion. The modification, commonly known as the Kjeldahl-Gunning-Arnold Method, is as follows:
Method in Absence of Nitrates. Weight of Sample. Fertilizers 0.7 to 3.5 grams. Soils 7 to 14 grams. Meat and meat products 2 grams. Milk 5 grams. The amount of the substance to be taken should be governed by its nitrogen content.¹

Acid Digestion.² The material is placed in a Kjeldahl flask of about 550 cc. capacity. Approximately 0.7 gram of mercuric oxide or an equivalent amount of metallic mercury together with 10 grams of powdered potassium sulphate followed by 20 to 30 cc. of concentrated sulphuric acid (sp.gr. 1.84) are added. The flask is placed in an inclined position, resting in a large circular opening of an asbestos board. The flask is heated with a small flame until the frothing has ceased. (A piece of paraffin may be added to prevent extreme frothing.) The heat is then raised and the acid brought to brisk boiling, the heating being continued until the solution becomes a pale straw color, or practically water white. (In case of leather, scrap, cheese, milk products, etc., a more prolonged digestion may be required. With a good flame from one-half to one hour of acid digestion is generally sufficient to completely decompose the material.) The flask is now removed from the flame and after cooling the solution is diluted with about 200 cc. of water and a few pieces of granulated zinc added to prevent “bumping” (50 mg. or so of No. 80 granulated zinc). The solution is now alkalinized strongly by addition of a mixture of sodium hydroxide and sodium sulphide solution (about 75 cc. of a mixture containing 25 grams of NaOH and 1 gram Na₂S). Phenolphthalein indicator added to the solution will show when the acid is neutralized. The flask is connected by means of a Hopkins distillation tube (Fig. 53) to a condenser and about 150 cc. of the solution distilled into an excess of standard sulphuric acid and the excess of the acid determined by titration with standard sodium hydroxide. (Methyl red indicator.)

The ammonia may be absorbed in a saturated solution of boric acid and titrated directly with standard acid. (Methyl orange indicator.)³

One cc. N/10 H₂SO₄ = 0.001704 gram NH₃.

²Fig. 50 shows a compact apparatus with several sets of flasks and condensers, which enable half a dozen or more determinations to be made at one time.
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In Presence of Nitrates. The procedure differs from the former in the preliminary treatment to reduce the nitrates. The material in the flask is treated with a mixture of 30 to 35 cc. of strong sulphuric acid containing 1 gram of salicylic acid and the mixture shaken and allowed to stand for five to ten minutes with frequent agitation. About 5 grams of sodium thiosulphate are now added and the solution heated for five minutes. After cooling, mercuric oxide or metallic mercury and potassium sulphate are added, and the solution treated as directed above.

Notes. Mercuric oxide or metallic mercury are added as a catalyst to assist the oxidation of the organic matter. The digestion process is shortened considerably by its use. In place of mercuric oxide or the metal, copper sulphate may be used. In this case the addition of sodium sulphide is omitted. Copper sulphate acts as an indicator in the neutralization of the sample with caustic.

Potassium sulphide is added to remove the mercury from the solution and prevent the formation of mercur-ammonium compounds, which are not completely decomposed by sodium hydroxide.

Ferric chloride, FeCl₃, may be used in place of copper or mercury salts or oxides to assist in the oxidation of organic matter.

Soils. Available Nitrates. Five hundred to 1000 grams of the air-dried soil is extracted with 1 to 2 liters of water containing 10 to 20 grams of dextrose. Fifteen to twenty hours of leaching is sufficient. An aliquot portion is taken for analysis.

Ammonium Salts. The sample is placed in the distillation flask with splash bulb as described in the modified Kjeldahl procedure for organic substances, and the material decomposed with ammonia-free caustic solution. The ammonia is distilled into an excess of standard acid or a saturated solution of boric acid (neutral to methyl orange), and the ammonia determined as usual, either by titration of the excess of acid, or by direct titration with acid, according to the absorbent used.

Nitrites. The sample, broken down as fine as possible, is dissolved in water, decomposed with Devarda alloy and distilled as described by the modified Devarda methods given later.

Nitrites. The material, dissolved in water, is titrated with standard permanganate solution according to the procedure described later.

Mixtures of Ammonium Salts, Nitrates, and Nitrites. Ammonia is determined by distillation with caustic as usual. The nitrite is titrated with permanganate. Total nitrogen is determined by the modified Devarda methods. Nitric acid is now estimated by difference, e.g., from the total nitrogen is deducted the nitrogen due to ammonia together with the nitrogen of the nitrite and the difference calculated to the nitrate desired. The nitrate may be determined in presence of nitrite and ammonia by direct titration with ferrous sulphate. The detailed procedures may be found under the Volumetric Methods.

Nitric Acid in Mixed Acid. This is best determined by the ferrous sulphate method for nitric acid. The nitrometer method is also excellent.

SEPARATIONS

Ammonia. No special separation need be considered in the determination of ammonia. The general method has already been mentioned by which ammonia is liberated from its salts by a strong base and volatilized by heat. This effects a separation from practically all substances.
Nitric Acid. The compound may be isolated as the fairly insoluble, crystalline nitron nitrate, C₆H₄N₄·HNO₃ by the following procedure.

Such an amount of the substance is taken as will contain about 0.1 gram nitric acid, and dissolved in about 100 cc. of water with addition of 10 drops of dilute sulphuric acid. The solution is heated nearly to boiling and about 12 cc. of nitron acetate solution added (10 grams of nitron in 100 cc. of 5% acetic acid). The solution is cooled and placed in an ice pack for about two hours, and then transferred to a Gooch or Munroe crucible (weighed crucible if gravimetric method is to be followed), and after draining it is washed with about 10 to 12 cc. of ice-water added in small portions. The nitrate may now be determined gravimetrically by drying the precipitate to constant weight at 110°C., 16.53% of the material being due to NO₂.

The base diphenyl-endo-anilo-hydro-triazole (nitron) also precipitates the following acids: nitrous, chromic, chloric, perchloric, hydrobromic, hydriodic, hydroferro- and hydroferricyanic, oxalic, picric and thiocyanic acids. Hence these must be absent from the solution if precipitation of nitric acid is desired for quantitative estimation.

Removal of Nitrous Acid. Finely powdered hydrazine sulphate is dropped into the concentrated solution. (0.2 gram substance per 5 or 6 cc.) Chromic acid is reduced by addition of hydrazine sulphate.

Hydrobromic acid is decomposed by chlorine water added drop by drop to the neutral solution, which is then boiled until the yellow color has disappeared.

Hydriodic acid is removed by adding an excess of potassium iodate to the neutral solution and boiling until the iodine is expelled.

PROCEDURES FOR THE DETERMINATION OF COMBINED NITROGEN

Ammonia

The volumetric procedures for determination of ammonia are preferred to the gravimetric on account of their accuracy and general applicability. The following gravimetric method may occasionally be of use:

Gravimetric Determination of Ammonia by Precipitation as Ammonium Platinochloride, (NH₄)₂PtCl₆

Ammonia in ammonium chloride may be determined gravimetrically by precipitation with chlorplatinic acid. The method is the reciprocal of the one for determining platinum.

Procedure. The aqueous solution of the ammonium salt is treated with an excess of chlorplatinic acid and evaporated on the steam bath to dryness. The residue is taken up with absolute alcohol, filtered through a weighed Gooch crucible, and washed with alcohol. The residue may now be dried at 130°C. and weighed as (NH₄)₂PtCl₆ or it may be gently ignited in the covered crucible until

1 M. Busch, Ber., 88, 861 (1905), Treadwell and Hall, "Analytical Chemistry."
2 Keep nitron reagent in a dark-colored bottle.
ammonium chloride has been largely expelled and then more strongly with free access of air. The residue of metallic platinum is weighed. If the ignition method is to be followed, the ammonium platinic chloride may be filtered into a small filter, the paper with the washed precipitate placed in a porcelain crucible and then gently heated until the paper is charred (crucible being covered) and then more strongly with free access of air until the carbon has been destroyed.

Factors.\(^1\) \((\text{NH}_4)_2\text{PtCl}_6\times 0.2400 = \text{NH}_4\text{Cl}\), or \(0.08095 = \text{NH}_4\), or \(\times 0.0767 = \text{NH}_4\). \(\text{Pt} \times 0.5453 = \text{NH}_4\text{Cl}\), or \(\times 0.1839 = \text{NH}_4\), or \(\times 0.1736 = \text{NH}_4\).

**VOLUMETRIC METHODS FOR DETERMINATION OF AMMONIA**

Two conditions are considered:

A. Estimation of free ammonia in solution.

B. Determination of ammonia in its salts—combined ammonia.

**Analysis of Aqua Ammonia**

Provided no other basic constituent is present, free ammonia in solution is best determined by direct titration with an acid in presence of methyl orange or methyl red as indicator.

**Procedure.** About 10 grams of the solution in a weighing bottle with glass stopper is introduced into an 800-cc. Erlenmeyer flask containing about 200 cc. of water and sufficient \(\frac{1}{4}\) normal sulphuric acid to combine with the ammonia and about 10 cc. in excess. The flask is stoppered and warmed gently. This forces out the stopper in the weighing bottle, the ammonia combining with the acid. Upon thorough mixing, the solution is cooled, and the excess of acid is titrated with half normal caustic.

One cc. \(\frac{1}{4}\) N. \(\text{H}_2\text{SO}_4\) = 0.0085 gram \(\text{NH}_3\).

Factor. \(\text{H}_2\text{SO}_4 \times 0.3473 = \text{NH}_3\).

**Note.** The aqua ammonia exposed to the air will lose ammonia, hence the sample should be kept stoppered. This loss of ammonia is quite appreciable in strong ammoniacal solutions.

**Determination of Combined Ammonia. Ammonium Salts.**

Strong bases decompose ammonium salts, liberating ammonia. This may be distilled into standard acid or into a saturated solution of boric acid (neutral to methyl orange) and titrated.

**Procedure.** About 1 gram of the substance is placed in a distillation flask (see Fig. 50) and excess of sodium or potassium hydroxide added and the ammonia distilled into a saturated solution of boric acid or an excess of standard sulphuric acid. Ammonia in boric acid solution may be titrated directly with standard acid (methyl orange or methyl red indicator) or in case a mineral acid

\(^1\) Factors recommended by Treadwell and Hall, "Analytical Chemistry," 2, John Wiley & Sons.
was used to absorb the ammonia, the excess of acid is titrated with standard
caustic solution.

One cc. half normal sulphuric acid = 0.0085 gram NH₃.
One cc. normal acid = 0.01703 gram NH₃.

Factors. \( H_2SO_4 \times 0.3473 = NH_3 \) and \( NH_3 \times 2.8792 = H_2SO_4 \).

**ANALYSIS OF AMMONIACAL LIQUOR**

The crude liquor by-product from coal gas in addition to ammonia contains
hydrogen sulphide, carbon dioxide, hydrochloric acid, sulphuric acid, combined
with ammonia, also sulphites, thiosulphates, thiocyanates, cyanides, ferrocyanides,
phenols.

**Determination of Ammonia**

**Volatile Ammonia.** This is determined by distillation of the ammonia into
an excess of standard sulphuric acid and titrating the excess of acid. With the
exception that caustic soda is omitted in this determination, the details are the
same as those for total ammonia as stated in the next paragraph.

**Total Ammonia.** The true value of the liquor is ascertained by its total
ammonia content. Ten to 25 cc. of the sample is diluted to about 250 cc. in
a distilling flask with a potash connecting bulb, as previously described, 20 cc.
of 5% sodium hydroxide are added and about 150 cc. of solution distilled into an
excess of sulphuric acid. The excess is then titrated according to the standard
procedure for ammonia.

One cc. N. \( H_2SO_4 = 0.01703 \) gram NH₃.

**Fixed Ammonia** is the difference between the total and the volatile ammonia.

**Carbon Dioxide**

Ten cc. of the liquor are diluted to 400 cc. and 10 cc. of 10% ammoniacal
calcium chloride added and the mixture, placed in a flask with Bunsen valve, is
digested on the water bath for two hours. The precipitated calcium carbonate
is washed, placed in a flask and an excess of \( N/2 \) HCl added and the excess acid
titrated with \( N/2 \) NaOH.

\( N/2 \) HCl = 0.011 gram CO₂.

**Hydrochloric Acid**

Ten cc. of the liquor is diluted to 150 cc. and boiled to remove ammonia.
Now hydrogen peroxide is added to oxidize organic matter, etc., the mixture being
boiled to remove the excess of the peroxide. Chlorine is titrated in presence of
potassium chromate as indicator by tenth normal silver nitrate after neutralizing
with dilute nitric acid.

One cc. \( N/10 AgNO₃ = 0.00364 \) gram HCl.
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Hydrogen Sulphide

To 10 cc. of the liquor are added an excess of ammoniacal zinc chloride or acetate, the mixture diluted to about 80 cc. and warmed to 40°. After settling for half an hour the zinc sulphide is filtered off and washed with warm water (40 to 50°); the precipitate is washed from the filter into an excess of N/10 iodine solution, the sulphide clinging to the paper washed into the main solution with hydrochloric acid. The mixture is acidified and the excess iodine titrated with N/10 sodium thiosulphate.

One cc. N/10 I = 0.0017 gram H₂S or 0.0016 gram S.

Sulphuric Acid

250 cc. of the liquor is concentrated to 10 cc., 2 cc. of concentrated hydrochloric acid added and the mixture heated to decompose any thiosulphate, sulphide or sulphite present. The concentrate is extracted with water, filtered and made to 250 cc. The sulphuric acid is now precipitated in an aliquot portion with barium chloride.

\[ \text{BaSO}_4 \times 0.4202 = \text{H}_2\text{SO}_4 \quad \text{or} \quad \times 0.1374 = S \quad \text{present as H}_2\text{SO}_4 \]

Total Sulphur. Fifty cc. of the liquor is run by means of a pipette into a deep beaker (250 cc. capacity), containing an excess of bromine covered by dilute hydrochloric acid. The mixture is evaporated to dryness on the steam bath and the residue taken up with water and diluted to 250 cc. Sulphur is now precipitated as barium sulphate as usual, preferably on an aliquot portion.

For a more complete analysis of crude liquor determining sulphite, thiosulphate, thiocyanate, hydrocyanic acid, ferrocyanic acid, and phenols the analyst is referred to Lunge, "Technical Methods of Chemical Analysis," Part II, Vol. II, D. Van Nostrand Co.

Determination of Traces of Ammonia

The determination of traces of ammonia is best accomplished by the colorimetric method with Nessler's reagent. Details of the procedure are given in the chapter on water analysis.

NITRIC ACID. NITRATES

The alkaliometric method for determining free nitric acid, and the complete analysis of the commercial product are given in the chapter on Acids. Special procedures for determining the combined acid are herein given.

Gravimetric Method for Determining Nitric Acid by Precipitation as Nitron Nitrate, \( \text{C}_{20}\text{H}_{16}\text{N}_{4} \cdot \text{HNO}_3 \)

As in case of ammonia the volumetric methods are generally preferable for determining nitric acid, combined or free. Isolation of nitric acid by precipitation as nitron nitrate may occasionally be used. The fairly insoluble, crystalline compound, \( \text{C}_{16}\text{H}_{24}\text{N}_{4} \cdot \text{HNO}_3 \) is formed by addition of the base diphenyl-endo-
anilo-hydro-triazole (nitron) to the solution containing the nitrate as directed under Separations. The precipitate washed with ice-water is dried to constant weight at 110° C. 16.53% of the compound is NO$_3$.

**Note.** The following acids should not be present in the solution, since their nitron salts are not readily soluble: nitrous, chromic, chloric, perchloric, hydrobromic, hydroiodic, hydroferrocyanic, hydroferricyanic, oxalic, picric and thiocyanic acids. Solubility of less soluble nitron salts in 100 cc. of water. Nitron nitrate = 0.0099 gram, nitron bromide = 0.01 gram, iodide = 0.017 gram, nitrite = 0.19 gram, chromate = 0.06 gram, chlorate 0.12 gram, perchlorate = 0.008 gram, thiocyanate = 0.04 gram. (Treadwell and Hall, "Analytical Chemistry, Quantitative Analysis.")

**VOLUMETRIC METHODS**

**Direct Estimation of Nitrates by Reduction to Ammonia.**

**Modified Devarda Method**

An accurate procedure for the determination of nitrogen in nitrates is Allen's modification of the Devarda method. The method is based upon the quantitative reduction of nitrates to ammonia in an alkaline solution by an alloy consisting of 45 parts of aluminum, 50 parts of copper and 5 parts of zinc. The ammonia evolved is distilled into standard sulphuric acid and thus estimated. The method, originally designed for the valuation of sodium or potassium nitrates, is also of value in the determination of nitric acid, nitrates or ammonia. In the latter case the alloy is omitted.

**Reagents Required.** *Devarda's Alloy.* Forty-five parts aluminum, 50 parts copper and 5 parts zinc. The aluminum is heated in a Hessian crucible in a furnace until the aluminum begins to melt, copper is now added in small portions until liquefied and zinc now plunged into the molten mass. The mix is heated for a few moments, covered and then stirred with an iron rod, allowed to cool slowly with the cover on and the crystallized mass pulverized.

**Standard Sulphuric Acid.** This is made from the stock C.P. acid by dilution so that 1 cc. is equal to 0.0057 gram H$_2$SO$_4$ 100 cc. of acid of this strength being equivalent to approximately 1 gram of sodium nitrate. (A tenth normal acid will do, a smaller sample being taken for analysis.) Since it is necessary to standardize this acid against a standard nitrate, it is advisable to have an acid especially for this determination rather than a common reagent for general use.

**Standardization of the Acid.** 11.6 grams of standard potassium nitrate, equivalent to about 9.9 grams of NaNO$_3$ is dissolved and made to volume in the weighing bottle (100 cc.), and 10 cc. is placed in the Devarda flask, reduced and the ammonia distilled into 100 cc. of the acid, exactly as the following method describes. The temperature of the acid is noted and its value in terms of H$_2$SO$_4$ KNO$_3$ and NaNO$_3$ stated on the container. The acid expands or contracts 0.029 cc. for every degree centigrade above or below the temperature of standardization, per 100 cc.

**Standard Potassium Nitrate.** The purest nitrate that can be obtained is reconstituted in small crystals, by stirring, during the cooling of the supersaturated concentrated solution, and dried first at 100° C. for several hours and then

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1 Paper by W. S. Allen, General Chemical Company, Eighth International Congress of Applied Chemistry.
at 210° C. to constant weight. Chlorides, sulphates, carbonates, lime, magnesia and sodium are tested for and if present are determined and allowance made.

**Standard Sodium Hydroxide.** This should be made of such strength that 1 cc. is equal to 1 cc. of the standard acid, 2 cc. methyl red being used as indicator. Ten cc. of the acid are diluted to 500 cc. and the alkali added until the color of the indicator changes from a red to a straw color.

**Methyl Red Solution.** 0.25 gram of methyl red is dissolved in 2000 cc. of 95% alcohol; 2 cc. of the indicator is used for each titration. As the indicator is sensitive to CO₂, all water used must first be boiled to expel carbonic acid.

(Baker & Adamson, manufacturers of methyl red.)

**Sodium Hydroxide—Sp.gr. 1.3.** Pure sodium hydroxide is dissolved in distilled water and boiled in an uncovered casserole with about 1 gram of Devarda's alloy to remove ammonia. This is cooled and kept in a well-stoppered bottle.

**Apparatus.** This is shown in the accompanying illustration, Fig. 51. It consists of the Devarda flask connected to the scrubber K', filled with glass wool. This

scrubber is heated by an electric coil or by steam passed into the surrounding jacket. The scrubber prevents caustic spray from being carried over into the receiving flask O. The form of the apparatus can best be ascertained from the sketch.

Weighing bottle with graduation at 100 cc. and a 10-cc. dropper with rubber bulb is used for weighing out the sample in solution. See Fig. 52.
Preparation of the Sample

**Weight.** It is advisable to take a large sample if possible, e.g., 100 grams of NaNO₃, 119 grams of KNO₃ or about 80 grams of strong HNO₃ (95%) or more if the acid is dilute. Solids are taken from a large sample, all lumps being broken down. After dissolving in water the sample is made up to 1 liter. (Scum is broken up by addition of a little alcohol.) One hundred cc. of this solution is placed in the weighing bottle, which has been previously weighed, being perfectly clean and dry. The difference is the weight of the 100-cc. sample.

**Manipulation.** All parts of the apparatus are washed out with CO₂-free water. All water used in this determination should be boiled to expel CO₂. Ninety-eight cc. of the standard acid is placed in flask O and washed down with 2 to 3 cc. of water. Two cc. of the standard acid is placed in flask P and washed down with 10 cc. of water and 13 to 14 drops of methyl red indicator added. Connections are made between the flasks and the scrubber. (The correction is made for the acid, the temperature being noted at the time of withdrawal.) A casserole, filled with cold water, is placed under F (see illustration). The stem E is removed from the Devarda flask and 10 cc. (or more) of the nitrate added by means of the dropper in the weighing bottle, a funnel having been inserted in the flask. The bottle is weighed before the weight of the sample removed, by difference. The nitrate is washed down with 10 cc. of water and 25 cc. of 20% caustic added (free from NH₃), the alkali washed down with 10 cc. more of water and then 3 grams of Devarda alloy placed in the flask by means of dry funnel. The stem E is quickly replaced, the stopcock being turned to close the tube. The reaction begins very soon. If it becomes violent, the reaction may be abated by stirring the water in the casserole, thus cooling the sample. After the reactive action has abated (five minutes), the casserole with the cold water is removed and the action allowed to continue for twenty minutes, meantime heat or steam is turned on in the scrubber. E is connected at C to the flask B containing caustic to act as a scrubber. It is advisable to have a second flask containing sulphuric acid attached to the caustic to prevent ammonia from the laboratory entering the system. A casserole with hot water is placed under F and the burner lighted and turned on full. A gentle suction is now applied at R, the stop-cock D being turned to admit pure air into the evolution flask; the rate should be about 5 to 6 bubbles per second. The suction is continued for thirty minutes, hot water being replaced in the casserole as the water evaporates. The heat is now turned off and the apparatus disconnected at M and J. The contents of this elbow and the condenser are washed into the flask O. The acid in O and P poured into an 800-cc. beaker and rinsed out several times. The volume in the beaker is made up to 500 cc., 1 cc. of methyl red added, and the free acid titrated with the standard caustic. The end-point is a straw yellow.

**Calculation.** The cc. of the back titration with caustic being deducted, the volume of the acid remaining (e.g., combined with ammonia) is corrected to the standard condition. Expansion or contraction per 100 cc.is 0.029 cc. per each degree C. above or below the temperature at which the acid was standardized. If the acid is exactly 0.057 gram H₂SO₄ per cc., the result multiplied by 0.989 and
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divided by the weight of the sample taken gives per cent nitrate. (In terms of NaNO₃.)

The Weight of the Sample. Ten times the difference of the weighings of the bottle W before and after removal of the 10 cc. and the product divided by the weight of the 100 cc. of the solution equals the weight of solid taken.

Example. Weight of the bottle +100 cc. sample = 218 grams. Weight of the bottle = 112 grams, therefore weight of 100 cc. NaNO₃ = 106 grams. Weight of the bottle +100 cc. sample = 218. Weight after removal of 10 cc = 207.4 grams, therefore sample taken = 10.6 grams, including the added water. Now from above the weight of the actual sample taken = 10.6 × 10 ÷ 106 = 1 gram.

Temperature Correction. Temperature of standardization = 20° C. Temperature of the sulphuric acid when taken for the analysis = 31° C. Back titration of the caustic = 2 cc. The correct volume = (100 - 2) - ((31 - 20) × 0.029) = 97.681 cc. H₂SO₄ combined with ammonia from the reduced nitrate. 97.681 × 0.989 + 1 = 96.62% NaNO₃.

Factors. H₂SO₄ × 2.06107 = KNO₃ or ÷ 1.7334 = NaNO₃ or × 1.2850 = HNO₃.

H₂SO₄ × 0.9587 = HNO₃ or ÷ 0.3473 = NH₃.

NH₃ × 3.6995 = HNO₃ or ÷ 4.9906 = NaNO₃ or ÷ 4.0513 = NaNO₃.

NaNO₃ × 1.1894 = KNO₃ and KNO₃ ÷ 0.8408 = NaNO₃.

ANALYSIS OF NITRATE OF SODA

The following impurities may occur in nitrate of soda: KNO₃, NaCl, Na₂SO₄, Na₂CO₃, NaClO₃, NaClO₄, Fe₂O₃, Al₂O₃, CaO, MgO, SiO₂, H₂O, etc. In the analysis of sodium nitrate for determination of NaNO₃ by difference, moisture, NaCl, Na₂SO₄ and insoluble matter are determined and their sum deducted from 100, the difference being taken as NaNO₃. Such a procedure is far from accurate, the only reliable method being a direct determination of niter by the Devarda method given in detail. The following analysis may be required in the valuation of the nitrate of soda.

Determination of Moisture

Twenty grams of sample are heated in a weighed platinum dish at 205 to 210° C. for fifteen minutes in an air bath or electric oven. The loss of weight multiplied by 5 = per cent moisture. (Save sample for further tests.)

Insoluble Matter

Ten grams are treated with 50 cc. of water and filtered through a tared Gooch. The increased weight dried residue (100° C.) multiplied by 10 = per cent insoluble matter. (Save filtrate.)

Sodium Sulphate

The moisture sample is dissolved in 20 cc. hot water and transferred to a porcelain crucible. It is evaporated several times with hydrochloric acid to dryness to expel nitric acid. (Until no odor of free chlorine is noticed when thus treated.) Fifty cc. of water and 5 cc. hydrochloric acid are now added and the
sample filtered. Any residue remaining is principally silica. The filtrate is heated to boiling, 10 cc. of 10% barium chloride solution added, and the precipitated sulphate filtered off, ignited and weighed.

\[ \text{BaSO}_4 \times 3.0445 = \text{per cent Na}_2\text{SO}_4. \]

**Iron, Alumina, Lime, and Magnesia**

These impurities may be determined on a 20-gram dried sample, the material being dried and evaporated as in case of the sodium sulphate determination. The filtrate from silica is treated with ammonium hydroxide and Fe(OH)_3 and Al(OH)_3 filtered off. Lime is precipitated from the iron and alumina filtrate as oxalate and magnesia determined by precipitation as phosphate from the lime filtrate by the standard procedures.

**Sodium Chloride**

The filtrate from the insoluble residue is brought to boiling and magnesia, MgO (Cl free), is added until the solution is alkaline to litmus. 0.5 cc. of 1% potassium chromate (K_2CrO_4) solution is added as an indicator and then the solution is titrated with a standard solution of silver nitrate until a faint red tinge is seen, the procedure being similar to the determination of chlorides in water by silver nitrate titration. The cc. AgNO_3 x factor for this reagent x 10 = per cent NaCl.

Silver nitrate is standardized against a salt solution.

**Carbonates**

This determination is seldom made. CO_2 may be tested for by addition of dilute sulphuric acid to the salt. Effervescence indicates carbonates. Any evolved gas may be tested by lime water, which becomes cloudy if CO_2 is present. For details of the procedure reference is made to the chapter on Carbon.

**DETERMINATION OF NITRIC NITROGEN IN SOIL EXTRACTS**

**Vamari-Mitscherlich-Devarda Method**

**Procedure.** Forty cc. of water, a small pinch of magnesia and one of magnesium sulphate are added to flask D of the Mitscherlich apparatus (Fig. 53). Twenty-five cc. of standard acid and 60 cc. of neutral distilled water are placed in flask F; 250 or 300 cc. of aqueous soil extract are placed in a 500-cc. Kjeldahl flask, 2 cc. of 50% sodium hydroxide added, the mouth of the flask closed with a small funnel to prevent spattering, and the contents of the flask boiled for thirty minutes. The water which has boiled off is replaced, and, after cooling, 1 gram of Devarda's alloy (60 mesh), and a small piece of paraffin are added and the flask connected with the apparatus; reduction and distillation are carried on for forty minutes. The receiver contents are then cooled, 4 drops of 0.02%
solution of methyl red added, the excess acid is nearly neutralized, the liquid boiled to expel CO₂, cooled to 10 to 15° and the titration completed.

![Diagram of apparatus](image)

**Fig. 53.**—Mitscherlich's Apparatus for Nitrogen Determination.

B. S. Davisson¹ recommends an improved form of scrubber, shown in Fig. 53a to be used in place of the Hopkins bulb (Fig. 53). The bulb and adaptor are made of Pyrex glass. Steam condenses in the bulb and the condensate acts as a scrubber preventing alkali mist from being carried over with the ammonia. During the test ammonia is completely volatilized into the absorption flask. The bulb of the adaptor, shown as II, prevents back suction into the distillation flask.

![Diagram of scrubber](image)

**Fig. 53a.**—Davisson's Scrubber.

Determination of Hydroxylamine—Method of Raschig

Hydroxylamine in hot acid solutions reduces ferric salts to ferrous condition quantitatively according to the reaction:

\[ 2\text{NH}_2\text{OH} + 2\text{Fe}_2(\text{SO}_4)_3 = 4\text{FeSO}_4 + \text{N}_2\text{O} + \text{H}_2\text{O}. \]

The amount of ferrous iron formed is a measure of the hydroxylamine originally present.

Procedure. Approximately 0.1 gram of hydroxylamine salt is dissolved in a little water in an Erlenmeyer flask and 30 cc. of cold saturated solution of ferric-ammonium alum added, followed by 10 cc. of dilute sulphuric acid (1:4). The solution is heated to boiling and kept at this temperature for five minutes, then diluted to 300 cc. and titrated immediately with standard permanganate solution.

1 cc. N/10 KMnO₄ = 0.001652 g. NH₂OH.

Iodometric Determination of Nitrates—Method of Gooch and Gruener

By this method the nitrate to be estimated is treated, in an atmosphere of carbon dioxide, with a saturated solution of manganous chloride (crystallized) in concentrated hydrochloric acid, the volatile products of the reaction (nitrogen dioxide, chlorine, etc.) are now distilled and caught in a solution of potassium iodide. The iodine set free is titrated by a standard solution of thiosulphate.

Procedure. The nitrate and the manganous mixture (saturated solution of crystallized manganous chloride and strong hydrochloric acid—20 cc. per 0.2 gram sample) following it are introduced into the pipette shown in Fig. 53a (marked III) suction being applied, if necessary, at the end of the absorption train (VI). The current of CO₂ is started immediately after putting in the mixture. When the air has been replaced by CO₂, heat is applied to the retort III and the distillation continued until nearly all the liquid has passed over into the receiver IV, which is cooled by water. (See illustration.) The contents of the receivers are united and the bulbs washed out by passing the wash water directly through III and IV. Introduction of manganous chloride into the distillate does not influence the accuracy of the titration. The liberated iodine is titrated with standard sodium thiosulphate as soon as possible after

1 Hydroxylamine may also be determined by reduction with an excess of titanous salt in acid solution with exclusion of air, and the excess titrated with permanganate.

Reaction: \( 2\text{NH}_2\text{OH} + \text{Ti}_2(\text{SO}_4)_3 = (\text{NH}_4)_2\text{SO}_4 + 4\text{TiOSO}_4 + \text{H}_2\text{SO}_4 \).


admitting air to the distillate, since traces of dissolved nitric oxide reoxidized by the air would react with the iodide liberating more iodine.

![Diagram of apparatus](image)

Fig. 53b. Gooch-Gruener Apparatus.

**DETERMINATION OF NITROGEN OF NITRATES (AND NITRITES) BY MEANS OF THE NITROMETER**

The nitrometer is an exceedingly useful instrument employed in the accurate measurement of gases liberated in a great many reactions and has therefore a number of practical applications. It may be used in the determination of carbon dioxide in carbonates; the available oxygen in hydrogen dioxide; in the valuation of nitrous ether and nitrites; in the valuation of nitrates and nitric acid in mixed acids.

The method for the determination of nitrogen in nitrates, with which we are concerned in this chapter, depends on the reaction between sulphuric acid and nitrates in presence of mercury:

$$2\text{KNO}_3 + 4\text{H}_2\text{SO}_4 + 3\text{Hg} = \text{K}_2\text{SO}_4 + 3\text{HgSO}_4 + 4\text{H}_2\text{O} + 2\text{NO}.$$  

The simplest type of apparatus is shown in the illustration, Fig. 54. The graduated decomposition tube has a capacity of 100 cc. It is connected at the base by means of a heavy-walled rubber tubing with an ungraduated leveling tube (b). At the upper portion of (a) and separated from it by a glass stop-cock (s) is a bulb (c) of about 5 cc. capacity; a second stop-cock enables completely enclosing the sample, as may be necessary in volatile compounds. The glass stop-cock (s), directly above the graduated chamber, is perforated so as
to establish connection with the tube (d) when desired and the graduated cylinder (a).

**Procedure.** The tube (b) is filled with mercury and the air in (a) now displaced by mercury, by turning the stop-cock to form an open passage between (a) and (d) and then raising (b). A sample of not over 0.35 gram potassium nitrate or a corresponding amount of other nitrates, is introduced into (c), the material being washed in with the least amount of water necessary (1 to 2 cc.). By lowering (b) and opening the stop-cock s the solution is drawn into the decomposition chamber, taking care that no air enters. This is followed by about 15 cc. of pure, strong sulphuric acid through s1 and s2, avoiding admitting air as before. NO gas is liberated by the heat of reaction between the sulphuric acid and the water solution. When the reaction subsides, the tube (a) is shaken to mix the mercury with the liquor and the NO completely liberated. The gas is allowed to cool to room temperature and then measured, after raising or lowering (b) so that the column of mercury is the calculated excess of height above that in (a) in order to have the gas under atmospheric pressure. The excess of height is obtained by dividing the length of the acid layer in (a), in millimeters, by 7 and elevating the level of the mercury in (b) above that in (a) by this quotient; i.e., if the acid layer =21 mm. the mercury in (b) would be 3 mm. above that in (a). The volume of gas is reduced to standard conditions by using the formula

\[ V' = \frac{V (P - w)}{760(1 + 0.003671)} \]

\[ V' = \text{volume under standard conditions; } V = \text{observed volume; } P = \text{observed barometric pressure in mm.; } w = \text{tension of aqueous vapor at the observed temperature, expressed in millimeters; } t = \text{observed temperature.} \]

One cc. gas = 4.62 milligrams of KNO₃, or 3.8 milligrams NaNO₃, or 2.816 milligrams HNO₃.

**Du Pont Nitrometer Method**

The Du Pont nitrometer, Fig. 55, is the most accurate apparatus for the volumetric determination of nitrates. By use of this, direct readings in per cent may be obtained, without recourse to correction of the volume of gas to standard conditions and calculations such as are required with the ordinary nitrometers.

The apparatus consists of a generating bulb of 300 cc. capacity E with its reservoir F connected to it by a heavy-walled rubber tubing. E carries two glass stop-cocks as is shown in illustration. The upper is a two-way stop-cock connecting either the cup or an exit tube with the chamber. D is the chamber-reading burette, calibrated to read in percentages of nitrogen, and graduated from 10 to 14%, divided in 1/100%. Between 171.8 and 240.4 cc. of gas must be generated to obtain a reading. A is also a measuring burette, that may be used in place of D where a wider range of measurement is desired. It is used for the measurement of small as well as large amounts of gas. It is most commonly graduated to hold 300.1 milligrams of NO at 20° C. and 760 mm. pressure and this volume is divided into 100 units (subdivided into teeths) each unit being equivalent to 3.001 milligrams of NO. When compensated, the gas from

---

ten times the molecular weight in milligrams of any nitrate of the formula RNO₃ (or five times molecular weight of R(NO₃)₃) should exactly fill the burette. This simplifies all calculations; for example the per cent nitric acid in a mixed acid would be

\[
\frac{R63.02}{100W} = \text{per cent HNO}_3
\]

\( R \) = burette reading, \( W \) = grams acid taken.\(^1\) \( C \) is the compensating burette very similar in form to the chamber burette \( D \). \( B \) is the leveling bulb, by the

Fig. 54.—Nitrometer.

Fig. 55.—Du Pont’s Nitrometer.

raising or lowering of which the standard pressure in the system may be obtained. The apparatus as shown in Fig. 55 is mounted on an iron stand. As in the more simple form of apparatus, previously described, mercury is used as the confining liquid. The parts are connected by heavy-walled rubber tubing, wired to the glass parts.

\(^1\) A. W. Betts, Chemist, E. I. DuPont de Nemours Powder Co., in letter to author.
**Standardizing the Apparatus.** The apparatus having been arranged and the various parts filled with mercury, the instrument is standardized as follows: 20 to 30 cc. of sulphuric acid are drawn into the generating bulb through the cup at the top, and at the same time about 210 cc. of air; the cocks are then closed, and the bulb well shaken; this thoroughly desiccates the air, which is then run over into the compensating burette until the mercury is about on a level with the 12.30% mark on the other burette, the two being held in the same relative position, after which the compensating burette is sealed off at the top. A further quantity of air is desiccated in the same manner and run into the reading burette so as to fill up to about the same mark; the cocks are then closed, and a small piece of glass tubing bent in the form of a U, half filled with sulphuric acid (not water), is attached to the outlet of the reading burette; when the mercury columns are balanced and the enclosed air cooled down, the cock is again carefully opened, and when the sulphuric balances in the U-tube, and the mercury columns in both burettes are at the same level, then the air in each one is under the same conditions of temperature and pressure. A reading is now made from the burette, and the barometric pressure and temperature carefully noted, using the formula

\[ V_t = \frac{V_o P_o (273 + t)}{P_s 273}, \]

the volume this enclosed air would occupy at 29.92 ins. pressure and 20° C. is found. The cock is again closed and the reservoir manipulated so as to bring the mercury in both burettes to the same level, and in the reading burette to the calculated value as well. A strip of paper is now pasted on the compensating burette at the level of the mercury, and the standardization is then complete.

Another rapid method of standardizing is to fill the compensating chamber with desiccated air as stated in the first procedure and then to introduce into the generating chamber 1 gram of pure potassium nitrate dissolved in 2 to 4 cc. of water, the cup is rinsed out with 20 cc. of 60° Béarn sulphuric acid, making three or four washings of it, each lot being drawn down separately into the bulb. The generated gas formed after vigorous shaking of the mixture, as stated under procedure, is run into the measuring burette. The columns in both burettes are balanced so that the reading burette is at 13.85 (100 per cent N in KNO₃). A strip of paper is pasted on the compensating burette at the level of the mercury, and standardization is accomplished. By this method the temperature and pressure readings, and the calculations are avoided.¹

**Procedure for Making the Test. Salts.** One gram of sodium or potassium nitrate, or such an amount of the material as will generate between 172 to 240 cc. of gas, is dissolved in a little water and placed in the cup of the generating bulb.

**Liquid Acids.** The acid is weighed in a Lunge pipette and the desired amount run into the funnel of the generating bulb, the amount of acid that is taken being governed by its nitrogen content.

The sample is drawn into the bulb; the funnel is then rinsed out with three or four successive washings of 95% sulphuric acid, the total quantity being 20 cc.

To generate the gas, the bulb is shaken well until apparently all the gas is

¹Standardization with "C. P. KNO₃ is the better, as it is less tedious and is not subject to the correction errors that cannot be escaped when standardizing with air. The KNO₃ must be of undoubted purity."—A. W. Betta.
formed, taking care that the lower stop-cock has been left open, this cock is then closed and the shaking repeated for two minutes. The reservoir is then lowered until about 60 cc. of mercury and 20 cc. of acid are left in the generating bulb. There will remain then sufficient space for 220 cc. of gas.

Note. If too much mercury is left in the bulb, the mixture will be so thick that it will be found difficult to complete the reaction, a long time will be required for the residue to settle and some of the gas is liable to be held in suspension by the mercury, so that inaccurate results follow.

The generated gas is now transferred to the reading burette, and after waiting a couple of minutes to allow for cooling, both burettes are balanced, so that in the compensating tube the mercury column is on a level with the paper mark as well as with the column in the reading burette; the reading is then taken.

If exactly one gram of the substance is taken the percentage of nitrogen may be read directly, but in case of other amounts being taken, as will invariably be the case in the analysis of acids, the readings are divided by the weight of the substance and multiplied by 4.5 to obtain the per cent of nitric acid monohydrate present.

The procedure may be used for determining nitrites as well as nitrates.

**Determination of HNO₃ in Oleum by Du Pont Nitrometer Method**¹

About 10 cc. oleum are weighed in a 30-cc. weighing bottle, 10 cc. 95⁰c reagent sulphuric acid added and mixed by shaking. This mixture is transferred to the nitrometer reaction tube and the weighing bottle and nitrometer cup rinsed with three 5-cc. portions of the reagent sulphuric acid which is drawn into the reaction tube. This is vigorously shaken for three minutes and the gas then passed to the measuring tube and allowed to stand for about five minutes, after which the mercury levels are adjusted and the reading taken.

It is obvious that this determination includes any nitrous acid in the oleum.

**Combined Nitric Acid**

The nitric acid in nitrates may be determined by titration with ferrous sulphate. The nitrate dissolved in a little water is run into strong sulphuric acid and titrated with standard ferrous sulphate according to the procedure described for determining free nitric acid in mixed acids (Vol. II, Acids).

**Determination of Free Nitric Acid**

Other acids being absent, free nitric acid may be determined by titration with standard alkali. Details for the analysis of nitric acid in presence of commonly occurring impurities are given in Volume II in the chapter on Acids.

1 cc. N/1 NaOH = 0.063018 g. HNO₃

¹ By courtesy of E. I. du Pont de Nemours Powder Co.
DETERMINATION OF NITRITES

Gravimetric Method of Buovold

One and one fourth to 1.5 gram of AgBrO₃ is dissolved in 100 cc. of water and 110 cc. of 2 N. acetic acid, in an Erlenmeyer flask. 200 cc. of the nitrite solution (1 g. NaNO₂) are added from a burette, stirring the mixture during addition of the nitrite. A pale green precipitate is obtained. 30 cc. of H₂SO₄ (1 : 4) are added, the mixture warmed to 85°. When the yellow precipitate settles it is filtered on a Gooch and washed with hot water, then dried and weighed as AgBr + AgCl—chlorine is determined on a separate portion and AgCl deducted. AgBr × 0.9070 = NaNO₂. The method is specially applicable to nitrites high in chlorine.

Volumetric Permanganate Method

Principle. Potassium permanganate reacts with nitrous acid or a nitrite as follows:

\[ 5\text{N}_2\text{O}_5 + 4\text{KMnO}_4 + 6\text{H}_2\text{SO}_4 = 5\text{N}_2\text{O}_4 + 2\text{K}_2\text{SO}_4 + 4\text{MnSO}_4 + 6\text{H}_2\text{O} \]

\[ 5\text{HNO}_3 + 2\text{KMnO}_4 + 3\text{H}_2\text{SO}_4 = 5\text{HNO}_2 + \text{K}_2\text{SO}_4 + 2\text{MnSO}_4 + 3\text{H}_2\text{O} \]

Since 2KMnO₄ in acid solution has five available oxygens for oxidation of substances (e.g., 2KMnO₄ − K₂O.2MnO + 5O equivalent to 10H) the molecular weights of the constituents divided by 20 in the first equation and by 10 in the second would represent the normal weights per liter, e.g., 5N₂O₅ divided by 20 = 76 divided by 4 = 19 grams N₂O₅ per liter. 4KMnO₄ divided by 20 or 2KMnO₄ divided by 10 = 158.03 divided by 5 = 31.61 grams of KMnO₄ per liter for a normal solution. In the second equation if Na represents the univalent element we would have 5NaNO₂ divided by 10 or 69 divided by 2 = 34.5 grams per liter. Hence 1 cc. of a normal KMnO₄ solution would oxidize 0.019 gram N₂O₅ or 0.0345 gram NaNO₂ to form N₂O₅ and NaNO₂ respectively.

Organic matter is also oxidized by KMnO₄ hence will interfere if present.

Special Reagents.

\textit{N/5 Potassium Permanganate.} The solution contains 6.322 grams KMnO₄ per liter.

\textit{N/5 Sodium Oxalate.} Na₂C₂O₄ reacts with KMnO₄ as follows:

\[ 5\text{Na}_2\text{C}_2\text{O}_4 + 2\text{KMnO}_4 + 8\text{H}_2\text{SO}_4 = \text{K}_2\text{SO}_4 + 2\text{MnSO}_4 + 5\text{Na}_2\text{SO}_4 + 10\text{CO}_2 + 8\text{H}_2\text{O} \]

Hence 5Na₂C₂O₄ divided by 10 or 134 divided by 2 = 67 grams per liter = a normal sodium oxalate solution. A N/5 solution requires 13.4 grams Na₂C₂O₄ per liter.

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Preparation of the Sample.

Soluble Nitrites. Ten grams of the nitrite are dissolved in water and made to 1000 cc.; 10 cc. contain 0.1 gram of the sample.

Water-insoluble Nitrites. 0.5 to 1.0 gram of the nitrite according to the amount of nitrous acid present is taken for analysis. An excess of KMnO₄ solution is added, followed by dilute H₂SO₄ and the excess standard permanganate titrated with sodium oxalate according to directions given under Procedure.

Nitrous Acid in Nitric Acid and Mixed Acids. This is present generally in very small amounts so that a large sample is taken. The amount and details of the procedures are given under the special subject.

For routine work where a number of daily determinations are made, a 50-cc. burette is generally preferred.

Trial Run. If the approximate strength of the salt is not known the following test may be quickly made to ascertain whether more than 50 cc. of solution is necessary and the approximate amount of KMnO₄ required for oxidation.

Ten cc. of the solution together with 100 cc. of water are placed in a 4-in. casserole and about 10 cc. of dilute H₂SO₄, 1 : 1, added. Standard KMnO₄ from a 50-cc. burette is now run into the sample until a permanent pink color is obtained. The cc. of KMnO₄ multiplied by 5 = the approximate amount of permanganate solution required for oxidation of 50 cc. of sample. An excess of 5 to 10 cc. should be taken in the regular run.

Titration of Nitrite. Sufficient standard N/5 KMnO₄ to oxidize the sample to be titrated (as ascertained by the trial run) and 10 cc. excess are placed in a casserole. The solution is acidified with 10 cc. of dilute (1 : 4) H₂SO₄ and 50 cc. of the nitrite solution is added slowly with constant stirring. The sample is placed on a hot plate until the mixture reaches a temperature of 70° to 80° C. and 25 cc. more of the dilute H₂SO₄ added. The excess permanganate is now titrated with N/5 Na₂C₂O₄, the oxalate being added slowly until the permanganate color is destroyed. Five cc. excess of the oxalate are added and the exact excess determined by titrating the hot solution with N/5 KMnO₄ to a faint pink color. The total permanganate solution taken minus the oxalate titration = cc. KMnO₄ required by the nitrite.

Standard ferrous sulphate, FeSO₄, may be used, in place of sodium oxalate. The titration then may be conducted in the cold.

One cc. N/5 KMnO₄ = 0.0038 g. N₂O₅, or 0.0069 g. NaNO₂, or 0.0085 g. KNO₂.

Detection of a Nitrate in a Nitrite Salt

Iridium salts are colored blue by HNO₃ but no color is produced by HNO₂. Use a 0.025% solution of IrO₂ or (NH₄)₂IrCl₄ per 100 cc. of 98-99% H₂SO₄ and heat to boiling. The solution should be kept in a stoppered bottle. Into the hot reagent in a test tube is dropped the solid substance tested. A blue color is produced by nitrites. If the nitrite is in solution, make alkaline with KOH, evaporate to dryness and test the residue. Chlorine interferes, but not FeCl₃.
Determination of Pyridine in Ammonium Nitrate

Dissolve 250 g. of sample in 300 cc. of distilled water, using a 1000 cc. Kjeldahl or Florence flask. Add a few drops of methyl orange and neutralize with 10% sodium hydroxide solution. Then add 15 cc. excess of 10% sodium hydroxide solution. Set up apparatus, note Fig. 55a, using 300 cc. hypobromite solution in the second flask and receiving the distillate in 25 cc. N/10 sulfuric acid. Distil until 100 cc. of distillate have been collected. The heating should be very slow until all the ammonia, driven off, has been destroyed. This point will be indicated first by an acid reaction of the methyl orange in the first flask and second by the gradual reduction of the amount of nitrogen given off, in very small bubbles, in the hypobromite. At this point the hypobromite flask should not be warm enough to burn the hand (not above 70° to 75° C.). It is now safe to increase the heat so that boiling occurs in the hypobromite in 10 to 15 min. and 100 cc. of distillate comes over in 20 to 25 min. after active boiling starts.

Titrate the liquid in the receiver, using N/10 sodium hydroxide solution with methyl orange as the indicator.

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Record the end-point; add \( \frac{1}{2} \) cc. of phenolphthalein (1 : 1000) solution and continue the titration until a red color which will persist for 30 sec. appears. Subtract the methyl orange end-point from that obtained with phenolphthalein, and multiply the difference by 0.0079. The result is the pyridine bases in grams. Methyl orange indicates pyridine plus ammonia. Phenolphthalein indicates ammonia. Difference is due to pyridine.

NOTES. Because of the fact that the methyl orange and phenolphthalein end-points are never quite the same and because an absorption of carbon dioxide by the sodium hydroxide solution may bring it about that they vary still more widely, it is necessary to standardize the solutions used to both end-points and to make a correction for their normal difference. This correction should be checked by a new standardization at least once a week. We found that with our solutions this difference was usually about 0.4 cc.

In case it is desired to use a sample of a different size, maintain the proportions indicated above, except that the total solution in the first flask should always be about 500 cc.

The hypobromite solution is made up as follows: 100 g. sodium hydroxide are dissolved in 800 cc. of water, 25 cc. of liquid bromine are added, and the mixture shaken until the bromine is entirely dissolved and made up to 1,000 cc. The solution should be made up a day in advance. It will maintain its strength for at least a week if kept in a stoppered, dark bottle. It will be brown in color. Should the brown color disappear during the distillation it would mean that an excess of ammonia is present. This should also be indicated and eliminated from the calculations by the double end-point called for, but in case this happens it is well to repeat the test, using more of the hypobromite solution.

The reactions involved and the calculations on which the proportions are based are indicated in the following equations:

\[
\text{NaOH} + \text{NH}_4\text{NO}_3 \rightarrow \text{NH}_3 + \text{H}_2\text{O} + \text{NaNO}_2
\]

\[
\frac{40}{17}
\]

15 cc. 10% sodium hydroxide solution contains 1.5 g. sodium hydroxide

1.5 g. sodium hydroxide will free 0.0375 g. ammonia

\[
2\text{NH}_3 + 3\text{NaBrO} \rightarrow 3\text{H}_2\text{O} + \text{N}_2 + 3\text{NaBr}
\]

\[
\frac{34}{357}
\]

0.638 g. ammonia is destroyed by 6.699 g. sodium hypobromite

\[
2\text{NaOH} + \text{Br}_2 \rightarrow \text{NaBrO} + \text{NaBr} + \text{H}_2\text{O}
\]

\[
\frac{80}{160} \frac{119}{119}
\]

25 cc. bromine = 79.5 g. bromine

300 cc. solution contains 17.7 g. hypobromite (approx.)
DETERMINATION OF NITROGEN IN STEEL

For the determination of nitrogen in steel, a modification of the method first published by A. H. Allen and modified by Prof. J. W. Langley is used.

By the following method the sample and standard distillates are prepared under similar conditions, and when treated with Nessler reagent, develop colors nearly identical in quality or tone, but proportional in intensity to the ammonia present.

If the Nessler reagent is carefully prepared and works properly, the color in sample and standard will develop almost instantly and is fully developed in less than one minute. The solutions treated with such reagent remain clear or do not cloud appreciably on standing for ten minutes; however, the comparison is best made after standing one minute, and all difficulty due to clouding avoided.

The difficulties of comparison are also reduced to a minimum by using an aliquot part of the distillate in the manner to be described instead of that corresponding to the whole sample.

Preparation of Reagents

Hydrochloric acid of 1.1 sp. gr., free from ammonia, which may be prepared by distilling pure hydrochloric acid gas into distilled water free from ammonia. To do this, take a large flask fitted with a rubber stopper carrying a separatory funnel-tube and an evolution-tube, fill it half full of strong hydrochloric acid, connect the evolution-tube with a wash-bottle connected with a bottle containing the distilled water. Admit strong sulphuric acid free from nitrous acid to the flask through the funnel-tube, apply heat as required, and distill the gas into the prepared water.

Test the acid by admitting some of it into the distilling apparatus, described farther on, and distilling it from an excess of pure caustic soda, or determine the amount of ammonia in a portion of hydrochloric acid of 1.1 sp. gr., and use the amount found as a correction.

Note. The ammonia-free hydrochloric acid may also be prepared as follows:

Dilute concentrated hydrochloric acid to specific gravity 1.10 and without addition of sulphuric acid distill it.

Hydrochloric acid of this strength distills without change in concentration.

The first 100-cc. distillate from one litre of acid will usually contain all the ammonia and is rejected; the portions distilled thereafter being collected for use but must, of course, be tested as usual to make sure it is free from ammonia.

Solution of caustic soda, made by dissolving 300 grams of fused caustic soda in 500 cc. of water and digesting it for 24 hours at 50° C. on a copper zine couple, made as described by Gladstone and Tribe, as follows:

Place from 25 to 30 grams of thin sheet zine in a flask and cover with a moderately concentrated, slightly warm solution of copper sulphate. A thick, spongy coating of copper will be deposited on the zine. Pour off the solution in about ten minutes and wash thoroughly with cold distilled water.

Nessler Reagent. Dissolve 35 grams of potassium iodide in a small quantity of distilled water, and add a strong solution of mercuric chloride little by little, shaking after each addition until the red precipitate formed dissolves. Finally the precipitate formed will fail to dissolve, then stop the addition of the mercury salt and filter. Add to the filtrate 120 grams of caustic soda dissolved in a small amount of water, and dilute until the entire solution measures 1 litre. Add to this 5 cc. of saturated aqueous solution of mercuric chloride, mix thoroughly, allow the precipitate formed to settle, and decant or siphon off the clear liquid into a glass-stoppered bottle.

\[1\] Methods of Analysis used in Laboratories of the Titanium Alloy Manufacturing Co. Contributed by L. E. Barton.
NITROGEN

Standard Ammonia Solution. Dissolve 0.0382 gram of ammonium chloride in 1 litre of water. 1 cc. of this solution will equal 0.01 milligram of nitrogen.

Distilled Water Free From Ammonia. If the ordinary distilled water contains ammonia, redistill it, reject the first portions coming over, and use the subsequent portions, which will be found free from ammonia. Several glass cylinders of colorless glass of about 150 cc. capacity are also required.

The best form of distilling apparatus consists of an Erlenmeyer flask of about 1500 cc. capacity, with a rubber stopper, carrying a separatory funnel-tube and an evolution-tube, the latter connected with a condensing-tube around which passes a constant stream of cold water. The inside tube, where it issues from the condenser, should be sufficiently high to dip into one of the glass cylinders placed on the working table.

Method of Determination

Distillation of Sample

In a distilling flask of 1000 to 1500 cc. capacity, fitted with separatory funnel and connected with condenser, place 40 cc. prepared caustic soda solution; add 500 cc. distilled water and distill until the distillate gives no reaction with Nessler reagent.

Dissolve a 5-gram sample of the steel in 40 cc. of ammonia-free hydrochloric acid, and by means of the separatory funnel add the solution slowly to the contents of the distilling flask, washing in finally with ammonia-free water.

Distill and collect 150 cc. of distillate in a graduated flask. Cork the flask and set aside. Experience has shown that 150 cc. of distillate will contain all the nitrogen in the sample.

Preparation of Standard

After distilling the sample—the apparatus then being free from ammonia but containing the residue of sample and reagents—25 cc. of standard ammonium chloride solution and 150 cc. of ammonia-free water are added to the contents of the flask, and distillation continued until a standard distillate of 150 cc. is collected in a graduated flask.

As before, the single distillate will contain all the ammonia from 25 cc. of standard solution.

To the standard distillate is added 6 cc. of Nessler reagent; and since the standard ammonium chloride solution is equivalent to .00001 g. nitrogen per cc., 1 cc. prepared standard distillate is equivalent to \(25 \times \frac{0.00001}{156} = 0.00001\), 6 g. nitrogen per cc. = .00016% nitrogen when using one gram sample.

Comparison and Determination

To make the determination, 30 cc. of sample distillate, equal to one gram of sample, are placed in one of a pair of Nessler jars and the color developed by addition of 1 cc. Nessler reagent.

The standard and sample are allowed to stand one minute to fully develop the color.

Into the other jar the standard distillate is run from a burette until the colors in standard and sample jars are of the same intensity; the final comparison being made after bringing the contents of the jars to the same volume by addition of ammonia-free water to one or the other.

The number of cc. of standard distillate multiplied by .00016 gives the percentage of nitrogen in the steel.

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DETERMINATION OF CONVERTER EFFICIENCY IN
OXIDATION OF AMMONIA TO NITRIC ACID

In place of determining the total ammonia used and the total products of oxidation, samples may be taken, during the operation, of gases entering and leaving the converter and analyzed according to the following simple and accurate procedure suggested by Gaillard; a method successfully used by the American Cyanamid Company at Warners, N. J., and by the United States nitrate plants at Sheffield and Muscle Shoals, Ala.

Principle. The gas to be analyzed is drawn into an evacuated bulb which has previously been weighed, and the increased weight due to the sample is obtained. The ammonia or nitrogen oxides in the bulb are then absorbed and titrated, and the percentage by weight of combined nitrogen in the gases is determined. The efficiency is the ratio of the combined nitrogen in the exit and inlet gases.

Sources of Error. Error may be caused by:
(a) Water condensation in the sampling tube during sampling.
(b) Air leakage into the tube during sampling.
(c) Ammonia escaping oxidation being drawn into the bulb. In presence of ammonia a cloudiness is readily observed.
(d) Changes in temperature, barometric pressure, and moisture conditions between successive weightings of the same bulb.

These errors are rendered negligible by careful manipulation. (The writer would suggest that a similar bulb tare weight be used and the procedure for weighing recommended in combustion carbon determinations be followed.)

On the right hand side of the illustration below is shown the bulb in the process of evacuation by means of a vacuum pump operated by an electric motor. Attached to the system is a mercury gauge or barometer which gives the degree of evacuation of the bulb.

**Fig. 55b.** Evacuation and Weighing of Bulbs for Converter Efficiency in Ammonia Oxidation.

On the left hand side of the illustration is shown a balance with a bulb suspended for weighing after being evacuated. It is advisable to have a bulb on the right hand arm of the balance acting as a tare weight. This counteracts the buoyancy error of the air, increasing the delicacy of weighing. If the stopcocks are not absolutely tight, the bulb will gain in weight owing to an intake of air.
PHOSPHORUS

P₄, at.wt. 31.02; sp.gr. \{ yellow 1.831 \}
\{ red 2.296 \}; m.p. 44°; b.p. 725°; oxides.

P₂O₅, PO₃, P₂O₅; acids, H₃PO₃, H₄PO₄, H₃PO₄, HPO₃, H₂P₂O₇.

DETECTION

Element. Phosphorus is recognized by its glowing (phosphorescence) in the air. The element is quickly oxidized to P₂O₅; if the yellow modification is slightly warm (34° C.) the oxidation takes place with such energy that the substance bursts into flame. The red form is more stable. It ignites at 200° C.

Boiled with KOH or NaOH it forms phosphine, PH₃, which in presence of accompanying impurities is inflammable in the air.

Phosphorus oxidized to P₂O₅ may be detected with ammonium molybdate, a yellow compound, (NH₄)₃PO₄·12MoO₃·3H₂O, being formed.

Acids. Hypophosphorous Acid, H₃PO₃, heated with copper sulphate to 55° C. gives a reddish-black compound, Cu₄H₂, which breaks down at 100° to H and Cu₄. Permanganates are reduced immediately by hypophosphorous acid. No precipitates are formed with barium, strontium or calcium solutions. Zinc in presence of sulphuric acid reduces hypophosphorous acid to phosphine, PH₃.

Phosphorous Acid, H₂PO₃. Copper sulphate is reduced to metallic copper and hydrogen is evolved, no Cu₄H₂ being formed as in case of hypophosphorous acid. Permanganates are reduced slowly. Added to solutions of barium, strontium or calcium white phosphites of these elements are precipitated. Alkali phosphites are soluble in water, while hypophosphites are not readily soluble.

Orthophosphoric Acid, H₃PO₄. Ammonium phosphomolybdate precipitates yellow ammonium phosphomolybdate from slightly nitric acid solutions. The precipitate is soluble in ammonium hydroxide.

Metaphosphoric Acid, H₂PO₄. Converted by nitric acid in hot solutions to the ortho form. Metaphosphoric acid is not precipitated by ammonium molybdate.

Pyrophosphoric Acid, H₃P₂O₇. Converted to orthophosphoric acid in hot solutions by nitric acid. No precipitate is formed with ammonium molybdate.

<table>
<thead>
<tr>
<th>Reagent</th>
<th>Orthophosphoric acid</th>
<th>Metaphosphoric acid</th>
<th>Pyrophosphoric acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonium molybdate</td>
<td>Yellow ppt.</td>
<td>No ppt.</td>
<td>No ppt.</td>
</tr>
<tr>
<td>Albumin</td>
<td></td>
<td>Coagulated</td>
<td>Not coagulated</td>
</tr>
<tr>
<td>Zine sulphate, cold, in excess</td>
<td>Yellow ppt., Ag₃PO₄</td>
<td>No ppt.</td>
<td>White ppt., Ag₃PO₄</td>
</tr>
<tr>
<td>Silver nitrate in neutral solution</td>
<td>White ppt.</td>
<td></td>
<td>White ppt.,</td>
</tr>
<tr>
<td>Magnesium salts</td>
<td></td>
<td></td>
<td>No ppt.</td>
</tr>
</tbody>
</table>

Chapter contributed by Wilfred W. Scott.

362
PHOSPHORUS

Phosphorous acids are distinguished from phosphoric acids by the phosphine formed with the former when acted upon with zinc. Acid phosphates are distinguished from normal phosphates as follows: Neutral silver nitrate added to an acid phosphate liberates free nitric acid (Litmus test), the following reaction taking place:

$$3\text{AgNO}_3 + \text{Na}_2\text{HPO}_4 = \text{Ag}_3\text{PO}_4 + 2\text{NaNO}_3 + \text{HNO}_3.$$ 

The solution resulting when silver nitrate is added to normal phosphate solution is neutral.

$$3\text{AgNO}_3 + \text{Na}_2\text{PO}_4 = \text{Ag}_3\text{PO}_4 + 3\text{NaNO}_3.$$ 

ESTIMATION

The determination of the pentoxide of phosphorus is required in a large number of substances, since it is widely distributed in the form of phosphates—calcium phosphate, $\text{Ca}_3(\text{PO}_4)_2$; fluorapatite, $3\text{Ca}_3(\text{PO}_4)_2 \cdot \text{CaF}_2$; chlorapatite, $3\text{Ca}_3(\text{PO}_4)_2 \cdot \text{CaCl}_2$; vivianite, $\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$; wavelite, $2\text{Al}_2(\text{PO}_4)_3 \cdot \text{Al}_2(\text{OH})_6 \cdot 9\text{H}_2\text{O}$; pyromorphite, $3\text{Pb}_4(\text{PO}_4)_3 \cdot \text{PbCl}_3$; phosphates of iron and calcium in phosphate ores, hence in slags of the blast furnace. It occurs in fertile soils, bones, plant and animal tissues.

The chemist is especially concerned in the determination of phosphoric acid ($\text{H}_3\text{PO}_4$), in the evaluation of materials used for the manufacture of the acid—bone ash and phosphate rock (see table below). Generally, determinations of lime, iron and alumina are also desired and frequently a more complete analysis. In the analysis of phosphoric acid certain impurities occurring in the crude material used are determined, e.g., iron, lime, magnesia, sulphuric, hydrochloric and hydrofluoric acids, etc. Phosphoric acid is determined in the evaluation of phosphate fertilizers, phosphates used in medicine, phosphate baking powders, etc.

The element is determined in iron, steel, phosphor bronzes, and other alloys.

**Typical Analyses**

<table>
<thead>
<tr>
<th>Substance</th>
<th>Bone Ash</th>
<th>Charlestown</th>
<th>Spanish</th>
<th>Sombrero</th>
<th>Redonda</th>
<th>Canadian Phosphates</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phosphoric oxide</td>
<td>39.55</td>
<td>27.17</td>
<td>33.38</td>
<td>35.12</td>
<td>35.47</td>
<td>37.68</td>
</tr>
<tr>
<td>Sulphur trioxide</td>
<td></td>
<td>3.30</td>
<td>0.57</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>4.43</td>
<td>4.96</td>
<td>4.10</td>
<td>7.40</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lime</td>
<td>52.46</td>
<td>44.03</td>
<td>47.16</td>
<td>51.33</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Magnesia</td>
<td>1.02</td>
<td>0.37</td>
<td>trace</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Alumina</td>
<td></td>
<td>1.44</td>
<td>0.80</td>
<td>+Fe</td>
<td>20.17</td>
<td>$\text{Fe}_2\text{O}_3$</td>
</tr>
<tr>
<td>Ferric oxide</td>
<td>0.17</td>
<td>0.43</td>
<td>2.59</td>
<td>1.02</td>
<td>8.85</td>
<td>$\text{Al}_2\text{O}_3$</td>
</tr>
<tr>
<td>Fluorine, etc.</td>
<td>2.38</td>
<td>4.01</td>
<td></td>
<td></td>
<td>F. etc.</td>
<td></td>
</tr>
<tr>
<td>Alkaline salts</td>
<td>0.87</td>
<td></td>
<td>0.42</td>
<td></td>
<td>9.70</td>
<td>$= 6.88$</td>
</tr>
<tr>
<td>Silica—sand, etc.</td>
<td>0.51</td>
<td>5.60</td>
<td>3.71</td>
<td>2.02</td>
<td></td>
<td>4.29</td>
</tr>
</tbody>
</table>


**Preliminary Remarks.** Practically all procedures for the determination of phosphorus depend upon its oxidation to ortho phosphoric acid and its precipitation by ammonium molybdate from a nitric acid solution as ammonium phospho-molybdate. It may now be determined either gravimetrically or volumetrically. Two procedures are of importance in the gravimetric deter-
mination of phosphorus; the first depends upon the direct weighing of the yellow phosphomolybdate, dried at 110° C.; the second, on the conversion of the yellow precipitate to the magnesium salt and its ignition to pyrophosphate. Two volumetric procedures, which are of special value in the determination of small amounts of phosphorus as in case of phosphorus in iron and steel, are to be recommended for their rapidity and accuracy. One of these is to dissolve the ammonium phosphomolybdate in a known amount of standard caustic, titrate the excess of alkali with standard acid, which indicates the alkali required to neutralize the molybdate acid in the yellow precipitate. From this the amount of phosphorus present may be calculated. A second procedure of equal accuracy and rapidity is to dissolve the molybdate in ammonia, add an excess of sulphuric acid, pass the warm solution through a column of zinc and titrate the reduced molybdate acid with standard potassium permanganate, the amount of permanganate required being a measure of the phosphorus present.

The impurities interfering in the procedures are silica and arsenic acid. The first may be eliminated by dehydration of the silicic acid in the solution and its removal as insoluble SiO₂ by filtration. Arsenic in small quantities does not interfere under certain conditions; in large quantities its removal is imperative.

Preparation and Solution of the Sample

Amount of the Sample Required. For accurate results it is advisable to take a fairly large sample, 5 to 10 grams, and when it has been dissolved, to dilute to a definite volume, 500 or 1000 cc. Aliquots of this solution are taken for analysis.

Iron Ores, Phosphate Rock and Minerals. Five to 10 grams of the pulverized material placed in a 3-in. porcelain dish are digested for an hour with 50 to 100 cc. of concentrated hydrochloric acid (sp.gr. 1.19), the dish being covered by a clock-glass and placed on a steam bath. The acid is now diluted with half its volume of water and the solution filtered into a porcelain dish of sufficient capacity to hold the filtrate and washings. The residue is washed with dilute hydrochloric acid (1:1) until free of visible iron discoloration. The filtrate and washings are evaporated rapidly on a hot plate to small volume and then to dryness over the steam bath. Meanwhile the insoluble residue and filter are ignited in a 20-cc. platinum crucible over a Méker burner or in a muffle furnace and the residue fused with ten times its weight of sodium carbonate. The fusion is removed by inserting a platinum wire into the molten mass, allowing to cool and then gently heating until the mass loosens from the crucible, when it may be removed on the wire. The cooled mass on the wire and that remaining in the crucible are dissolved in dilute hydrochloric acid, and the filtered solution added to the main solution. The combined solutions are evaporated to dryness, and heated gently to dehydrate the silica. The residue is taken up with a few cc. of hydrochloric acid, the solution diluted, filtered and the SiO₂ washed with dilute nitric acid solution. The combined filtrates are made up to 500 or 1000 cc. Aliquots of this solution are taken for analysis.

Iron and Steel. Five to 10 grams of the drillings or filings are dissolved in an Erlenmeyer flask with 50 to 100 cc. of dilute nitric acid, 1:1, more acid being added if necessary. When dissolved, a strong solution of KMnO₄ is added until a pink color appears; on boiling brown manganese dioxide forms in the solution if a sufficient amount of permanganate has been added. This is dis-
solved by adding 2% sodium sulphite solution in just sufficient quantity to
dissolve the precipitate. The solution is diluted to a convenient volume for
analysis. Where a number of determinations are to be made, it is advisable
to weigh the amount of sample desired for the determination and to precipitate
the ammonium phosphomolybdate in the flask in which the drillings have
been dissolved.

**Ferro-Silicon, Iron Phosphide and Acid Insoluble Alloy Steels.** Decom-
position is best accomplished by fusing 1–2 grams with 10–15 grams of a
mixture of sodium carbonate and magnesium oxide (2:1). (A blank should
be run on the reagents and allowance made for any phosphorus present.)
The fusion is dissolved in hydrochloric acid, then taken to dryness and the
SiO₂ filtered off. The SiO₂ is treated with H₂SO₄ in a platinum dish and taken to fumes. The residue is fused with Na₂CO₃ and
the fusion dissolved in HCl and the solution added to the main filtrate
containing the iron and phosphate, etc. This filtrate is concentrated to
near dryness, 10 cc. nitric acid added and the evaporation repeated. This
concentrate is diluted to about 25 cc. and phosphorus precipitated with
ammonium molybdate solution as usual.

**Ferro-Titanium, Metallic Titanium.** The fusion, obtained as directed for
ferro-silicon, is extracted with water to dissolve out the sodium phosphate.
The residue is fused with sodium carbonate and again extracted with water.
The water extracts of the two fusions is examined for phosphorus. The
extracts are made acid with nitric acid, the solution evaporated to near dry-
ness, nitric acid added and the concentrated solution treated as directed for
steel. Iron, in this case, has been removed with titanium.

**Materials Containing Tungsten.** The alloy is dissolved in dil. HNO₃ and
evaporated to dryness, HCl is now added and the solution again evaporated
to dryness, the residue is taken up with HCl and again evaporated. This
residue is extracted with dil. HCl and washed with acid ammonium nitrate.
Iron and phosphorus are in solution, Si and W remain insoluble.

**Ores Containing Titanium.** Titanium may be recognized by the red color
produced by hydrogen peroxide, H₂O₂, added to the sulphuric acid extract; also
by the reduction test with zinc, which causes a play of colors, the solution becom-
ing colorless by the reduction of iron, then, in presence of titanium, pink, purple
and finally blue. (Vanadium gives similar tests.) Solutions containing titanium
frequently appear milky when the solution is diluted before filtering off the insol-
uble residue. Since titanium forms an insoluble compound with phosphoric acid
and iron oxide the final residue, obtained by the method of solution for ores,
phosphate rock and minerals, should be moistened with sulphuric acid and the
silica expelled with hydrofluoric acid. The solution is evaporated to dryness and
to SO₂ fumes, the residue fused with sodium carbonate and taken up with boiling
water. TiO₂ remains insoluble, while P₂O₅ passes into the filtrate.

**Determination of Phosphorus in Organic Matter.** Decompose the organic
matter with nitric acid in a sealed tube according to the method of Cassius
described on page 145, and determine the phosphoric acid formed.

**Soluble Phosphates, Phosphate Baking Powder, etc.** A water extract
is generally sufficient to get the material in solution. In case iron, alumina, lime
and magnesia salts are present, as may occur in baking powders, an extraction
with dilute 3% nitric acid is necessary. It is advisable to dissolve a 5- to 10-gram
sample and take an aliquot part of the solution made up to a definite volume.
Before precipitating with ammonium phosphomolybdate, 5 grams of ammonium
nitrate should be added for each gram of the sample taken for analysis.
GRAVIMETRIC METHODS FOR DETERMINATION OF PHOSPHORUS

A. Direct Weighing of the Ammonium Phosphomolybdate Precipitation of Ammonium Phosphomolybdate

Precipitation of ammonium phosphomolybdate is common to all subsequent methods for determination of phosphorus.

Reaction.

\[ \text{H}_3\text{PO}_4 + 12(\text{NH}_4)_2\text{MoO}_4 + 21\text{HNO}_3 = (\text{NH}_4)_2\text{PO}_4 + 12\text{MoO}_3 + 21\text{NH}_4\text{NO}_3 + 12\text{H}_2\text{O} \]

Amount of Sample Required for Analysis. In volumetric procedures the amount of sample should be such that the phosphorus content will be between 0.005 and 0.05 gram phosphorus. In gravimetric procedure twice this amount is desirable.

Ammonium Molybdate Reagent. See pages 368, and the chapter on Reagents.

Precipitation. The free acid of the solution is nearly neutralized by addition of ammonium hydroxide. In analysis of phosphate rock or materials comparatively low in iron, it is advisable to add ammonium hydroxide in quantity sufficient to cause a slight permanent precipitate followed by just sufficient HNO₃ to dissolve the precipitate. In iron and steel analysis ammonium hydroxide is added until the precipitated iron hydroxide dissolves with difficulty and the solution becomes a deep amber color or cherry red. In analysis of soluble phosphates, litmus paper dropped into the solution indicates the neutral point. Nitric acid is added to the neutral or slightly acid solution, 5 cc. of acid for every 100 cc. of solution. A volume of 150 to 200 cc. of solution is the proper dilution for samples taken in amounts above recommended. To the warm solution (not over 80° C.) ammonium molybdate is added, 60 cc. of the reagent being required for every 0.1 gram of P₄O₁₀ present. The solution is stirred, or shaken, if in a flask, until a cloudy precipitate of ammonium phosphomolybdate appears.

It is then allowed to settle on the steam bath at a temperature of 40 to 60° C., for one hour, then again agitated and allowed to settle in the cold for an hour longer. The filtrate should be tested with additional ammonium molybdate for phosphorus. The yellow precipitate is filtered and washed with 1% HNO₃ solution followed by a 1% solution of KNO₃, or NH₄NO₃ or (NH₄)₂SO₄ as the special case requires. Filtration through asbestos in a Gooch crucible is to be recommended. When a large number of determinations are to be made, as in case of iron and steel, filter paper is more convenient.

A. Direct Weighing of the Ammonium Phosphomolybdate

The sample being dissolved and the ammonium phosphomolybdate precipitated according to directions already given above, the supernatant solution is filtered through a weighed Gooch crucible and washed twice by decantation with dilute nitric acid (1%), the precipitate washed into the Gooch, followed by two washings with 1% KNO₃ or NH₄NO₃ (neutral solutions) and finally with water. The precipitate, free from contaminating impurities, is dried for two hours in an oven at 110° C., then cooled in a desiccator and weighed. Weight of precipitate \( \times 0.0165 = P \), or \( \times 0.03784 = P_{P_2O_5} \).

Note. If this procedure is to be followed it will be convenient to take 1.65 grams sample, if the phosphorus content will allow. Each 0.01 gram of precipitate will then equal 1% P.
B. Determination of Phosphorus as Magnesium Pyrophosphate

**Magnesia Mixture.** For precipitation of ammonium magnesium phosphate, 110 grams of magnesium chloride (MgCl₂·6H₂O) are dissolved in a small amount of water. To this are added 280 grams of ammonium chloride and 700 cc. of ammonia (sp.gr. 0.90); the solution is now diluted to 2000 cc. with distilled water. The solution is allowed to stand several hours and then filtered into a large bottle with glass stopper. Ten cc. of the solution should be used for every 0.1 gram P₂O₅ present in the sample analyzed. As the reagent becomes old it will be necessary to filter off the silica that it gradually accumulates from the reagent bottle.

**Procedure.** The ammonium phosphomolybdate, obtained as directed (page 365), is filtered onto a 12½ S. & S. No. 589 filter paper and washed four or five times with dilute 1% HNO₃. The precipitate is now dissolved from the filter by a fine stream of hot ammonium hydroxide, 1:1, catching the solution in the beaker in which the precipitation was made. The solution and washings should be not over 100 to 150 cc. Hydrochloric acid is added to the cooled solution to neutralize the excess of ammonia, the yellow precipitate, that forms during the neutralization, dissolving with difficulty, when sufficient acid has been added. To the cooled solution cold magnesia mixture is added drop by drop (2 drops per second) with constant stirring. Ten cc. of the reagent will precipitate 0.1 gram P₂O₅. When the solution becomes cloudy the stirring is discontinued and the precipitate allowed to settle ten minutes. Ammonium hydroxide is added until the solution contains about one-fourth its original volume of strong ammonia (e.g. 25 cc. NH₄OH, 90 to 100 cc. of solution). The solution is stirred during the addition and then allowed to settle for at least two hours. It is filtered preferably, through a Gooch crucible (or through an ashless filter paper), and the precipitate washed with dilute ammonium hydroxide, 1:4, then placed in a porcelain crucible, a few drops of saturated solution of ammonium nitrate added and the precipitate heated over a low flame till decomposed (or until the paper chars). The lumps of residue are broken up with a platinum rod and again ignited over a Scimatico or Mäker burner, the heat being gradually increased. If the heating is properly conducted, the resultant ash will be white or light gray, otherwise it will be dark. The addition of solid ammonium nitrate aids the oxidation in obstinate cases, but there is danger of slight mechanical loss. The crucible is cooled in a desiccator and the residue weighed as magnesium pyrophosphate.

\[
\text{Mg}_3\text{P}_2\text{O}_7 \times 0.2787 = \text{P} \quad \text{and} \quad \text{Mg}_3\text{P}_2\text{O}_7 \times 0.6379 = \text{P}_2\text{O}_5.
\]

**Direct Precipitation of Magnesium Ammonium Phosphate**

In the absence of heavy metals whose phosphates are insoluble in an ammoniacal solution, the magnesia mixture may be added directly to the neutral solution containing the phosphate, without previous precipitation of ammonium phosphomolybdate. The magnesium ammonium phosphate is washed and ignited according to directions given above, and weighed as magnesium pyrophosphate.

The use of the Gooch crucible for the ammonium phosphomolybdate and the ammonium magnesium phosphate precipitates is recommended in preference to filter paper. See precautions on page 375.
PHOSPHORUS

VOLUMETRIC METHODS FOR THE DETERMINATION OF PHOSPHORUS

These volumetric procedures are especially applicable for determining small amounts of phosphorus such as are present in steel and in alloys.

C. Alkalimetric Method

The method is based on the acid character of ammonium phosphomolybdate, the following reaction taking place with an alkali hydroxide:

\[
2(NH_4)_2\cdot12\text{MoO}_3\cdot\text{PO}_4\cdot46\text{NaOH} = 2(NH_4)_2\text{HPO}_4\cdot(NH_4)_2\text{MoO}_4\cdot23\text{Na}_2\text{MoO}_4\cdot22\text{H}_2\text{O}.
\]

From the reaction 46 molecules of sodium hydroxide are equivalent to one molecule of \(\text{P}_2\text{O}_5\), hence 1 cc. of N/10 solution of sodium hydroxide neutralizes the yellow precipitate containing an equivalent of .000309 gram of \(\text{P}_2\text{O}_5\) (N equivalent of \(P = 31 + 23 = 1.35\)).

Solutions Required. Nitric Acid for Dissolving: Mix 1000 cc. of HNO\(_3\), sp.gr. 1.42, and 1200 cc. of distilled water.

Nitric Acid for Washing: Mix 20 cc. of HNO\(_3\), sp.gr. 1.42, and 1000 cc. of distilled water.

Ammonium Molybdate: Solution No. 1. Place in a beaker 100 g. of 85 per cent molybdic acid, mix it thoroughly with 240 cc. of distilled water, add 140 cc. of NH\(_4\)OH, sp.gr. 0.90, filter and add 60 cc. of HNO\(_3\), sp.gr. 1.42.

Solution No. 2. Mix 400 cc. of HNO\(_3\), sp.gr. 1.42, and 960 cc. of distilled water.

When the solutions are cold, add solution No. 1 to solution No. 2, stirring constantly; then add 0.01 gram of ammonium phosphate dissolved in 10 cc. of distilled water and let stand at least 24 hours before using.

Potassium Nitrate, 1 per cent: Dissolve 10 g. of KNO\(_3\) in 1000 cc. of distilled water.

Phenolphthalein Indicator: Dissolve 0.2 g. of phenolphthalein in 50 cc. of 95 per cent ethyl alcohol and 50 cc. of distilled water.

Standard Sodium Hydroxide: Dissolve 6.5 g. of purified NaOH in 1000 cc. of distilled water, add a slight excess of 1 per cent solution of barium hydroxide, let stand for 24 hours, decant the liquid, and standardize it against a steel of known phosphorus content as determined by the molybdate-magnesia method, so that 1 cc. will be equivalent to 0.01 per cent of phosphorus on the basis of a 2-g. sample (see notes). A 0.1 N or N/10 solution contains 4 g. NaOH (100%) per 1000 cc.

Protect the solution from carbon dioxide with a soda-lime tube.

Ferric Chloride: Dissolve 100 g. of ferric chloride (phosphorus free) in 100 cc. of distilled water.

Standard Nitric Acid: Mix 10 cc. of HNO\(_3\), sp.gr. 1.42, and 1000 cc. of distilled water. Titrate the solution against standardized NaOH, using phenolphthalein as indicator, and make it equivalent to the NaOH by adding distilled water. 0.1 N or N/10 solution contains 6.3 g. HNO\(_3\) per 1000 cc.

Determination of Phosphorus in Ores and Minerals. See page 371.

Determination of Phosphorus in Iron and Steel. See page 1045, Vol. II.
Determination of Phosphorus in Copper Alloys

In a 400-cc. casserole dissolve 1 g. of copper alloy metal in 10 cc. of HNO₃, sp.gr. 1.42. Add 20 cc. of HCl, sp.gr. 1.20, and evaporate to dryness. Moisten with HCl, evaporate to dryness again, and bake to dull redness. Moisten with HCl again (add 3 cc. of ferric chloride solution unless iron is already present) and dilute to about 200 cc. with distilled water. Add NH₄OH, sp.gr. 0.90, until the basic salts of copper have dissolved and the solution has become a deep blue. Boil, allow to settle, and filter on a loosely woven filter paper. Wash with dilute ammonia and with hot water. Dissolve the precipitate on the filter with hot dilute HCl, dilute the solution to about 200 cc., add NH₄OH, sp.gr. 0.90, until the precipitate which forms at first dissolves rather slowly, and saturate with H₂S gas. Filter off and reject the precipitate. Boil the filtrate to expel H₂S, and add HNO₃, sp.gr. 1.42, until the iron is oxidized. Add NH₄OH, sp.gr. 0.90, until the solution is alkaline. Boil and filter on a loosely woven filter paper. Wash with dilute ammonia and with hot water. Dissolve the precipitate on the filter with HNO₃ (sp.gr. 1.42), receiving the solution in a 350-cc. Erlenmeyer flask. Add NH₄OH, sp.gr. 0.90, until the iron is entirely precipitated, and then add HNO₃, sp.gr. 1.42, cautiously until the solution just becomes clear. Bring the solution to a temperature of about 80° C., and add 40 cc. of ammonium molybdate at room temperature. Allow to stand for one minute, shake or agitate for 3 minutes, and filter on a 9-cm. paper. Wash the precipitate three times with the 2 per cent HNO₃ solution to free it from iron, and continue the washing with the 1 per cent KNO₃ solution until the precipitate and flask are free from acid.

Transfer the paper and precipitate to a solution flask, add 20 cc. of distilled water, 5 drops of phenolphthalein solution as indicator, and an excess of standard NaOH solution. Insert a rubber stopper and shake vigorously until solution of the precipitate is complete. Wash off the stopper with distilled water and determine the excess of NaOH solution by titrating with standard HNO₃ solution. Each cubic centimeter of standard NaOH solution represents 0.01 per cent of phosphorus.

Accuracy. Duplicate determinations should check within 0.01 per cent of phosphorus.

Notes. The ammonium-molybdate solution should be kept in a cool place and should always be filtered before using.

All distilled water used in titrations should be freed from carbon dioxide by boiling or otherwise.

Method for Steel

Procedure. Preparation of the sample. Consult pages 364 and 366. After oxidation of the sample by adding a strong solution of KMnO₄ and boiling, and dissolving the precipitated MnO₂ by reduction with sodium sulphite, the greater part of the free acid is neutralized by addition of ammonia. The solution will appear a deep cherry red color. No iron precipitate should be present. Ammonium phosphomolybdate is now precipitated by addition of ammonium molybdate according to the procedure outlined on page 366. This is filtered into a Gooch crucible containing asbestos, and washed once
or twice with water containing 1% nitric acid, and then several times with a 1% neutral solution of potassium nitrate until the washings are free of acid, as indicated by testing with litmus paper. The asbestos mat containing the precipitate is transferred to a No. 4 beaker, 100 cc. of CO₂ free water added, followed by about 20 cc. of N/10 NaOH measured from a burette. The crucible is rinsed out with 5 to 10 cc. of N/10 NaOH, the exact amount being noted and then with water, adding the rinsings to the main solution. Phenolphthalein indicator is added, and the excess of caustic titrated with N/10 HNO₃.¹ The total NaOH added minus the acid titration equals the cc. of the caustic required to react with the yellow precipitate.

One cc. of 0.1 N or N/10 NaOH = 0.000136 gram of P.

The exact factor should be determined as directed under Reagents.


D. Zinc Reduction and Titration with Potassium Permanganate

Permanganate. Ferric-Alum Method. This method is based on the assumption that ammonium phosphomolybdate, (NH₄)₆Mo₇O₂₄PO₄, is reduced, in acid solution, by zinc, the molybdic acid, MoO₃, forming the lower oxide MoO₂, in which form it reacts with ferric iron in the receiving flask, reducing a corresponding equivalent of ferric salt to ferrous condition, being itself oxidized to MoO₃. When the ferric solution is not placed in the receiving flask, a slight oxidation takes place, the oxide MoO₄²⁻ apparently being formed.

Special Apparatus Required

Jones’ Reductor. Details of the reductor are given under the determination of iron by the permanganate method, also under the Volumetric Determination of Molybdenum.

Solutions Required.

Dilute Ammonia. Mix 100 cc. of NH₄OH, sp.gr. 0.90, and 900 cc. of distilled water.

Dilute Hydrochloric Acid. Mix 500 cc. of HCl, sp.gr. 1.20, and 500 cc. of distilled water.

Dilute Sulphuric Acid for Dissolving. Mix 200 cc. of H₂SO₄, sp.gr. 1.84, and 800 cc. of distilled water.

Dilute Sulphuric Acid for Reductor. Mix 500 cc. of H₂SO₄, sp.gr. 1.84, and 500 cc. of distilled water.

Ammonium Molybdate. Solution No. 1. Place in a beaker 100 g. of 85 per cent molybdic acid, mix it thoroughly with 240 cc. of distilled water, add 140 cc. of NH₄OH, sp.gr. 0.90, filter and add to 60 cc. of HNO₃, sp.gr. 1.42.

Solution No. 2. Mix 400 cc. of HNO₃, sp.gr. 1.42, and 960 cc. of distilled water.

When the solutions are cold, add solution No. 1 to solution No. 2, stirring constantly, then add 0.1 g. of ammonium phosphate dissolved in 10 cc. of distilled water, and let stand at least 24 hours before using.

Acid Ammonium Sulphate. Mix 25 cc. of H₂SO₄, sp.gr. 1.84, and 1000 cc. of distilled water, and then add 15 cc. of NH₄OH, sp.gr. 0.90.

Ferric Alum. Dissolve 200 g. of ferric ammonium sulphate crystals in

¹ If a large quantity of yellow precipitate is present, five minutes should be allowed for the alkali to react before titrating the excess with standard acid.
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1950 cc. of distilled water. Add 50 cc. of H₂SO₄, sp.gr. 1.84, and 80 cc. of phosphoric acid, 85 per cent.

**Potassium Permanganate.** Dissolve from 3.0 to 3.2 g. of KMnO₄ in 1000 cc. of distilled water. Allow the solution to stand for about one week, and then filter it through an asbestos filter. Standardize by using about 0.200 g. portions of pure sodium oxalate—29.85 cc. of 0.1 N solution. See pages 13 and 790.

**Standard for Phosphorus in Steel.** The exact value of the permanganate solution may be accurately and rapidly determined in terms of phosphorus by standardizing against a sample of standard steel containing a known amount of phosphorus, the ultimate standard being steel drillings furnished by the Bureau of Standards. The drillings are dissolved in nitric acid, oxidized with KMnO₄, the excess of the reagent being destroyed by sulphite solution. Ammonia is added until the solution becomes a deep amber color. The phosphorus is precipitated as ammonium phosphomolybdate. The following procedure is the same as is given in the volumetric method following: The permanganate titration of the reduced molybdcic acid divided into the amount of phosphorus known to be present in the solution will give the value of the permanganate in terms of phosphorus.

\[
\frac{\text{Wt. of P in sample}}{\text{cc. KMnO}_4 \text{ required}} = \text{amount of P per cc. of KMnO}_4.
\]

**Method.** In a 400-cc. casserole dissolve 1 g. of the metal in 10 cc. of HNO₃, sp.gr. 1.42. Add 20 cc. of HCl, sp.gr. 1.20, and evaporate to dryness. Moisten with HCl, evaporate to dryness again, and bake to dull redness. Moisten with HCl again, and dilute to about 200 cc. with distilled water and filter if cloudy. To the solution add NH₄OH, sp.gr. 0.90, until the iron is entirely precipitated, and then add HNO₃, sp.gr. 1.42, cautiously until the solution just becomes clear, the solution having an amber color. Bring the solution to a temperature of about 80° C., and add 40 cc. of ammonium molybdate at room temperature. Allow to stand for one minute, shake or agitate for 3 minutes, filter on a 9-em. paper, and wash very thoroughly (about 25 times) with acid ammonium sulphate. Dissolve the precipitate on the paper using 50 cc. of dilute ammonia. Add 10 cc. of H₂SO₄, sp.gr. 1.84, and immediately pass the solution through a Jones reductor, which has the reductor tube prolonged and reaching nearly to the bottom of the flask, dipping into 50 cc. of ferric-alum solution.¹ Wash through the reductor with 150 cc. of distilled water, and follow with an additional 100 cc. of distilled water. Titrate with standard KMnO₄.

By this method the molybdenum in passing through the reductor is reduced entirely to the form Mo₇O₂₃, and is oxidized by the ferric alum to the form MoO₄, an equivalent amount of iron being reduced to the ferrous condition. As the yellow precipitate contains one atom of phosphorus to each twelve molecules of MoO₄, and as three atoms of oxygen oxidize two of molybdenum, eighteen oxygens or thirty-six irons are equivalent to one phosphorus. Therefore, the iron value of the permanganate multiplied by the factor P/36×Fe (or 0.01540) gives the value of the permanganate in terms of phosphorus.

**Accuracy.** Duplicate determinations should check within 0.005 per cent of phosphorus.

¹ It is not required to heat the solution for reduction as is sometimes stated in text books.
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Notes. The ammonium-molybdate solution should be kept in a cool place and should always be filtered before using.

A blank determination should be made on corresponding amounts of acid and water, passing through the reductor into the usual amount of ferrie-alum solution in the flask.

A small quantity of liquid should always be left in the reductor funnel, and air should never be allowed to enter the reductor.

Description of the Jones reductor is given on pages 319 and 320.

In absence of ferrie iron the reduced molybdate is an amber or brown color. During titration with KMnO₄ the color changes to a reddish yellow and fades to a colorless solution, and then the permanganate pink color is obtained.

Calculation. Case 1. If ferrie sulphate is in the receiver (6Mo₂O₇ + 18O = 12MoO₃ in the molecule containing 1P), 18O are equivalent to 36H, hence N/10 P according to this reaction equals at wt. P divided by (36 x 1000) = P for 1 cc. of N/10 KMnO₄ = .0000862 g. P.

Case 2. No ferrie salt in receiver. Mo₆O₁₇ + 35O = 24MoO₃ + 2P (35O = 70H). Dividing by 2 we get at wt. P divided by (35 x 1000) = P for 1 cc. of N/10 KMnO₄ = .0000887.

Notes. In case the alkametric method is chosen, it will be necessary to wash the precipitate free of acid by washing with neutral ammonium nitrate. (Washing with pure water is prohibited owing to the solubility of the precipitate.) A litmus paper test of the filtrate coming from the funnel is the usual practice of ascertaining whether this washing is complete. Sufficient time should be allowed for the standard alkali to react with the precipitate before addition of standard acid in the titration of the excess alkali, otherwise the results will be low; this is specially true if much "yellow precipitate" is present. If the permanganate method has been chosen, washing the precipitate with ammonium sulphate is the general practice, as the presence of nitrate salts in the precipitate would cause error in this reduction method.

As ammonium molybdate is apt to deteriorate after standing for several weeks, it is advisable to test the reagent before use. A fresh solution should be made up every ten or fifteen days.

In precipitating phosphorus it must be remembered that overheating the solution will cause the precipitation of molybdic oxide; should this be suspected, the magnesium phosphate method will correct results.

Special Steels and Alloys. Steels containing titanium, tungsten, vanadium, etc., require special treatment in preparing these for analysis, in the determination of phosphorus. Directions are given for these on the following page, 370a.

Ferro-Silicon, Iron Phosphide and Acid-Insoluble Alloy Steels. Decomposition is best accomplished by fusing 1–2 grams with 10–15 grams of a mixture of sodium carbonate and magnesium oxide (2 : 1). (A blank should be run on the reagents and allowance made for any phosphorus present.) The fusion is dissolved in hydrochloric acid, then taken to dryness and the SO₃ filtered off. The SO₃ is treated with HF and a few drops of H₂SO₄ in a platinum dish and taken to fumes. The residue is fused with Na₂CO₃, and the fusion dissolved in HCl and the solution added to the main filtrate containing the iron and phosphate, etc. This filtrate is concentrated to near dryness, 10 cc. nitric acid added, and the evaporation repeated. This concentrate is diluted to about 25 cc. and phosphorus precipitated with ammonium molybdate solution as usual.

Ferro-Titanium, Metallic Titanium. The fusion, obtained as directed for ferrosilicon, is extracted with water to dissolve out the sodium phosphate. The residue is fused with sodium carbonate and again extracted with water. The water extracts of the two fusions are examined for phosphorus. The extracts are made acid with nitric acid, the solution evaporated to near dryness, nitric acid added and the concentrated solution treated as directed for steel. Iron, in this case, has been removed with titanium.
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Preparation of Cast Iron and Alloy Steels for the Determination of Phosphorus. Cast Iron. One gram or more of the sample is dissolved in 50 cc. of dilute nitric acid, the solution evaporated to dryness and baked at 200° C. for an hour, 15 cc. of hydrochloric acid (d. 1.2) are added and the solution again evaporated to dryness. 15 cc. hydrochloric acid are added to the residue and 20–30 cc. of water and the silica is filtered off and washed with water. The filtrate is evaporated to pasty consistency, 15 cc. of nitric acid are added and the solution evaporated to near dryness, this treatment is repeated and the residue then taken up with 15 cc. of water. Phosphorus is now precipitated according to the directions for phosphorus in the steel solution.

Iron Containing Titanium. The material is treated as in case of cast iron. Any residue remaining from the nitric acid evaporation is treated with HF and H₂SO₄ as in case of cast iron. (Use platinum dish.) The residue remaining from the HF treatment is taken up with a little HCl and filtered. The filtrate being added to the main solution containing iron and phosphorus. The solution is heated to boiling and an ammonium acid sulphite solution is added, dropwise (2 cc. of NH₄OH saturated with SO₂ and 10 cc. NH₄OH). A precipitate will form, which dissolves. In case it does not, on stirring, the solution is cleared by adding a few drops of HCl, and the addition of sulphite continued. When all but 1–2 cc. of the reagent is added, the solution is heated. Ammonium hydroxide is now added drop by drop to the hot solution until a slight greenish precipitate is formed in the solution, which remains undissolved on stirring. Now the remaining 1–2 cc. of the sulphite is added. If a precipitate forms (titanium hydroxide) which does not redissolve on stirring, HCl is added drop by drop until the solution clears. The odor of SO₂ should be evident. If not, more sulphite should be added and the solution again cleared. 5 cc. HCl are added, CO₂ passed through the solution, which is heated to boiling to expel excess of SO₂, the iron remaining in the reduced form. Sufficient ferric chloride is now added to combine with all the phosphorus and a slight excess.

The solution is cooled under tap water and ammonium hydroxide added drop by drop until green ferrous iron precipitate redissolves, and then a white precipitate of titanium hydroxide and ferric phosphate remains and an additional drop causes a distinct reddish tint and the appearance of a green precipitate with one more. If the red color does not appear, the green precipitate is dissolved with a few drops of HCl and additional ferric chloride solution is added. The addition of ammonia is now repeated. A reddish color of excess of ferric hydroxide should be evident.

A few drops of acetic acid (d. 1.04) are added to dissolve the green precipitate, the red remaining undissolved, and 1 cc. excess. The solution is diluted to about 450 cc. with hot water, boiled 1 minute, then rapidly filtered, and washed once or twice with hot water. The filtrate passes through clear, but will become cloudy upon oxidation of iron.

The residue is dried, separated from the filter, the latter burned and its ash added to the main residue. This is mixed with 5 grams of sodium carbonate and about 0.2 g. potassium nitrate and fused in a platinum crucible for half an hour. The fusion is extracted with water and the solution filtered. The filtrate contains all the phosphorus as sodium phosphate.

1 Traces of P in residue are recovered by treating with HF and H₂SO₄ and expelling SiO₂.
The filtrate is acidified with nitric acid and evaporated to near dryness, then taken up with a few cc. of water and to a volume of 25 cc. is added the ammonium molybdate solution according to the procedure for iron and steel. The procedure from this stage is the same as for steel.

**Vanadium Steel.** In presence of vanadium the ammonium phosphomolybdate will be contaminated with vanadium, so that its presence requires a special treatment. If less than 2.5% is present, the regular procedure for steel is followed with the exception that just before adding the ammonium molybdate, 5–10 cc. nitric acid are added.

If more than 2.5% of vanadium is present, the following procedure is recommended by C. M. Johnson (J. I. E. C., 11, 113 (1919)): 1 gram of steel is treated in a covered 250-cc. porcelain dish with a mixture of 30 cc. concentrated hydrochloric acid and 30 cc. concentrated nitric acid, and the solution is heated for an hour. The cover is rinsed off into the main solution, 100 cc. of strong nitric acid is added and the solution evaporated to dryness and baked for 5 minutes at 200° C. The oxides are dissolved in 35 cc. of concentrated hydrochloric acid and the solution evaporated to about 10 cc. 10 cc. of nitric acid are added and the covered solution heated for a few minutes. The solution is filtered through asbestos, on a small wad of glass wool in a funnel. The vanadium oxide residue is washed 15 times with small portions of a solution containing 200 cc. concentrated nitric acid, 100 cc. water and 20 grams of ferric nitrate (free from phosphorus). The filtrate is concentrated to 10 cc. If a precipitate forms V₂O₅, it is filtered off and the washing repeated, the filtrate is again evaporated and filtered if necessary. If no precipitation occurs in the filtrate upon concentration, 40 cc. of nitric acid are added and the phosphorus precipitated with ammonium molybdate as usual.

Note. Vanadium may also be precipitated by concentration to about 20 cc., neutralizing the greater part of the acid and adding ammonium chloride solid to saturation. The precipitate is washed with a saturated solution of NH₄Cl.

¹Johnson recommends ammonium molybdate that contains 55 grams of ammonium molybdate, 50 grams of ammonium nitrate, 40 cc. ammonium hydroxide, and 700 cc. water. After heating for half an hour, the solution is diluted to 1000 cc. The solution is allowed to settle for 24 hours and is filtered. It is slightly ammoniacal.
Report of the Committee on Research and Analytical Methods—
Phosphate Rock

The following tentative standard methods for sampling and determination of moisture, phosphoric acid and iron and alumina in phosphate rock are recommended to the Division.

Methods of Sampling and Determination of Moisture

I. Gross Sample. A. Car Shipments. One hundred pounds sample per car.

1. Sampling from the Car. In sampling car shipments in the car at least ten scoops of equal size shall be taken from each car at approximately equal distances from each other so as to average the car. Care shall be taken to see that each scoopful shall cover the entire face of the pile from floor to top.

2. Sampling from the Cart or Barrow. A small hand scoopful of 1 to 2 lbs. shall be taken from each cart or barrow either as it is being loaded or as it leaves the car.

B. Cargo Shipments. One hundred pounds minimum sample per vessel.

1. Sampling in Hoisting Tub. In sampling cargoes generally running from 1000 tons upward a small hand scoopful shall be taken from approximately every tenth tub before it is hoisted from the hold.

2. Sampling from Conveyor. If unloading is being done with automatic bucket and conveyor, periodical sections of the entire discharge of the conveyor shall be taken of such intervals and quantity as to give a sample equivalent to approximately 1 lb. per each 10 tons of cargo.

3. Sampling from Conveying Vehicle. Samples shall be taken with a hand scoop from various cars at such regular intervals and in such quantities as to give approximately 1 lb. for each 10 tons of cargo.

II. Laboratory Sample. The resulting gross sample obtained by any one of the methods outlined shall be crushed to pass a four-mesh screen, thoroughly mixed on a clean, hard surface and quartered down to a 10-lb. average sample.

A. Crushing. This 10-lb. sample shall all be crushed to pass an eight-mesh screen.

B. Mixing and Quartering. This eight-mesh sample shall be carefully mixed and quartered down to two 2-lb. samples.

C. Grinding. 1. Moisture Sample. One of these 2-lb. samples shall be held in an air-tight container. This sample is to be used for the determination of moisture.

2. Analytical Sample. The other 2-lb. sample shall be further mixed and quartered down to a 2- or 4-oz. sample which is then to be ground to pass a sixty-mesh screen or preferably a sixty-five mesh screen. This sample is to be used for the analytical determination.

Note. It is essential that the taking of the gross sample be done with small hand scoops and that the practice of taking the sample in the hand be absolutely prohibited, for it has been found that there is considerable selective action in the finer materials sifting through the fingers while a scoop retains the entire sample.

The dimensions of the screens referred to above are to be as follows:

<table>
<thead>
<tr>
<th>No. of Mesh</th>
<th>Size of Opening Inches</th>
<th>Diameter of Wire Inches</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>0.185</td>
<td>0.065</td>
</tr>
<tr>
<td>8</td>
<td>0.093</td>
<td>0.032</td>
</tr>
<tr>
<td>65</td>
<td>0.0082</td>
<td>0.0072</td>
</tr>
</tbody>
</table>

III. Determination of Moisture. Moisture is to be determined on both the moisture sample and analytical sample. Of the moisture sample not less than 100 grams are to be weighed out for each determination. Of the analytical sample approximately 2 grams are to be weighed out for each determination. Both are to be dried to constant weight at a temperature of 105° C. in a well-ventilated oven, preferably with a current of dry air passing through the oven. The containers in which moisture is determined should be provided with well-fitting covers so that the samples may be cooled and weighed in the well-covered container.

1 Journ. Ind. and Eng. Chem.
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IV. Calculation of Results. The percentages of phosphoric acid and iron and alumina as determined on the analytical sample are to be calculated to a moisture-free basis and subsequently to the basis of the original sample as shown by the moisture content of the moisture sample.

Determination of Phosphoric Acid

Reagents. To be prepared as in Official Methods, A. O. A. C. Bureau of Chemistry, Bulletin 107 (Rev.), 1910, p. 2. Preparation of reagents (c), (d), (e) and (f), except that the ammonium nitrate solution in (d) is changed to 5% instead of 10%.

Method of Solution. To 5 grams of the sample add 30 cc. of conc. hydrochloric acid (sp.gr. 1.20) and 10 cc. of conc. nitric acid (sp.gr. 1.42) and boil down to a syrupy consistency. The residue, which should be nearly solid after cooling, is taken up with 5 cc. of conc. nitric acid and 50 cc. of water. Heat to boiling, cool, filter and make up to 500 cc. through the filter. This procedure eliminates practically all of the silica and it is necessary to filter as quickly as possible after digestion so as to avoid redissolving the silica.

Determination. Draw off an aliquot portion of 50 cc., corresponding to 0.5 gram, neutralize with ammonia, then add nitric acid until the solution is just clear. Add 15 grams of ammonium nitrate (free from phosphates), heat the solution to 50° C. and add 150 cc. of molybdate solution. Digest at 50° C. for fifteen minutes with frequent stirring. Filter off the supernatant liquid and test the filtrate with molybdate solution to see if precipitation has been complete. (If not, add more molybdate to the filtrate and digest for fifteen minutes longer.) Wash with 5% percent ammonium nitrate solution by decantation, retaining as much of the precipitate as possible in the beaker. Dissolve the precipitate in the beaker in the least possible quantity of ammonium hydroxide (sp.gr. 0.90) and dilute this solution with several times its volume of hot water. Dissolve the remainder of the precipitate on the filter with this solution, washing beaker and filter with hot water and keeping the volume of the filtrate between 75 and 100 cc. Neutralize with hydrochloric acid, cool to room temperature and add 25 cc. of magnesia mixture from a burette, drop by drop, stirring vigorously with a rubber-tipped rod, then add 15 cc. of ammonium hydroxide (sp.gr. 0.90) and allow to stand for four hours or overnight at room temperature. The time of standing may be reduced to two hours if kept in a refrigerator or still better in an ice-water bath. Filter through a platinum or porcelain Gooch crucible, fitted with a platinum or asbestos nap carefully made and ignited to constant weight. Wash with 2.5% ammonium hydroxide until practically free from chlorides; dry, ignite, cool and weigh as magnesium pyrophosphate. If desired, filtration may be made through an ashless filter paper, igniting in the usual manner. Calculate to P₂O₅ by multiplying by 0.6378 (log 80468).

Determination of Iron and Aluminum together as Phosphates

I. Solutions Required: 1. Hydrochloric acid (1 : 1); prepared by mixing 1 part by volume of concentrated HCl (sp.gr. 1.19) with 1 part of distilled water.
2. A saturated solution of ammonium chloride, which should be filtered before use.
3. A 25% solution of ammonium acetate, faintly acid to litmus paper.
4. A solution of ammonium phosphate (10%) prepared by dissolving 20 grams of (NH₄)₂HPO₄ in 180 cc. of distilled water and filtering. (This should be prepared frequently in small quantity, as it attacks glass containers on standing.)
5. A standard solution of ferrous ammonium sulphate, containing iron equivalent to about 0.0100 gram of Fe₂O₃ in 10 cc. and 50 cc. conc. HCl per liter.
6. A solution of calcium and magnesium phosphates for blank determinations, prepared as follows: Dissolve 4 grams of MgO and 35 grams of CaCO₃ (both free of iron and aluminum) in 100 cc. concentrated HCl, add an aqueous solution of 30 grams of (NH₄)₂HPO₄, make up to 2 liters and filter.
7. A solution of ammonium nitrate (3%) for washing precipitates. About 400 cc. are required for each determination.

All reagents used should be as pure as practicable and all solutions should be free of suspended matter.

II. Preparation of Rock Solution. Place 2.5 grams of pulverized rock with 50 cc. of 1 : 1 HCl in a graduated 250-cc. flask, the glass of which contains less than 1%
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of iron and aluminum oxides. Boil gently with occasional shaking for one hour in such a manner as to avoid concentrating the solution to less than half of its original volume. Dilute, cool to room temperature, make up to volume and mix; filter immediately through a dry filter into a dry flask, discarding the first few cc of the filtered solution.

Pipette a 50-cc aliquot, representing 0.5 gram of rock, into a platinum dish and evaporate nearly to dryness. Cool, take up with a few cc of water and when the salts are loosened from the dish, add 5 cc of 1 : 1 sulphuric acid and evaporate to fumes. Increase the temperature and evaporate nearly to dryness. Cool, dilute with about 50 cc of distilled water, add 10 cc of conc. HCl and heat, with occasional stirring, until sulphates are dissolved. Filter into a 600-cc. Jena glass beaker through a 9-em. paper (S. & S. No. 597), washing the paper thoroughly with dilute HCl and hot water.

III. First Precipitation with Ammonium Acetate. To the solution in the beaker, add 25 cc of the standard iron solution when the amount of combined iron and aluminum oxides in the rock does not exceed 5% and 50 cc of the standard iron solution when the combined oxides exceed 5%. Oxidize with about 3 cc of bromine water and boil in covered beaker for about fifteen minutes to expel the excess of bromine. Rinse cover and sides of beaker with distilled water and cool to room temperature.

(Run a blank determination containing 10 cc of 1 : 1 HCl, 25 cc of the calcium and magnesium phosphate solution, and the same quantity of standard iron solution as is added to the rock solution.)

Add 100 cc of saturated ammonium chloride solution, 3 cc of 10% ammonium phosphate solution, 2 drops of methyl-orange indicator and conc. ammonium hydrate (free of spangles and dissolved mineral matter) to alkaline reaction. Then add dilute HCl (about 1 : 20) drop by drop, with constant stirring, until the solution becomes faintly acid and the pink color of the methyl orange is just restored.

Dilute to 450 cc with distilled water, heat to boiling, and add 25 cc of 25% ammonium acetate solution. Continue heating for about five minutes, after adding ammonium acetate, filter on a 12.5 cm. ashless filter paper (S. & S. No. 589 "White Ribbon"

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1 Experiments have shown that the solution cannot be made in flasks made of glass containing a higher percentage of alumina, because the fluorine in the rock partially dissolves the glass and adds alumina to the solution. Neither "Nonsol," "Jena," nor "Weber's" resistant glass "R" is suitable. Flasks made of glass containing little alumina, such as "Kavalier," "F Z resistant glass" or other Bohemian glass of lower alumina content have proven satisfactory. See "Chemical Glassware," P. H. Walker, J. Am. Chem. Soc., 27, 865.

2 This may be accomplished by heating the flask over a low Bunsen flame or on a hot platé which is just hot enough to keep the solution boiling. A glass tube about 12 ins. long by 1 in. in diameter with a bulb in the middle makes a very satisfactory condenser when placed in the neck of the flask.

3 It is advisable to remove as much of the HCl as possible before adding sulphuric acid so as to minimize the chances of loss by effervescence or bumping. The evaporation may be conducted in glass beakers of low alumina content. Kavalier glass has been used satisfactorily. In no case should the evaporation be conducted in porcelain.

It is best to remove as much sulphuric acid as possible so that the calcium sulphate which might hold iron will dissolve readily in HCl.

It has been found that when iron oxide is present in considerable excess over aluminum oxide the precipitation of the phosphates is more complete, the combined phosphates are more readily ignited to constant weight, and the precipitate does not turn orange red on ignition.

Ammonium chloride in large quantity increases the solubility of calcium and magnesium phosphates and decreases the solubility of iron and aluminum phosphates.

This method of adjusting acidity was suggested by F. B. Carpenter and was found to give satisfactory results.

All our work has confirmed Brown's statement (see Wiley's "Principles and Practice of Agricultural Analysis," 2d edition, 1908, Vol. II, p. 245) that the separation from calcium under the conditions of the method depends upon sufficient dilution.
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is suitable), in a 3-in. rapid filtering funnel, keeping the contents of the beaker and funnel hot. Wash three times with hot 5% ammonium nitrate solution, each time cutting the precipitate loose from the filter and stirring it thoroughly with the stream from the wash bottle and filling to within about 3/4 in. of its upper edge. About 30 cc. are required for each washing. Return the precipitate to the precipitating beaker by washing it out of the filter with a stream of hot water. Dissolve the precipitate with dilute HCl (1:6), pouring about 50 cc. through the filter in successive washings and using about 25 cc. to wash down inside the beaker. Finish filter paper with distilled water.

IV. Second Precipitation with Ammonium Acetate. Cool the solution to room temperature, add 50 cc. saturated ammonium chloride solution, 4 cc. of 10% ammonium phosphate solution, 2 drops of methyl orange, and adjust acidity as before. Dilute to 300 cc. with distilled water. Heat to boiling; add 15 cc. of 25% ammonium acetate solution and continue heating for about five minutes. Filter on the same paper as used for the first filtration, scrubbing the inside of the beaker with a rubber-tipped stirring rod and rinsing with hot 5% ammonium nitrate solution. Wash the precipitate ten times with hot 5% ammonium nitrate solution, each time cutting the precipitate loose, stirring it thoroughly as before and breaking up all lumps that it may contain. About 300 cc. of wash solution are required.

As a control measure, boil the filtrate and washings from both the first and second precipitates, and recover any additional precipitate.

V. Ignition of Precipitate. Transfer filter with precipitate to a weighed deep-form porcelain crucible (40 mm. in diameter is a good size) and heat gently over a low flame until the contents are dry. Increase the temperature a little and continue heating until the paper is charred, increase the temperature again and continue heating until the paper is entirely burned. Ignite the uncovered porcelain crucible for one-hour periods over blast lamp No. 4 Meker burner to constant weight, each time cooling to room temperature in desiccator before weighing. Deduct the weight of blank from each determination, and after subtracting the weight of FePO₄ equivalent to the amount of iron found in 0.5 gram of rock by titration, calculate the remainder to Al₂O₃. Al₂O₃ × 0.4184 = Al₂O₃.

Determination of Iron

I. Solutions Required. 1. Standard Potassium Permanganate, N/40, containing 0.79015 gram of KMnO₄ per liter, and having a value of 0.001998 (or practically 0.002) gram of Fe₂O₃ per cc. Standardize with pure sodium oxalate (Bureau of Standards standard sample No. 40.)

2. Stannous Chloride. Dissolve 50 grams of the crystallized salt in 100 cc. of hot conc. HCl and make up to 1 liter with distilled water.


4. Manganese Solution. (Preventive solution): (a) Dissolve 200 grams of crystallized manganese sulphate in 1000 cc. of water. (b) Pour slowly, with constant stirring, 400 cc. of conc. sulphuric acid into 600 cc. of water and add 1000 cc. of phosphoric acid of 1.3 sp. gr. Mix solutions (a) and (b).

II. Analytical Procedure. Determine iron according to Jones' and Jeffrey's modification of the Zimmermann-Reimhardts method as follows: Place in a 250-cc. beaker an aliquot of the rock solution, containing not more than 5 cc. of conc. HCl, boil and reduce with the smallest possible excess of stannous chloride, added drop by drop while agitating the solution. Wash sides of beaker with distilled water and cool rapidly. Add 10 cc. of mercuric chloride solution and stir vigorously for about thirty seconds. Pour the mixture into a large porcelain casserole or dish containing 20 cc. of the manganese solution in about 500 cc. of water which has just been treated with the permanganate solution.

1 The contents of the funnel will remain hot if the solution in the beaker is kept hot over a low flame and filtration is fairly rapid.

2 Heat over Bunsen to redness before placing over blast in order to prevent loss of precipitate by blowing out of crucible.

3 Analyst, 34 (1909), 306.

4 Barneby has shown that only a short interval of time is necessary between the addition of mercuric chloride and manganese sulphate, if the solution is thoroughly agitated. J. Am. Chem. Soc., 36 (1914).
Titrating with N/40 permanganate solution, to original tint and correct result by the volume of KMnO₄ required for a blank containing the same quantity of HCl (diluted), adding 2 or 3 drops of stannous chloride to the hot solution, cooling, adding 10 cc. of mercuric chloride and titrating similarly.

When the rock solution contains carbonaceous matter it is necessary first to oxidize this with a little potassium chlorate, evaporate to dryness to eliminate chlorine, and redissolve with 5 cc. cone. HCl and about 10 cc. of water.

Calculate the Fe₂O₃ found to FePO₄, using the factor 1.8808, and after deducting from the weight of combined phosphates found, calculate the difference (Al₂PO₄) to Al₂O₃.

**Volumetric Determination of Free Phosphoric Acid**

Phosphoric acid may be titrated directly by means of standard sodium or potassium hydroxide. The choice of the indicator is important as may be seen by the following reactions:

\[ \text{H₃PO₄} + \text{NaOH} = \text{H₂O} + \text{NaH₂PO₄} \text{ (neutral to methyl orange, acid to phenolphthalein)} \]
\[ \text{H₃PO₄} + 2\text{NaOH} = 2\text{H₂O} + \text{Na₂HPO₄} \text{ (neutral to phenol, and acid to methyl orange)} \]

The slight dissociation of Na₂HPO₄ causing an alkaline reaction to phenolphthalein prevents the endpoint being sharp. This dissociation may be repressed by titrating in a cold concentrated solution containing sodium chloride. The first reaction with methyl orange indicator is more satisfactory. By the electrometric method J. S. Coye has proven that the endpoint of phenolphthalein is the full color of the alkaline salt, not a faint pink.

Reference is made to the chapter on Acidity and Alkalinity, Volume 2, for titrating phosphoric acid in presence of its salts.

**Sources of Error in the Determination of Phosphoric Acid**

McCandless and Burton have shown that discrepancies in the gravimetric determination of phosphorus in high grade materials are chiefly due to variations in the amount of HCl used in neutralizing the ammoniacal solution of the yellow precipitate. A solution made neutral, using litmus paper as indicator, has the proper neutrality. Plus errors are caused by adding the acid in excess of the neutral point, and minus errors by having ammonia in excess of neutrality.

The yellow precipitate contained in a small filter (7.5 cm.) is dissolved by adding NH₄OH drop by drop from a burette in just sufficient amount to dissolve the precipitate. The filter is washed free of the phosphate, the washing continued until the volume of the filtrate is 100-150 cc. To the cooled filtrate is added, drop by drop, dilute HCl (1 : 1), with constant stirring, until the color of the litmus paper, placed in the solution, changes to a violet, verging on blue rather than red. Magnesium mixture is now added, drop by drop, in slight excess. After 15 minutes NH₄OH (sp.gr. 0.90) is added, 12 cc. NH₄OH to 100 cc. filtrate or 18 cc. NH₄OH, if the volume is 150 cc. The precipitate is washed thoroughly with 2.5\% NH₄OH water, and finally with a strong NH₄NO₃ solution in ammonia water. The Gooch and asbestos is ignited over the blast lamp before use.

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PLATINUM

Pt, at. wt. 195.23; sp. gr. 21.48; m.p. 1755° C.; oxides PtO, PtO₂

DETECTION

Platinum is a gray, lustrous, soft and malleable metal. It is not altered by ignition in the air, but fuses in the oxy-hydrogen flame. It does not dissolve in any of the single acids, but a fusion with acid potassium sulphate attacks the metal slightly. The action of chlorine in general, and nitro-hydrochloric acid (aqua regia), the main solvent, converts the metal to hydrochloroplattinic acid, H₂PtCl₆, which forms many double salts, or platinichlorides. If platinic chloride is gently heated it breaks up into platinous chloride, PtCl₂, and chlorine.

If, however, the platinum is alloyed with silver, it dissolves in nitric acid to a yellow liquid, provided sufficient silver is present in the alloy.

The oxides can be formed by carefully igniting the corresponding hydroxides. These are very unstable, decomposing into metal and oxygen by gentle ignition.

The chlorides are the most important compounds of platinum. Two complex acids are formed with hydrochloric acid when the metal is dissolved in aqua regia.

PtCl₄ + 2HCl = H₂PtCl₆ (chloroplatinic acid), orange-red crystals.

PtCl₄ + 2HCl = H₂PtCl₄ (chloroplatinous acid), only known in solution.

An aqueous solution of the former is yellowish-orange, while an aqueous solution of the latter is dark brown, the former being by far the more important.

Potassium iodide precipitates platinum iodide, but it dissolves quite readily, giving a pink to a dark blood-red liquid, depending on the concentration of the solution. Nitric acid should be absent. Heat destroys this color, as well as hydrogen sulphide, sodium thiosulphate and sulphite, sulphurous acid, mercuric chloride and certain other reducing reagents.

Hydrogen sulphide precipitates black platinum disulphide, PtS₂, with the other elements of the hydrogen sulphide group. The solution should be hot, as precipitation takes place more quickly. It is difficultly soluble in ammonium sulphide. It will be found in the extract with the arsenic, antimony, tin, gold, molybdenum, etc., and is precipitated with these elements upon addition of hydrochloric acid. Platinum sulphide is soluble in aqua regia. Addition of MgCl₂ solution prevents formation of colloidal PtS₂.

Ammonium chloride added to a concentrated solution of platinum chloride precipitates yellow (NH₄)₂PtCl₆, which is slightly soluble in water, and less so in dilute ammonium chloride solution and alcohol.

Potassium chloride precipitates yellow K₂PtCl₆, which is slightly soluble in water, but insoluble in 75% alcohol.

Chapter by R. E. Hickman and Edward Wichers.
PLATINUM

Ferrous sulphate precipitates metallic platinum on boiling from a neutral solution. Neutralize with Na₂CO₃. Free mineral acids (except dilute H₂SO₄) prevent the precipitation (difference from gold).

Stannous chloride does not reduce platinum chloride to metal, but reduces hydrochloroplatinic acid to hydrochloroplatinous acid.

$$H₂PtCl₄ + SnCl₂ → H₂PtCl₄ + SnCl₄$$

Oxalic acid does not precipitate platinum (difference from gold).

Sodium hydroxide with glycerine reduces hydrochloroplatinic acid on warming to black metallic powder.

Formic acid precipitates from neutral boiling solutions all the platinum as a black metallic powder.

Thallium protoxide precipitates from the platinum bichloride solution a pale yellow salt, thallium platinocloride. When the salt is heated to redness it leaves an alloy of thallium and platinum.

Sodium hydroxide added to platinic chloride and then acidified with acetic acid produces a pale yellow to orange precipitate of platinic hydroxide, Pt(OH)₄. This dissolves in acids readily, except acetic acid.

Metallic zinc, magnesium, iron, aluminum and copper are the most important metals that precipitate metallic platinum.

$$H₂PtCl₄ + 3Zn → 3ZnCl₂ + H₂ + Pt$$

ESTIMATION

Platinum may be present under the following conditions:

1. Native grains usually accompanied by the other so-called platinum metals, iridium, palladium, ruthenium, rhodium, osmium, and gold and silver (alloyed with one or more of the allied metals).

   Ore concentrates containing the native grains as above with the base metals, iron, copper, chromium, titanium, etc. The associated minerals high in specific gravity in the gravels may be expected to appear with the platinum nuggets, such as chromite, magnetite, garnet, zircon, rutile, small diamonds, topaz, quartz, cassiterite, pyrite, epidote, and serpentine; with gold in syenite; ores of lead and silver.

2. Scrap platinum containing, oftentimes, palladium, iridium, gold, silver and iron.

3. Small amounts of platinum in the presence of large amounts of iron, silica, carbon, magnesia: platinum residues, nickel and platinum contacts, photography paper, jewelers' filings and trimmings, dental and jewelers' sweeps and asbestos, etc.

4. Platinum alloyed with silver, gold, tungsten, nickel, copper, lead, etc.

5. Platinum solutions and salts.

Preparation and Solution of the Sample

The best solvent for platinum is aqua regia. The metal is also acted upon by fusion with the fixed alkalies—sodium or potassium hydroxide and sodium peroxide or potassium or sodium nitrate; also by chlorates in the presence of
HCl. Platinum, when highly heated, alloys with other metals, as lead, tin, bismuth, antimony, silver, gold, copper, etc. The element dissolves in nitric acid when alloyed with silver. This gives a method for the determination of gold in the presence of silver and platinum alloy.

All salts of platinum are soluble in water. The less soluble salts are the chloroplatinates of potassium, ammonium, rubidium, and caesium. Heat increases the solubility while the presence of alcohol decreases the solubility.

Ores. When the free grains of platinum, gold and osmiridium are desired the following method is recommended: Five to 10 grams of the ore are taken from a well-mixed pulverized sample and placed in a large platinum dish that has been weighed. Twenty-five to 50 ec. of strong hydrofluoric acid together with 5 to 10 ec. of concentrated sulphuric acid is mixed with the ore in the dish and evaporated on the water bath, when SiF₄ and the excess of HF are expelled. The material is gently heated until SO₃ fumes are given off. This is repeated with HF if necessary. The material is washed into a casserole with about 200 ec. of hot water and digested over a water bath for fifteen or twenty minutes, and is then washed by decantation, several times pouring the supernatant liquor through a filter to save any floating material that might be washed out. The filter is cautiously burned and the residue is added to the unattacked material. This is transferred from the dish to a beaker or a porcelain dish and treated with aqua regia. The platinum and a small amount of iridium that dissolves with the platinum on account of its being alloyed can be precipitated with ammonium chloride. The remaining residue in the dish will be a small amount of sand and osmiridium. The silica is driven off with HF as described above and the bright grains weighed as osmiridium, or the sand and osmiridium are fused with silver and borax, then extracted with dilute nitric acid, leaving the osmiridium grains free from sand.

Platinum Scrap. One-half gram to a gram is dissolved in aqua regia and evaporated with HCl to get rid of the HNO₃.

If the platinum is alloyed with a large amount of copper, silver, lead and other impurities, a sample of 1 to 5 grams is dissolved in 15 to 25 ec. of HNO₃, whereby the copper, silver, lead and other impurities alloyed with the platinum as well as a large amount of platinum will dissolve. The residue after washing will be platinum and gold. These are dissolved in aqua regia as described above and the platinum precipitated with ammonium chloride. The platinum is recovered from the nitric acid solution and added to the aqua regia solution and the whole is evaporated to get rid of the HNO₃.

Small Amounts of Platinum in the Presence of Large Amounts of Iron; Iron Scale, Fe₂O₃; Sulphate of Iron, Magnesia, Sulphate of Magnesia, Silica, etc. The material is carefully weighed and the coarse scales are separated from the finer material containing the platinum by passing the fines through a 20-in. mesh or finer wire sieve. The coarse scale seldom contains platinum, but it is advisable to quarter this down to 1 kilogram or a fairly good-sized sample and test for platinum on a portion of the ground sample. This can be tested by a wet or a fire assay. The fines are quartered down to about 1 kilogram and ground to pass a 60- to 80-in. mesh sieve. One hundred to 500 grams of the material are taken for analysis. This is placed in one or more casseroles, depending on the amount taken. Each 100-gram portion is extracted by digestion on the steam bath with about 300 to 400 ec. of 10% H₂SO₄. The iron, magnesia, etc., soluble in H₂SO₄ will go into solution, leaving the platinum with the
insoluble residue. Filter (a Büchner funnel may be necessary) and wash the residue with water. Test the filtrate for platinum and if any is present precipitate with zinc as described below.

After the filter is ignited in a large platinum dish, the residue is moistened with H₂SO₄, and HF is added completely covering the material. The solution is evaporated on the water bath until SO₃ fumes are given off. If necessary, repeat the treatment with H₂SO₄ and HF until all the silica is driven off as SiF₄. The residue is transferred to a casserole and digested with aqua regia according to directions given under Ores and Platinum Scrap. It is sometimes very difficult to precipitate all of the platinum in the presence of a large amount of iron, magnesium, etc., not having the solution concentrated enough for the platinum. It is advisable to reduce the platinum by iron or zinc, filter, wash with water and redissolve the black metallic platinum in aqua regia. The HNO₃ is expelled by evaporation and adding concentrated HCl from time to time and finally the platinum is precipitated with ammonium chloride.

SEPARATIONS

A careful review of the paragraph on Detection will be very helpful oftentimes in making separations from other metals and substances.

Separation of Platinum from Gold. The platinum is precipitated first with ammonium chloride, as (NH₄)₂PtCl₄. After the precipitate has settled it is filtered and washed free from gold with 20% ammonium chloride solution and alcohol. The gold is precipitated with a concentrated solution of ferrous sulphate or iron protochloride as metallic gold. (See also page 387a.)

Oxalic acid precipitates the gold, leaving the platinum in solution. The oxalic acid is added and the solution heated until the gold is entirely precipitated. Filter and wash the precipitate of metallic gold free from platinum. The filtrate is evaporated as far as possible without crystallizing, and the platinum is precipitated with ammonium chloride as (NH₄)₂PtCl₄, or it may be reduced with zinc and the black dissolved in aqua regia and treated as described above.

Separation of Platinum from Iridium. The platinum and the iridium are precipitated by iron or zinc and the black residue is washed free from impurities and the platinum is dissolved in dilute aqua regia with gentle heating, leaving the iridium as metallic iridium. The platinum solution is evaporated as described above and precipitated with NH₄Cl as (NH₄)₂PtCl₄.

If the platinum and iridium are precipitated together, the salt is filtered and washed with ammonium chloride solution and finally ignited. The sponge is redissolved and evaporated as above to expel the HNO₃. The platinum and the iridium are precipitated with NaOH, which brings down the platinum and iridium as Pt(OH)₄ and Ir(OH)₄. Boil this mixture with alcohol, which reduces the Ir(OH)₄ to Ir(OH)₃, but does not affect the Pt(OH)₄. Dissolve these hydroxides in HCl, forming PtCl₄ and IrCl₃ in solution, and the platinum is precipitated with NH₄Cl free from iridium.

See Deville-Stas-Gilchrist method on page 390.

Separation of Platinum from Palladium. Platinum is precipitated with ammonium chloride, and palladium is precipitated from the filtrate by means of dimethylglyoxime (1% alcoholic solution).

Palladium may be precipitated in presence of platinum by adding a one percent solution of dimethylglyoxime (1% salt in 95% alcohol) to the cold, slightly acid chloride solution of the elements. If the solution is hot the palladium precipitate will be badly contaminated with platinum. (E. Wichers.)
Separation of Platinum from Ruthenium. From the chloride of platinum and ruthenium the metals are precipitated with ammonium or potassium chloride and filtered. The filter is washed with dilute ammonium chloride solution or dilute potassium chloride solution and alcohol until free from ruthenium. If a large quantity is handled it may be necessary to ignite to platinum sponge and dissolve in aqua regia, expel the HNO₃ as described above, and reprecipitate with NH₄Cl, filter and wash free from ruthenium. (See also page 387a.)

Separation of Platinum from Rhodium. The separation is accomplished by adding freshly precipitated barium carbonate to the chloride solution of platinum and rhodium, previously brought nearly to the neutral point by addition of sodium hydroxide. After boiling for two or three minutes rhodium hydroxide precipitates. The precipitate is filtered off, dissolved in HCl, the solution again nearly neutralized and the rhodium precipitation repeated.

Other platinum metals will also precipitate if present. These should be removed prior to the separation of platinum and rhodium. (E. Wichers.)

Separation of Platinum from Osmium. Both metals are reduced with zinc as a fine black powder. The metallic residue is washed and carefully ignited at a high temperature under a hood, as the fumes are poisonous and disagreeable like chlorine. The osmium will be converted into OsO₄, which is very volatile. The residue is dissolved in aqua regia and the platinum is precipitated with NH₄Cl. See Osmium.

GRAVIMETRIC METHODS FOR THE DETERMINATION OF PLATINUM

A. Weighing as Metallic Platinum

1. When the platinum contains only a small amount of impurities a sample of 1/10 gram or more is taken and dissolved in aqua regia. The solution is gently heated until all is dissolved, adding another portion of aqua regia if necessary. The solution is evaporated, adding HCl from time to time in order to expel the HNO₃. Filter and evaporate again to concentrate the solution. Precipitate with ammonium chloride. After stirring, let stand until the precipitate, (NH₄)₂PtCl₆, settles, overnight if convenient. Filter, wash with alcohol or ammonium chloride solution and alcohol, and ignite to metal, in a reducing atmosphere, or ignite slowly in paper filter. Cool in a desiccator and weigh as metallic platinum.

\[
\frac{\text{Wt. of Pt found}}{\text{Wt. of sample taken}} \times 100 = \text{per cent of Pt in the material.}
\]

2. When the platinum solution contains a large amount of impurities, as iron, nickel, magnesium, etc., it is advisable to reduce the platinum to black metallic platinum with zinc, iron or magnesium as follows: The solution is made acid (2 to 5% free HCl) by adding HCl. The Zn, Fe or Mg is added in small quantities at a time until the solution becomes colorless or until the platinum is completely precipitated. After action has ceased the platinum black metal is filtered onto an ashless filter paper and washed with warm dilute HCl to remove any excess Zn, Fe, or Mg that might be present. The filter and its contents are

\[\text{FeCl}_3\] in presence of HCl has a solvent action on platinum, hence the iron should be completely reduced.
carefully ignited and afterwards dissolved in aqua regia and treated as directed under A, 1.  

3. If none of the other Hydrogen Sulphide Group metals are present the platinum can be precipitated by hydrogen sulphide, filtered, washed with hot water and ignited to metal. If impurities are present in the sulphide, dissolve in aqua regia and proceed as under A, 1. The solution should be boiling and have an acidity of 3% HCl or H₂SO₄.

B. Weighing as a Salt

1. The procedure is the same as under A. The (NH₄)₂PtCl₆ precipitate is washed on a weighed Gooch crucible with alcohol. The crucible and contents are dried at a temperature below 100°. Cool in a desiccator and weigh as (NH₄)₂PtCl₆.

\[
\text{Wt. of } (\text{NH}_4)_2\text{PtCl}_6 \text{ found} \times \frac{\text{Mol. wt. of Pt}}{\text{Mol. wt. of } (\text{NH}_4)_2\text{PtCl}_6} \times \frac{100}{\text{Wt. of sample}} = \text{per cent of Pt in material.} \]

2. After proceeding as described under A, the platinum is precipitated with potassium chloride as K₂PtCl₆. Transfer to a weighed Gooch crucible and wash well with alcohol. Dry below 100°, cool in a desiccator and weigh as K₂PtCl₆.

\[
\text{Wt. of } K_2\text{PtCl}_6 \text{ found} \times \frac{\text{Mol. wt. of Pt}}{\text{Mol. wt. of } K_2\text{PtCl}_6} \times \frac{100}{\text{Wt. of sample}} = \% \text{ of Pt in material.} \]

C. Determination of Platinum by Electro-analysis

When platinum solutions are acidulated with sulphuric acid and acted upon by a feeble current they give up the metal as a bright deposit upon the electrode. If platinum is used as the electrode, first coat it with a layer of copper and deposit the platinum upon the copper. Wash with water and alcohol and after drying weigh.

\[
\text{Wt. of electrode} + \text{Cu} + \text{Pt} - \text{Wt. of electrode} + \text{Cu} = \text{Wt. of Pt.}
\]

\[
\frac{\text{Wt. of Pt}}{\text{Wt. of sample taken}} \times 100 = \text{per cent of Pt in material.}
\]

Dr. E. F. Smith, in his work on “Electro-Analysis” recommends that the K₂PtCl₆ be dissolved in water and slightly acidulated with H₂SO₄ (2 or 3% by vol.) and after heating to about 60 to 65° and electrolyzing with N.D₁₀₀ = .05 ampere and 1.2 volts, the platinum will be completely precipitated in from four to five hours in a perfectly adherent form. A rotating anode will precipitate the platinum much quicker.

1 If iron and lead are suspected, the platinum residue is washed with 10% solution of ammonium chloride and then with 10% solution of ammonium acetate and finally with 80% alcohol.

* Factor (NH₄)₂PtCl₆ to Pt = 0.4393.

* Factor K₂PtCl₆ to Pt = 0.4013.
PALLADIUM

*Element, Palladium.* Pd. at.wt. 106.7; sp.gr. 11.9; m.p. 1549° C.; oxides, PdO, PdO₂.

DETECTION

This metal is also found associated with platinum and iridium as well as ruthenium, rhodium, and osmium. It occurs in the metallic state sometimes with gold and silver. It resembles platinum as to luster and color. Palladium sponge when heated slightly gives a rainbow effect due to the formation of oxides. Hydrogen passed over the sponge restores it to the original color. It dissolves in HNO₃ and boiling H₂SO₄. HCl has little action upon it. It is readily soluble in aqua regia, forming PdCl₂. PdCl₄ is unstable.

Palladium monoxide, PdO, is formed by a long-continued heating of the spongy metal in a current of oxygen at a temperature from 700 to 840° or by heating a mixture of a palladium salt with potassium carbonate. The pure hydrated oxide is best prepared by the hydrolysis of the nitrate.

It acts as a powerful oxidizing agent to organic substances, and is reduced to metal by hydrogen peroxide.¹

Palladium dioxide, PdO₂, is obtained in an impure hydrated form as a brown precipitate by the addition of caustic soda to potassium palladichloride. This is soluble in acids, but becomes less soluble when preserved. It can be obtained free from alkali and basic salts by the anodic oxidation of the nitrate, but it is not quite free from monoxide. The dioxide very readily decomposes into the monoxide and oxygen, and cannot be obtained in the anhydrous state. It acts as a vigorous oxidizing agent and decomposes hydrogen peroxide.

Alkalis precipitate in a concentrated solution a dark-brown precipitate soluble in an excess of the reagent. If boiled a brown palladous hydroxide is precipitated. The anhydrous oxide is black.

Ammonia added to a concentrated solution gives a flesh-red precipitate. Pd(NH₄)₂Cl₂, soluble in excess of ammonia. If HCl is added to this solution, the yellow compound of palladamine chloride, Pd(NH₄Cl)₂, is deposited.

Sulphur dioxide precipitates the metal from the nitrate or sulphate solution but not from the chloride.

Cuprous chloride precipitates the metal from the sulphate, nitrate and chloride solution when they are not too strongly acid.

Mercuric cyanide precipitates a yellowish-white gelatinous precipitate, Pd(CN)₂, insoluble in dilute acids, but dissolving in ammonia and in potassium cyanide to K₂Pd(CN)₄.

Potassium iodide precipitates black palladous iodide, PdI₂, insoluble in water, alcohol, and ether, but soluble in an excess of reagent (Rk also ppts.).

Hydrogen sulphide precipitates black palladous sulphide, PdS, soluble in HCl and aqua regia, but insoluble in (NH₄)₂S.

Ferrous sulphate slowly produces a black precipitate of metallic palladium from the nitrate.

¹ "Treatise on Chemistry," Roscoe and Schorlemmer.

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Ammonium chloride precipitates palladium as (NH₄)₂PdCl₄ from the nitrate.

Formic acid, zinc and iron reduce to metallic palladium.

Soluble carbonates precipitate brown palladous hydroxide, Pd(OH)₂, soluble in excess, and reprecipitated on boiling.

Phosphuretted hydrogen gas precipitates palladium phosphide. (Difference from Pt, Rh, and Ir.)

Alcohol precipitates, on boiling, metallic palladium.

Alkaline tartrates and citrates form yellow precipitates in a neutral solution from the nitrate.

Stannous chloride produces a brownish-black precipitate, soluble in hydrochloric acid to an intense green solution.

Potassium bisulphate attacks the metal readily.

An alcoholic solution of iodine dropped on the metal will turn black.

Acetylene gas passed through an acidified solution containing Pd produces a brown precipitate which, upon ignition, yields Pd. In this way Pd may be quantitatively separated from Cu.

ESTIMATION

Palladium is determined in alloys, ores, jeweler's sweeps, etc.

Preparation and Solution of the Sample

The solubility of palladium has been taken up under Detection. Palladium when alloyed with platinum, or an alloy of platinum, iridium and palladium, dissolves with the other metals in aqua regia as the chloride. When palladium is alloyed with silver the palladium and silver are dissolved in HNO₃, from which the silver can be separated.

Separations

Separation of Palladium from Platinum and Iridium. The chlorides of palladium, platinum and iridium in solution must be free from HNO₃. The platinum and the iridium are precipitated with NH₄Cl, leaving the palladium in solution. The precipitate is put on a filter and washed free from Pd with NH₄Cl solution and alcohol.

Separation of Palladium from Silver and Gold. At least three times the weight of the gold in silver should be present in the alloy in order to separate the silver and palladium from the gold. The silver and the palladium will dissolve in HNO₃, leaving the gold as the residue. This is filtered off and the silver may be precipitated with HCl. The silver chloride is filtered off and washed with hot water acidulated with HCl until free from palladium. Since AgCl tends to retain palladium it is advisable to redissolve the silver with HNO₃ after reduction of AgCl and reprecipitate the chloride to obtain a complete separation of palladium.

Separation of Palladium from Platinum. The chlorides of platinum and palladium being free from HNO₃ and having an excess of HCl is diluted with water. A 10% solution of potassium iodide is added until all of the palladium is precipitated. Avoid adding a large excess. The precipitate of PdI₂ is filtered off and washed free from platinum and alkali with water slightly acidulated with HCl. The filter is ignited to metallic sponge in a current of hydrogen. See glyoxime method on page 379.
GRAVIMETRIC METHODS FOR THE DETERMINATION OF PALLADIUM

1. The palladium is precipitated from the solution by granulated zinc, the solution having a small amount of free hydrochloric acid. The residue, after the zinc is dissolved, is put on a filter and washed free from impurities. Ignite the filter and dissolve in a small amount of aqua regia and evaporate to a syrupy consistency. Dilute with a small amount of water and add a few drops of HNO₃; precipitate the palladium with NH₄Cl crystals. Heat for a few minutes and let cool. Filter, wash with alcohol, and ignite. Reduce in hydrogen or moisten with formic acid to reduce to metal any oxide that may have formed. Dry and weigh as metallic palladium.

2. With the solution containing about one-fifth the volume of free HCl, the palladium is precipitated with 10% KI solution. Heat to nearly boiling, filter, wash free from iron, etc., with 1:4 HCl. Ignite, cool, reduce in hydrogen or moisten with formic acid, dry and weigh as metallic Pd.

3. The filtrate from the platinum precipitation or the nearly neutral solution containing the Pd is made to about 150 cc., and the Pd is precipitated by adding a solution of dimethylglyoxime (1% solution in alcohol). Bring to boiling and let stand overnight if convenient. Filter on a weighed Gooch crucible and wash with hot water slightly acidified with HCl, then with alcohol. Dry and weigh as (C₅H₅N₂O₄)Pd, which contains 31.67% Pd.

4. The nitric acid in the palladium solution is expelled by evaporating with HCl. Neutralize the chloride solution almost completely with sodium carbonate and mix the solution with a solution of mercuric cyanide, Hg(CN)₂, and heat gently for some time. Let stand until cool, overnight if convenient. A yellowish-white precipitate of Pd(CN)₂ is formed. Filter, wash with 1% Hg(CN)₂ solution, ignite and reduce in hydrogen to metal, or reduce with formic acid, dry, and weigh as metallic Pd.

5. The filtrate from the platinum precipitation is made neutral or slightly alkaline with Na₂CO₃ solution and an excess of formic acid is added. Boil until all the palladium is precipitated or the solution becomes clear. Filter, wash with hot water, ignite, reduce in hydrogen or with formic acid and weigh as metallic Pd.
DETERMINATION OF PLATINUM AND PALLADIUM

Special Methods

Gold Bar. Dissolve a 100-gram sample in aqua regia, and expel the nitric acid by evaporation and the addition of small amounts of hydrochloric acid. Take up with a few cc. of dilute hydrochloric acid. If there should be present a large amount of reduced gold, add a few drops of nitric acid and heat the solution for a few minutes. Dilute to 800 cc. with water, and let it stand in a cool place until solution clears. Filter off silver chloride and wash it with cold water. Pass sulphur dioxide gas through the filtrate to reduce the gold (palladium, etc., is also reduced). Decant the clear solution on a tight filter paper, and wash several times with hot water by decantation. Then pour over the gold in the beaker, 50 cc. of nitric acid, and boil for a few minutes to dissolve the reduced palladium. Add 50 cc. of hot water and filter on the same filter paper and wash several times with hot water. Add 15 cc. of sulphuric acid to the filtrate, evaporate and heat to heavy fumes. Cool, dilute to 200 cc. with water and boil for a few minutes, and filter off any gold and lead sulphate if present. Now pass hydrogen sulphide gas through the hot solution to precipitate the sulphides of platinum and palladium, etc. Filter and wash with hot water. Place the filter paper with the precipitate in a porcelain crucible, dry, burn and ignite. Now touch the residue with the reducing flame of a Bunsen burner to reduce to metal any oxide of palladium that may have formed. Dissolve the residue with a few cc. of aqua regia, and transfer the solution to a tall 300-cc. beaker, and evaporate carefully to dryness on a steam or sand bath. Then moisten the residue with hydrochloric acid and evaporate to dryness again. Moist the dry residue once more with hydrochloric acid and evaporate to dryness.

Now take up with 16 cc. of hydrochloric acid and 4 cc. of water, cover beaker and boil gently for a moment. Filter on a small filter paper and wash with a small stream of hot water. Discard the residue. Dilute filtrate to 60 cc., cover beaker and heat to near boiling point. Then add 16 grams of ammonium chloride and heat gently to near boiling until all ammonium chloride is in solution. Remove beaker from the hot plate, and let it stand over night in a cool place. Filter rapidly (using suction) on a tight, double filter paper, and wash with ammonium chloride solution (200 grams per liter of water). As the ammonium chloroplatinate is somewhat soluble if exposed to air, the precipitate should be covered with the wash solution all the time during filtration. Then before the ammonium chloride solution is all sucked through, wash once or twice with 95% grain alcohol. Save filtrate for palladium determination. Place the filter paper with the precipitate in a porcelain crucible, so that the precipitate does not come in contact with the sides of the crucible; if it does, a platinum mirror will form, that cannot be removed. Dry gently and smoke off the filter paper (without burning it with a flame), and finally ignite at a bright red heat. Cool and weigh metallic platinum.

Add to the filtrate from the ammonium chloroplatinate precipitate, 16 cc. of nitric acid, stir, cover beaker, placing a glass triangle under the watch glass, and let it stand over night on steam plate. When the solution is supersaturated, as indicated when half of the solution is filled with ammonia salts,

1 Contributed by F. Jaeger, Chemist, Nichols Copper Co.
remove the beaker from the steam plate and cool the solution. Filter off the ammonium chloropalladate just like the platinum salt and wash with ammonium nitrate solution (200 grams per liter of water). Finally wash with 97% grain alcohol. The solubility of ammonium chloropalladate is greater than of the platinum salt when exposed to air, therefore great care must be taken in filtering it. Place the precipitate with the filter paper in a porcelain crucible, dry, smoke off filter paper and finally ignite at a bright red heat. When cool, reduce any oxide that may have formed with the reducing flame of a Bunsen burner. Cool and weigh metallic palladium.

To confirm that all platinum and palladium is precipitated, neutralize the filtrate from the ammonium chloropalladate with a saturated solution of sodium carbonate, then add 30 cc. of formic acid, and boil for about one hour. Any platinum or palladium if still present will be precipitated as black powder.

Note. All evaporations should be made on a steam or sand bath, if not incomplete precipitation of platinum will be obtained.

Refined Silver. Weigh out 1,000 gram sample and dissolve it with dilute nitric acid. Filter off the gold and any undissolved platinum, and then separate the gold from the platinum as described under "Gold Bar," and add the solution to the main filtrate. Dilute the filtrate from the gold residue, so that there will be 10 grams of silver per liter of solution, and then add a slight excess of hydrochloric acid to precipitate all the silver. Stir well and let it settle. Decant the clear solution and wash the precipitate on a Buchner funnel with cold water. Evaporate the filtrate to a small volume. Now mix the silver chloride, with about ten times its weight, with soda ash (which contains a small amount of corn starch) and dry. Place the mass in 30 grams crucibles, and fuse for about 30 minutes. Pour in molds. When cool, hammer off excess of slag, and finally boil with hydrochloric acid to clean the silver buttons. Then dissolve with dilute nitric acid and precipitate silver as silver chloride as already described. Another silver chloride precipitation will be necessary to separate all platinum and palladium from the silver.

Combine all filtrates and evaporate to dryness on steam plate. Take up with a few cc. of hydrochloric acid and water, filter off the silver chloride and wash with cold water. This small amount of silver chloride carries down considerable platinum and palladium. Therefore place the filter paper with the silver chloride in a 3-inch scoriﬁer, dry, add 40 grams of test lead and a pinch of borax and scoriﬁ. Then cupel the lead button. Dissolve the silver buttons with dilute nitric acid and reprecipitate silver with hydrochloric acid. Finally when the pure white color of the silver chloride indicates that it is free from platinum and palladium, evaporate the filtrate to dryness on steam plate. Take up with 16 cc. of hydrochloric acid and 4 cc. of water. Boil for a minute, filter, and precipitate platinum and palladium as described under "Gold Bar."

Copper Anode Slimes. Take a 1,000-gram sample. Weigh out 3 gram portions into 3-inch scoriﬁers and mix each with 40 grams of test lead and a pinch of borax and litharge. Scoriﬁ and cupel. Dissolve silver buttons with dilute nitric acid, and proceed as described under "Refined Silver."
Determination of Platinum and Palladium in Refined Gold

The sample may be in the shape of drillings, but from a bar it is easier to roll the gold into a thin ribbon.

Fifty grams of gold sample is sufficient for gold which has been parted with sulphuric and nitric acids.

Dissolve sample in a 1,500 cc. beaker with 50 cc. of nitric acid (1.42) and 150 cc. of hydrochloric acid (1.19) using no water. Heating is not necessary. After complete solution of the sample, evaporate solution to a syrup of about 40 cc. volume, taking care not to evaporate too far; otherwise, some gold will become reduced and separate out: add 100 cc. of hydrochloric acid and re-evaporate the solution to syrup, repeating this operation four times in order to remove all nitric acid.

After the last evaporation, dilute with hot water, boil, add about 50 cc. hydrochloric acid (1.19) to clear up solution: volume of solution should be about 500 cc.

To the boiling solution gradually add a mixture of 50 grams ammonium oxalate and 50 grams oxalic acid, which should precipitate all the gold, but should there be any doubt add more of the mixture of the salts. Dilute the solution to about 1,000 cc. in volume and allow to settle in a warm place over night.

Filter off the gold, washing by decantation into a 1,500 cc. beaker. For extreme accuracy, this gold may be redissolved, re-evaporated and reprecipitated, this time with sulphur dioxide gas. This is more of a precautionary measure, for as a rule, no platinum or palladium will be found with the gold.

To the solution from the gold add 5 grams of 30 mesh C.P. zinc. This precipitates any gold left in the solution along with the silver, platinum, palladium, tellurium, copper, etc.

Filter as soon as precipitation is complete and wash by decantation keeping as much of the precipitate in the beaker as possible. Ignite filter paper and transfer residue and precipitate to a 250 cc. beaker, dissolve in 10 cc. aqua regia and after complete solution, add 5 cc. sulphuric acid (1.84) evaporate to fume of SO₂ and fume well, cool, dilute to 100 cc. Bring solution to boiling and add 1 drop of hydrochloric acid to precipitate the silver, filter in a 400 cc. beaker, dilute filtrate to 200 cc. volume, add 5 cc. hydrochloric acid (1.19),

1 Contributed by S. Skowronski, Chemist, Raritan Copper Works, Perth Amboy, N. J.
2 For gold which has been electrolytically refined by the Wohlwill process, 100 grams of gold should be taken as a sample, doubling the quantity of acid necessary for the solution.
3 Sulphur dioxide gas is not recommended for the precipitation of gold as gold bullions contain a trace of tellurium, and in the presence of tellurium, palladium is precipitated as a telluride by sulphur dioxide gas. The gold precipitated with oxalic acid is free from palladium telluride and therefore may be reprecipitated with sulphur dioxide gas if a reprecipitation is thought necessary.
4 The platinum and palladium after solution in aqua regia, and addition of sulphuric acid, should be well fumed, in order to reduce any gold remaining in the solution to the metallic condition, it is very essential that all the gold is removed at this stage, otherwise it is liable to contaminate the palladium di-methyl glyoxime.
and precipitate palladium with .5 grams of dimethyl glyoxime dissolved in 50 cc. of boiling water.  

Palladium dimethyl glyoxime, canary yellow in color, which possesses the same physical characteristics as the corresponding nickel salt, at once separates out. Allow to settle in a warm place for about five minutes. Filter in a Gooch crucible, wash with hot water, dry at 110° C. and weigh. Factor .3168.

To the filtrate from the palladium add 2 grams of 30-mesh C.P. zinc, which precipitates the platinum. Filter, ignite, precipitate and dissolve in aqua regia. Remove nitric acid by three evaporations with hydrochloric acid (1.19), taking care not to evaporate solution to dryness. After the last evaporation, take up with not more than 10 cc. of water, and a few drops of hydrochloric acid. If necessary, filter, keeping volume of 10 cc. add 2 grams of ammonium chloride, stir well, add 10 cc. of alcohol, and let stand one hour with an occasional stirring.

Filter off ammonium chlor-platinate in small Gooch crucible and ignite to platinum in the usual manner.

Separation of Platinum and Gold. In place of the procedures given on page 379 it is often preferable to precipitate gold first by means of sulphur dioxide, then reprcipitating with oxalic acid from weakly acid solution to obtain gold free from platinum.

Separation of Platinum and Ruthenium. According to Deville and his co-workers the ammonium chloride separation is unsatisfactory owing to contamination of the ammonium chlor-platinate with ruthenium. The ruthenium may be separated by volatilization with chlorine passed into the alkaline solution of platinum and ruthenium. See page 387b.

1 Palladium is best precipitated with di-methyl glyoxime in a 3–5% acid solution, gold if present will be reduced to the metallic condition and should be removed before hand. Alcohol is not recommended as the solvent for the dimethyl glyoxime, as it slows up the precipitation of the palladium. A hot water solution works quicker, and should be filtered to remove insoluble matter before addition to the palladium solution.

The precipitation should be carried out in a cold solution, since platinum will contaminate the palladium precipitate if the dimethylglyoxime reagent is added to a hot solution.

2 Any solutions containing platinum should never be evaporated to dryness, as platinum is easily reduced in baking to the “platinous” condition which is not precipitated with ammonium chloride.
QUANTITATIVE SEPARATION OF THE ELEMENTS OF THE PLATINUM GROUP

Dissolve the material in aqua regia and filter off the insol. Ignite the residue and fuse in a nickel crucible with Na₂O₃. Cool, place in a beaker containing a little water and acidify with HCl. Combine the solutions, place in a distillation flask, make alkaline with NaOH and distil with a current of chlorine gas, catching the distillate in NaOH.

<table>
<thead>
<tr>
<th>Distillate: Ru, Os. Acidify with HCl and pass in H₂S. Filter off sulphides and ignite in a boat in a combustion tube in a current of oxygen, catching the volatile OsO₄ in a solution of NaOH and alcohol. Determine Os in this solution, and weigh RuO₂ remaining in the boat.</th>
</tr>
</thead>
<tbody>
<tr>
<td>The remaining solution is boiled to expel chlorine and then concentrated HN₄Cl solution is added and sufficient 55% alcohol to double the volume of the solution.</td>
</tr>
<tr>
<td>Precipitate: Pt, Ir, some Rh, traces of Pd. Ignite in an atmosphere of hydrogen, extract residue with dilute aqua regia (1 part acids to 4 parts water).</td>
</tr>
<tr>
<td>Filtrate: Rh, Pd, some Pt, Ir, and any Fe, Ni, Cu that was present in sample. Nearly neutralize with NH₄OH and pass in H₂S gas.</td>
</tr>
<tr>
<td>Residue: Ir, Rh. Fuse with KHSO₄, extract with water and dilute H₂SO₄. Repeat fusion and extraction. Combine filtrates, washing residue.</td>
</tr>
<tr>
<td>Solution: Pt with traces of Pd, Ir, Rh.</td>
</tr>
<tr>
<td>Precipitate: sulphides of Pd, Rh, Au, Cu. Ignite and digest with HCl, filter and repeat ignition and extraction of residue. Combine extracts.</td>
</tr>
<tr>
<td>Filtrate: Ni, Fe, some Au and Rh. Evaporate to dryness with HNO₃ and ignite. Extract Fe and Ni with HCl. Ignite residue (B) and combine with (A) and (C).</td>
</tr>
<tr>
<td>Residue (C): Rh. Combine with (A) and (B).</td>
</tr>
<tr>
<td>Filtrate: Pd, Cu. Add KCl and alcohol. If Pd is present, it will precipitate as K₂PdCl₄.</td>
</tr>
<tr>
<td>Combine residues (A), (B) and (C) containing Au and Rh. Dissolve out Au by extraction with aqua regia. Rh is left as a residue.</td>
</tr>
</tbody>
</table>
RARER ELEMENTS OF THE ALLIED PLATINUM METALS

IRIDIUM

Element, Iridium. Ir. at. wt. 193.1; sp. gr. 22.3; m.p. 23.50° C. Oxides, IrO₂, Ir₂O₇.

DETECTION

Iridium is found associated with platinum. The element is insoluble in all acids, including aqua regia. Chlorine is the best reagent which forms the chlorides of iridium and yields compounds with other chlorides as K₂IrCl₄, which is insoluble. If the element is heated in a stream of chlorine in the presence of potassium chloride there forms a salt, K₂IrCl₆, which is sparingly soluble and is used in the separation of iridium.

The oxide, Ir₂O₃, is formed when K₂IrCl₆ is mixed with sodium carbonate and gently fused at a dull red heat.

\[ 2\text{K}_2\text{IrCl}_4 + 4\text{Na}_2\text{CO}_3 = \text{Ir}_2\text{O}_3 + 8\text{NaCl} + 4\text{KCl} + 4\text{CO}_2 + \text{O} \]

The fusion is dissolved in water containing ammonium chloride; filter the residue and after ignition, to expel the ammonium chloride, is treated with dilute acid in order to remove the small quantity of alkali. A bluish-black powder is thus obtained which begins to decompose when heated above 800 degrees, and at temperatures somewhat above 1000 degrees is completely broken up into oxygen and the metal.²

The dioxide, IrO₂, is a black powder obtained by heating the hydroxide in a current of carbon dioxide. It is insoluble in acids.²

Caustic Alkalies produce in a boiling solution a dark-blue precipitate of Ir(OH)₄ insoluble in all acids except HI.

Potassium chloride forms the double salt of K₂IrCl₆, which is black and is difficulty soluble in water.

Ammonium chloride precipitates black (NH₄)₂IrCl₆, which is difficulty soluble in water.

Hydrogen sulphide precipitates black Ir₃S₈, soluble in (NH₄)₂S.

Metallic zinc precipitates from an acid solution black metallic iridium.

Formic acid and sulphurous acid precipitate black metallic iridium from hot solutions.

Lead acetate gives a gray-brown precipitate.

“Treatise on Chemistry,” Roseoc and Schorlemmer.

Chapter contributed by R. E. Hickman and Edward Wickers.
PLATINUM GROUP

ESTIMATION

Substances in which iridium is determined are: platinum scrap, jewelers' sweeps, contact points, ores. Iridium is weighed as the metal.

Preparation and Solution of the Sample

Platinum scrap and contact points, etc., containing iridium dissolve with difficulty in aqua regia, depending on the amount of iridium present. The alloy is dissolved more quickly if it is rolled or hammered to a very thin sheet or ribbon. The alloy of platinum and iridium with an iridium content up to 10% dissolves in aqua regia slowly; an alloy of iridium content of 15% dissolves in aqua regia very slowly and the aqua regia will likely have to be replenished from time to time. An alloy of 25% iridium is practically insoluble in aqua regia. The filings from sweeps, etc., can be dissolved by aqua regia the same as the scrap. After expelling the HNO₃ the platinum and the iridium are precipitated together with NH₄Cl as (NH₄)₂PtCl₆ and (NH₄)₂IrCl₆. The iridium imparts a pinkish to a scarlet color to the salt.

If the iridium content is too high to be dissolved in aqua regia the metal can be mixed with NaCl, heated to a dull red heat in a porcelain or silica tube, and moist chlorine passed over the mixture. The iridium will be in the form of a chloride which dissolves in water. After filtering the solution and evaporating with HCl, the iridium as well as the platinum is precipitated with NH₄Cl or H₂S. This is a convenient way on a larger scale to dissolve osmiridium in ores. The writer has had good results with this operation.

When the iridium is contaminated with a large amount of impurities, it may be reduced from the solution with zinc, and the impurities dissolved by HNO₃ and dilute aqua regia; the residue is washed and dried as iridium.

Clean osmiridium grains are also brought into solution by a fusion of KNO₃, NaNO₃ or KCIO₃ and NaOH or KOH, leaving the iridium as Ir₂O₃.

SEPARATIONS

Separation of Iridium from Platinum. See Separation of Pt from Ir.

If the platinum and iridium are alloyed with at least ten times their weight of silver or lead and the alloy dissolved in HNO₃, the silver or lead and the platinum dissolves, leaving the iridium insoluble. After washing the residue, treat with a small amount of dilute aqua regia to dissolve any platinum that may be present.

Separation from Osmium. Osmium is removed by distillation. See Os.

For other separations see under Rh and Ru. See all section 3 following.
GRAVIMETRIC METHODS FOR THE DETERMINATION OF IRIDIUM

1. By Reduction with Zinc

The solution of iridium or iridium and platinum is treated with C.P. granulated zinc and 5% free HCl. The iridium and the platinum are precipitated as fine black metal. The black metal is washed free from impurities and the platinum is dissolved in dilute aqua regia as described under the Separations. The insoluble portion is dried, ignited, reduced with hydrogen and weighed as metallic iridium.

2. By Igniting the Salt (NH₄)₂IrCl₄

The percentage of iridium in the salt may be judged fairly well by the color, by comparing with standard iridium-platinum salts. The salt is filtered, washed with alcohol and carefully ignited and weighed as iridium-platinum sponge metal. The percentage of iridium in the sample can be calculated from the weight of the iridium obtained. The two metals are treated as stated under 3 below.

3. By Obtaining it as a Residue

The iridium and the platinum, etc., are alloyed with at least ten times its weight of silver and the alloy dissolved in HNO₃. The residue will be a small amount of platinum, gold, if any present, and iridium. Add a small amount of dilute aqua regia, which will dissolve the gold and the rest of the platinum, leaving the iridium as a black residue. This is filtered, washed and ignited, reduced by hydrogen and weighed as metallic iridium.

One part of the iridium material is alloyed with ten parts of lead. This is packed in a graphite capsule, and the whole embedded in charcoal in an ordinary assay crucible. Heat to a high temperature in a furnace for several hours. When the crucible and contents are cold, remove the lead and clean well. Treat the lead with dilute HNO₃, thus removing the lead and leaving the iridium as the residue. Wash thoroughly and treat the residue with dilute aqua regia, which leaves the residue as pure iridium. If other metals of the platinum group are present, see separations under those metals.

4. Determination of Iridium

Method of Deville and Stas, Modified by Gilchrist

1st Lead Fusion. Fuse the carefully sampled platinum alloy with ten times its weight of granular test lead for a period of one hour at a temperature of about 1000°. A covered crucible, whose outside dimensions are 4 cm. in diameter and 7 cm. in height, machined from Acheson graphite, is suitable for fusions made with 20 to 40 grams of lead. The inside of the crucible should possess a slight taper to facilitate the removal of the cooled ingot. Do not pour the fusion from the crucible, but allow it to solidify, since the iridium has largely settled to the bottom of the crucible. The crucible is best heated with an electric furnace.

2. Disintegration with Nitric Acid. Brush the cooled lead ingot free from carbon with a camel's hair brush and place it in a beaker. Add nitric acid of the concentration one volume of nitric acid (d. 1.42) to 4 volumes of water, using 1 cc. of acid per g. of lead. Place the beaker on the steam bath or on a hot-plate, which maintains the temperature of the solution at about 85°. Disintegration of the lead ingot is usually complete in about two hours and leaves a rather voluminous, grayish-black mass. Dilute the solution to twice its volume and decant the liquid through a double filter, consisting of a 9-cm. paper of fine texture, on which is superimposed a 7-cm. paper of looser texture. Wash the residue quite thoroughly with hot water and pass the washings through the filters. The residue is not transferred to the filters at this point. The lead nitrate solutions and washings are best caught in an Erlenmeyer flask to make easier the detection of the presence of any residue which has passed through the filters. This is done by whirling the liquid in the flask. Return the filters to the beaker without ignition.

3. Solution of the Lead-Platinum Alloy with Aqua Regia. Add in order —15 cc. of water, 5 cc. of hydrochloric acid (d. 1.18) and 0.8 cc. of nitric acid (d. 1.42) for each gram of the platinum-alloy sample taken. Heat the solution in the beaker on the steam-bath or on a hot-plate which maintains the temperature at about 85°. The lead-platinum alloy is usually completely dissolved within one and a half hours. Dilute the solution with twice its volume of water and filter through a double filter similar to the one used for the lead nitrate solution, the iridium, insoluble in aqua regia, is in the form of fine crystals, possessing a bright metallic luster and having a high density. Pass the clear solution through the filter first and then transfer the thoroughly macerated paper. It is very important to examine the beaker to see that no iridium remains. To do this the interior of the beaker is wiped with a piece of filter paper to collect any metal adhering to the sides. Then by whirling a small quantity of water in the beaker any iridium remaining gravitates towards one place whence it can be removed with a piece of paper. Wash the filters and iridium thoroughly, first with hot water, then with hot dilute hydrochloric acid (1 : 100), and lastly with hot water. The chlorplatinitic acid filtrate and washings should be examined for iridium, which may have passed through the filters, in the manner described under the nitric acid treatment. The last washings should be tested for the absence of lead.

4. Ignition and Reduction of the Iridium. Place the washed filters and iridium in a porcelain crucible and dry, before igniting in air. After the destruction of the filter paper, ignite the iridium strongly with the full heat of a Tirrill burner. After all the carbon is burned out, cover the crucible with a Rose lid, preferably of quartz. Introduce into the crucible a stream of hydrogen, burning from the tip of a Rose delivery tube (a quartz tube preferred). After five minutes remove the burner and a few minutes later extinguish the hydrogen flame by momentarily breaking the current of hydrogen. This is best done by having a section of the rubber delivery tube replaced by a glass tube, one end of which can easily be disconnected. Allow the iridium to cool in an atmosphere of hydrogen and then weigh as metallic iridium.

Notes. In commercial analysis no effort is made to correct the weight of iridium for small amounts of ruthenium. Correction, if desired, can be made according to the original directions of Deville and Stas. (“Procès-verbaux, Comité International des Poids et Mesures,” 1877, p. 185.) The correction for iron can be made by the procedure
suggested by W. H. Swanger, U. S. Bureau of Standards. The iridium is fused with zinc, the excess zinc removed with hydrochloric acid, and the zinc-iridium alloy fused with potassium pyrosulphate. The fusion is digested with dilute sulphuric acid, which leaves a residue of iridium free from iron but contaminated with silica. Silica is now removed by the usual manner and pure iridium remains. This purification is necessary if iron is present in the sample since this separates with iridium. Palladium, rhodium and gold have no effect in the determination. Ruthenium separates quantitatively with the iridium. The loss of weight of iridium during the ignition periods is insignificant.

RUTHENIUM

_Element, Ruthenium._ Ru. _at.w._ 101.7; _sp.gr._ 12; _m.p._ 2450° C.? _oxides,_
Ru₂O₃, RuO₂, RuO₄.

DETECTION

This element is found in platinum ores, and as laurite, Ru₂S₅. It is barely soluble in aqua regia and insoluble in acid potassium sulphate. It dissolves when fused with KOH and KNO₃. The solution of the fusion when dissolved in water forms potassium ruthenate, K₂RuO₄, from which HNO₃ precipitates the hydroxide, which is soluble in HCl. The treatment with chlorine and KCl at a high temperature yields a salt of K₂RuCl₄. The salts that are most common are K₂RuCl₃ and K₂RuCl₂.

The oxide, Ru₂O₃, is formed when finely divided ruthenium is heated in the air, forming a blue powder which is insoluble in acids. It can also be obtained by heating the trihydroxide, Ru(OH)₃, in dry carbon dioxide which forms a black, scaly mass.

Ruthenium dioxide, RuO₂, is obtained by roasting the disulphide or sulphate in contact with air. It is likewise formed when the metal is fused in an oxidizing atmosphere, when it burns with a sparkling smoky flame, and evolves an ozone-like smell.

Ruthenium tetroxide, RuO₄, is formed in small quantities when the metal is heated at 1000° in a current of oxygen, although when heated alone it decomposes about 106°. It is prepared by passing chlorine into a solution of potassium nitrosylchlororuthenate, or of potassium ruthenate or sodium ruthenate prepared by fusing the metal with sodium peroxide; the liquid becomes heated and the tetroxide distills over and is deposited in the receiver. The moist oxide quickly decomposes. In the dry state it is fairly stable, but decomposes in sunlight with the formation of lower oxides. It dissolves slowly in water, and the solution when it contains free chlorine or HCl may be kept without alteration for some days if light be excluded, but when pure slowly deposits a black precipitate.

In addition to the above oxides, salts corresponding to the acidic oxides RuO₂ and Ru₂O₇ have been prepared.

_Potassium hydroxide_ precipitates a black hydroxide easily soluble in HCl.
_Hydrogen sulphide_ slowly produces brown Ru₂S₅.
_Ammonium sulphide_ precipitates brownish black sulphide.
_Metallic zinc_ precipitates metallic ruthenium, the solution first turning blue.
_Potassium sulphocyanate_ gives on heating a dark brown solution.
_Silver nitrate_ gives a rose red precipitate.
_Mercurous nitrate_ produces a bright blue precipitate.
_Zinc chloride_ produces a bright yellow precipitate which darkens on standing.

Potassium iodide after a time by heating precipitates the black sesquiiodide.

ESTIMATION

Ruthenium is generally estimated in alloys and ores or residues.

Preparation and Solution of the Sample

When ruthenium is alloyed with platinum or gold, aqua regia dissolves these metals, forming the chlorides of platinum, gold and ruthenium. The ruthenium in ores is in the form of an alloy with platinum or osmiridium. This is fused with KNO₃ and KOH in a silver crucible, the osmium and the ruthenium forming salts as described above, while the iridium remains as an oxide.

Separations

Separation of Ruthenium from Platinum. The two metals are precipitated with KCl and the potassium rutheniochloride is dissolved out with cold water containing a very small amount of KCl and alcohol. The ruthenium is then precipitated from an acid solution by additions of granulated zinc.

A separation may be made by alloying with silver and dissolving the platinum and silver by HNO₃, the ruthenium remaining as the residue.

From a concentrated solution of these metals precipitate the platinum with NH₄Cl. Evaporate the filtrate with potassium nitrate to dryness and boil the residue with alcohol when the residual platinum will remain behind and the ruthenium goes into solution.

Separation of Ruthenium from Iridium. The two metals are fused with KOH and KNO₃ as described above, the ruthenium forming a salt soluble in water and the iridium remaining as an oxide.

To the solution of the two metals, sodium nitrite is added in excess, with sufficient sodium carbonate to keep the liquid neutral or alkaline. The whole is boiled until an orange color appears. The ruthenium and the iridium are converted into soluble double nitrites. Sodium sulphide is then added, small quantities at a time until the precipitated ruthenium sulphide is dissolved in the excess of alkaline sulphide. At first the addition of the sulphide gives the characteristic crimson tint due to ruthenium, but this quickly disappears and gives a bright chocolate-colored precipitate. The solution is boiled for a few minutes, and allowed to become perfectly cold and then dilute HCl cautiously added until the dissolved ruthenium sulphide is precipitated and the solution is faintly acid. The solution is filtered and the precipitate washed with hot water. The filtrate will be free from ruthenium.¹

The fusion with KOH and KNO₃ as described above is dissolved in water in a flask or retort; chlorine is passed through this solution and thence into two or three flasks containing a solution of KOH and alcohol. The two or three flasks which form the condensing apparatus should be kept as cold as possible. The ruthenium is transformed into volatile RuO₃ which condenses in the flasks, while the iridium remains in the retort.

Separation of Ruthenium from Rhodium. The mixed solution of the two metals is treated with potassium nitrite as described above. The orange-yellow solution is evaporated to dryness upon the water bath and treated with absolute alcohol. The rhodium remains undissolved and can be filtered off and washed with alcohol. The rhodium salt can be ignited with NH₄Cl and after washing yields metallic rhodium. See Separation of Rhodium from Ruthenium.

Separation of Ruthenium from Osmium. See Separation of Osmium from Ruthenium.

GRAVIMETRIC METHODS FOR THE DETERMINATION OF RUTHENIUM

Ruthenium is weighed as the residue or metallic ruthenium after it has been separated from the other metals.

The residue containing ruthenium or osmiridium is fused in a silver crucible with five grams KOH and one gram KNO₃ at a low temperature from one-half to one hour. The mass is cooled and extracted with water. The orange-colored solution containing potassium ruthenate is gently distilled in a current of chlorine whereby the volatile ruthenium tetroxide passes over into the receivers. All connections should be ground glass so that no Ru will be reduced in the joints. The solution in the distilling flask must be kept alkaline to prevent iridium chloride from distilling over with the Ru. Add a small piece of KOH after the first distillation and distill as before. Oftentimes it will be necessary to fuse again with KOH and KNO₃ and distill as stated above. Continue to pass chlorine through the alkaline solution until all effervescence ceases. Disconnect the chlorine and draw air through the apparatus, heating the solution nearly to boiling.

1. Receivers containing KOH solution (10 to 15% KOH) and alcohol.
   a. This alkaline solution containing the ruthenium tetroxide distillate is evaporated to a smaller volume and the ruthenium is precipitated by boiling with absolute alcohol. Filter, wash well with hot water, dilute HCl and again with hot water. Ignite, reduce in hydrogen and weigh as metallic Ru.
   b. The alkaline solution from the receivers is made acid with HCl and the Ru is precipitated from the hot solution with hydrogen sulphide gas. Filter, wash, ignite at a high temperature, reduce in hydrogen and weigh as metallic Ru.

2. Receivers containing hydrochloric acid.
   a. This acid solution containing the ruthenium tetroxide distillate is heated to nearly boiling and the ruthenium is precipitated with hydrogen sulphide gas as under 1b.
   b. The acid solution containing the Ru is evaporated to a concentrated solution and transferred to a weighed porcelain crucible. Evaporate to dryness, bake and ignite. Reduce in hydrogen and weigh as metallic Ru.
   c. Ruthenium may be estimated by precipitation with magnesium from solutions of its salts. The precipitate is washed with dilute sulphuric acid to remove excess of magnesium, dried, ignited in a current of hydrogen, cooled in carbon dioxide and weighed as metal.¹

RHODIUM

*Element, Rhodium. Rh. at.wt. 102.91; sp.gr. 12.1; m.p. 1950° C.; oxides, RhO, Rh₂O₃, RhO₂.*

DETECTION

Rhodium is found only in platinum ores. It is a white metal, difficultly fusible, and insoluble in acids. Rhodium, however, dissolves in aqua regia when alloyed with platinum, to a cherry red solution. It is also soluble in molten phosphoric acid and dissolves when fused with acid potassium sulphate with the formation of K₂Rh(SO₄)₂. If the metal is treated with chlorine in the presence of sodium chloride there forms a soluble salt, Na₂RhCl₄.

Rhodium monoxide, RhO, is obtained by heating the hydroxide Rh(OH)₃, by cupellation of an alloy of rhodium and lead, or by igniting the finely-divided metal in a current of air. It is a grey powder with a metallic appearance, and is not attacked by acids, and when heated in hydrogen is reduced with evolution of light.¹

The oxide, Rh₂O₃, is obtained as a grey iridescent spongy mass by heating the nitrate. It is also formed as a crystalline mass when sodium rhodochloride is heated in oxygen. It is perfectly soluble in acids.¹

Rhodium dioxide, RhO₂, is obtained by repeated fusions of the metal with KOH and KNO₂. It is attacked neither by alkalies nor by acids and is reduced by hydrogen only at a high temperature.¹

**Hydrogen sulphide** precipitates rhodium sulphide, when passed into a boiling hot solution containing rhodium.

**Potassium hydroxide** precipitates at first a yellow hydroxide, Ph(OH)₃ + H₂O soluble in an excess of the reagent. If boiled, a dark gelatinous precipitate separates. A solution of Na₂RhCl₄ does not show this reaction immediately, but the precipitate appears in the course of time. An addition of alcohol causes a black precipitate immediately.

**Ammonium hydroxide** produces a precipitate which dissolves in excess NH₄OH on heating. Addition of HCl now produces a yellow precipitate, insoluble in HCl but soluble in NH₄OH.

**Potassium nitrite** precipitates from hot solutions a bright yellow precipitate of double nitrite of potassium and rhodium.

**Zinc, iron and formic acid** precipitate rhodium as a black metal.

**Hydrogen** reduces rhodium salts.

To detect small amounts of rhodium in the presence of other metals, evaporate the solution and displace with a fresh solution of sodium hypochlorite; the yellow precipitate formed is soluble after an addition of acetic acid. After a long agitation the solution changes to an orange-yellow color and after a short time the color passes and finally a grey precipitate settles and the solution turns sky-blue.²

¹ "Treatise on Chemistry," Roscoe and Schorlemmer.
² Prescott and Johnson.
ESTIMATION

Rhodium is estimated mainly in ores, thermo couples and salts.

Preparation and Solution of the Sample

When rhodium is estimated in thermo couples or other alloys of platinum and rhodium the wire or sample is rolled to a thin ribbon and dissolved in aqua regia. Both metals will go into solution, forming the chlorides of rhodium and platinum. The aqua regia will have to be replaced from time to time, as the alloy dissolves slowly.

The rhodium from salts is precipitated with zinc and the black metallic rhodium cleaned with dilute aqua regia, filtered, washed, ignited and reduced with hydrogen.

Some alloys and ores are alloyed with silver and the silver and platinum are dissolved in HNO₃. The residue is cleaned with aqua regia, dried, and weighed as metallic rhodium. If the residue is ignited reduce with hydrogen.

The material or residue containing rhodium is fused with KHSO₄ for some time at a low red heat and the mass leached with hot water acidified with HCl. The rose-red solution contains the rhodium. Several fusions are generally necessary.

Separations

Separation of Rhodium from Platinum. Alloys and ores containing platinum and rhodium dissolve slowly in aqua regia as stated above. After expelling the HNO₃ add NH₄Cl. The precipitate is filtered and washed with dilute ammonium chloride solution, which dissolves the rhodium salt. A very small amount of rhodium will color the filtrate pink to a rose-red color, depending on the amount of rhodium present. A green tinge in the ammonium chloroplatinate indicates the presence of rhodium.

A solution of NaOH is added to the HCl solution of the two metals until yellow rhodium hydroxide begins to separate. After neutralizing, the volume of the solution should be so adjusted that the estimated total content of Pt and Rh does not exceed 1 gram per 100 cc. A mixture of equal volumes of solutions containing 90 grams of crystallized barium chloride and 36 grams of anhydrous sodium carbonate per liter, respectively, is added. Not less than 5 cc. of each solution is taken. After the suspension of barium carbonate is added, the solution is rapidly heated to boiling and boiled for two or three minutes. The residue is filtered off and washed several times with a hot 2% solution of sodium chloride, after which it is returned, with the filter paper, to the original beaker and digested with 25 cc. HCl (1HCl to 4H₂O) until solution is complete. Dilute with water and filter off the paper pulp. Adjust the volume to about 150 cc., heat to incipient boiling for 30 to 45 minutes while a current of hydrogen sulphide is passed in. After the precipitation the rhodium sulphide is filtered off at once, washed with water containing a little ammonium chloride, and ignited in a weighed porcelain crucible. The ignited sulphide is reduced and cooled in hydrogen, and weighed as metallic Rh.¹

Separation of Rhodium from Iridium. See Separation of Rh from Pt.

A separation can be made by adding sodium nitrite in excess to the solution of the two metals, with a sufficient quantity of sodium carbonate to make the

solution neutral or alkaline; this is boiled until the solution assumes a clear orange color. The rhodium and iridium are converted into soluble double nitrates. A solution of sodium sulphide is added in slight excess and the liquid made slightly acid. The rhodium is precipitated as dark-brown rhodium sulphide.

A solution of rhodium and iridium is evaporated with HCl and displaced with a large excess of acid sodium sulphite, NaHSO₃, and allowed to stand sometime when a pale yellow double salt of rhodium and sodium sulphite slowly separates out while the solution becomes nearly colorless. Wash out the precipitate, and heat with hot concentrated H₂SO₄ till the sulphurous acid is driven off. Heat the material in a crucible until rid of all free sulphuric acid. Then the iridium is dissolved out as a sulphate with a deep chrome-green color, while a double salt of sodium sulphate and rhodium oxide remains behind. This is flesh color insoluble in water and acids. Boil with aqua regia, wash, dry, heat and it decomposes into rhodium and sodium sulphate.¹

Rhodium can also be separated from iridium, when the latter is present as an iridic salt such as Ir(SO₄)₂, by precipitating the mixed salts with caustic potash, dissolving the hydroxides in dilute sulphuric acid and adding caesium sulphate. The sparingly soluble rhodium caesium-alum separates in the cold, and can readily be purified by re-crystallization and then by electrolysis.²

The residue of rhodium and iridium is melted or scorified with test lead. The lead button is cleaned and dissolved in dilute HNO₃. After filtering and washing the residue, do not ignite, but wash the contents of the filter into a beaker and fume with H₂SO₄ from one to three hours. When cool, dilute with water and let stand over night. The residue contains the iridium and a small amount of PbSO₄, while the solution contains the rhodium as the sulphate. To make a further separation from impurities present, the sulphate solution is made alkaline with NaOH and boiled. Let stand until cold and filter off the rhodium hydroxide. Digest with HCl until all the hydroxide has dissolved. Filter and wash with hot water. Evaporate the filtrate to dryness, dissolve in hot water and add about 15 cc. of sodium nitrate solution (40% NaNO₂). Heat until all action ceases, then add sodium carbonate to the hot solution until no more precipitate forms. Let cool, filter and wash with hot water. Acidify the filtrate with dilute acetic acid and add potassium chloride solution (20% KCl) until all the Rh is precipitated. Let stand over night at 50 to 60°C. When cold, filter the white precipitate, washing with 20% KCl solution containing a little NaNO₂. The white precipitate of potassium rhodium nitrite is digested with HCl, filtered and washed with hot water. Evaporate the HCl solution to dryness, add ammonium formate and heat until dry. Ignite, reduce in hydrogen and cool in CO₂, wash free from salts with hot water, ignite and reduce in hydrogen as before and weigh as metallic Rh.

Separation of Rhodium, Platinum and Palladium. Having the three in solution precipitate the platinum with NH₄Cl as described under Platinum. After filtering off the (NH₄)₂PtCl₆ precipitate, and after neutralizing the filtrate with Na₂CO₃ add mercuric cyanide to separate the palladium as Pd(CN)₂ as described under palladium. The filtered solution is evaporated to dryness with an excess of HCl. On treating the residue with alcohol, the double

¹ "Hand Book of Chemistry," Dammer.
² "Treatise on Chemistry," Roscoe and Schorlemmer.
chloride of rhodium and sodium is left undissolved as a red powder. By heating this in a tube through which hydrogen is passed the rhodium is reduced to the metallic state and the sodium chloride is washed out with water leaving a grey powder of metallic rhodium.

The residue containing these three metals is scorified with test lead, and the resultant lead button cupelled with silver. The silver bead is dissolved in dilute HNO₃; the solution filtered, washed with hot water, ignited, and the residue treated with dilute aqua regia to dissolve any platinum or palladium that may be present. Filter, wash with hot water, ammonia water, and again with hot water. Ignite and reduce in hydrogen as metallic Rh.

**Separation of Rhodium from Ruthenium.** The solution containing the two metals is treated with sodium nitrate as above and evaporated to dryness. The residue is powdered and treated in a flask with absolute alcohol. After filtering and washing with alcohol the rhodium remains undissolved.

The substance or residue containing the rhodium and ruthenium may be fused with KHSO₄ in a porcelain or platinum crucible causing the rhodium to go into solution as already described. The ruthenium remains insoluble.
GRAVIMETRIC METHODS FOR THE DETERMINATION OF RHODIUM

1. The solution containing rhodium is treated with zinc and the residue is washed well with hot water acidulated with HCl. The residue is then cleaned with dilute aqua regia and the black metallic rhodium is filtered off, dried, and ignited in hydrogen. Cool and weigh as metallic rhodium.

2. The metals may be melted with lead or silver and the buttons dissolved in dilute HNO₃, leaving a residue which is treated with dilute aqua regia to dissolve any platinum that might be present. The residue is treated with salt and chlorine and the melt dissolved in water as described under Iridium. The iridium is precipitated with NH₄Cl and the rhodium with zinc. The rhodium black is cleaned with dilute aqua regia, filtered, washed and ignited. Reduce in hydrogen and weigh as metallic rhodium.

3. The solution containing the rhodium is made alkaline with KOH and then acid with formic acid, boil, and the rhodium will be precipitated as finely divided metallic rhodium. After filtering proceed in the usual manner.

4. After the platinum and the palladium are eliminated, the residue of Ir, Rh and Ru is fused with K₂H₂O₄ in a porcelain crucible and the melt dissolved in water. Filter, wash with hot water, and after acidulating with HCl the Rh is precipitated with C.P. powdered zinc, hydrogen sulphide gas or both. Filter, wash with hot water and ignite. Clean the residue with dilute HNO₃, then with dilute aqua regia, wash with hot water, ignite in hydrogen and weigh as metallic Rh.

5. The residue containing Ir, Rh, Ru and Os is fused with five grams KOH and one gram KNO₃, and the Ru and Os are distilled with chlorine as explained under ruthenium. The solution in the distilling flask is zinced well, filtered, washed and ignited. The residue of impure Ir and Rh is scorified with test lead, the lead button dissolved in dilute HNO₃ and the residue treated with H₂SO₄ as explained under Separation of Rh from Ir. The clear rhodium sulphate solution is treated with C.P. powdered zinc, hydrogen sulphide gas or both, and the precipitate is treated as explained above and weighed as metallic Rh.

6. The solution from the distilling flask is zinced well as explained above. The residue is filtered, washed, ignited and boiled with a few cc. of HNO₃ and boiled with H₂SO₄ for one to three hours as explained above. The rhodium sulphate solution is made alkaline with KOH and boiled with alcohol until all the rhodium is precipitated and the solution is clear. Filter, wash with hot water, dilute HNO₃ and again with hot water. Ignite, reduce in hydrogen and weigh as metallic Rh.

7. Rhodium is conveniently estimated by precipitation with magnesium from solutions of its salts. The precipitate is washed with dilute H₂SO₄ to remove excess of magnesium, dried, ignited in a current of hydrogen, cooled in carbon dioxide and weighed as metal.¹

OSMIUM

Element, Osmium. Os. at.wt. 190.9; sp.gr. 22.4; m.p. 2700° C.? oxides, OsO₄, Os₂O₃, OsO₂, OsO₃.

DETECTION

Osmium occurs with platinum ores as a natural alloy with iridium (Osmiridium) and remains undissolved in the form of hard, white metallic-looking grains when the ores are treated with aqua regia. The chlorides, OsCl₂ and OsCl₄, combine with the alkali chlorides. Through the action of HNO₃, aqua regia or heating in a stream of moist chlorine, osmic tetroxide is formed. OsO₄ is very volatile and the fumes are poisonous. It is detected readily by the odor when heated, as the fumes are highly corrosive and disagreeable like chlorine. Chlorine passed over hot osmium mixed with KCl gives K₂OsCl₄, which dissolves in cold water.

The oxy-hydrogen flame oxidizes the metal but does not melt it. When strongly heated in contact with air, the finely divided osmium burns and is converted into OsO₄, commonly called osmic acid.

Osmium monoxide, OsO, is obtained when the corresponding sulphide mixed with sodium carbonate is ignited in a current of carbon dioxide. It is a greyish-black powder insoluble in acid.¹

The oxide, Os₂O₃, is a black insoluble powder obtained by heating its salts with sodium carbonate in a current of carbon dioxide.¹

Osmium dioxide, OsO₂, is obtained from its salts in a similar way to the foregoing oxides. It is likewise formed when its hydroxide is heated in a current of carbon dioxide.¹

Osmium tetroxide, OsO₄. Very finely-divided metallic osmium oxidizes slowly at the ordinary temperature, and at about 400° takes fire with formation of OsO₄. The denser the metal the higher is the temperature needed for oxidation.¹

Hydrogen sulphide precipitates dark brown osmium sulphide, OsS₂, but only in the presence of some strong mineral acid; from an aqueous solution of osmic acid there forms a dark brownish-black sulphide, OsS₄. These are insoluble in ammonium sulphide.

Potassium hydroxide precipitates reddish-brown osmium hydroxide, Os(OH)₃.

Ammonium hydroxide precipitates the osmium hydroxide.

Zinc and formic acid precipitate black metallic osmium.

Hydrogen reduces osmium compounds to the metal.

Potassium nitrite added to a solution of osmic acid reduces it to osmous acid which unites with an alkali forming a beautiful red salt.

Sodium sulphite yields a deep violet coloration and a dark blue osmium sulphite separates out gradually.

Phosphorus reduces osmium from an aqueous solution.²

Mercury precipitates osmium from an aqueous solution of osmic acid mixed with HCl.

Stannous chloride produces a brown precipitate, soluble in HCl to a brown fluid.

¹ "Treatise on Chemistry," Roscoe and Schorlemmer.

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PLATINUM GROUP

ESTIMATION

Osmium is estimated mainly in osmiridium and platinum residues.

Preparation and Solution of the Sample

After the platinum is extracted the residue or osmiridium is mixed with two or three times its weight of common table salt. The mixture is put in a porcelain or silica tube and heated to a dull red heat; moist chlorine is then passed through the tube and thence through receivers containing KOH and C₂H₅OH to catch the Os and Ru that pass over. The mass is cooled and dissolved with water. After several treatments the entire group of platinum metals will be in solution.

The osmium material may also be fused with KOH and KNO₃ and the melt dissolved in water. The osmium will be in solution as potassium osmate, K₂OsO₄, while the iridium remains as residue.

Cold selenic acid has no appreciable action on osmium; at about 120°, however, the metal is dissolved to a colorless solution which contains selenious acid and OsO₄, but no selenate.

Separations

In most cases osmium is separated from the other metals present by distillation or volatilization. See next page.

1 "Chemical Abstracts," April 10, 1918.

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GRAVIMETRIC METHODS FOR THE DETERMINATION OF OSMIUM

The osmium is very difficult to ascertain on account of the element being very volatile.

1. The potassium osmate, K₂OsO₄, solution is put in a small retort and boiled with HNO₃; the OsO₄ is conducted into receivers containing NaOH solution and C₆H₅OH. After acidifying with a little HCl the osmium can be precipitated with Na₃S₂O₅ as a brown precipitate of OsO₄ which is filtered, washed, dried and weighed as the oxide, or reduced in hydrogen and weighed as the metal. The osmate solution from the receivers above is heated gently and strips of aluminum are plunged in; the osmium will be deposited in metallic form, while the aluminum dissolves in the soda. Care must be taken not to add too much aluminum, as an aluminate might be precipitated which is troublesome. When the solution is discolored, the dense precipitated osmium is washed by decantation with water to remove the sodium aluminate, and then with 5% H₂SO₄ solution to remove the excess aluminum. The osmium is dried in a bell-jar filled with hydrogen, then heated to a dull redness and cooled in a current of hydrogen. The osmium is weighed as the metal. As a check the osmium may be driven off in the form of OsO₄ by heating to redness with plenty of air, or better, in a current of oxygen and weighing again.¹

2. The osmate solution from the condensing receivers or from the fusion of KOH and KNO₃ containing the ruthenium and osmium is placed in a retort and HCl is added. A slow current of air or oxygen is passed through the retort and thence through receivers containing KOH and alcohol similar to the ones mentioned above. These receivers are kept as cold as possible. The osmium is distilled over as OsO₄ while the ruthenium remains in the retort. Combine the solutions in the receivers and proceed to determine the osmium as described above.

3. The potassium or sodium osmate solution from the receivers above or where osmium tetroxide is dissolved in potassium hydroxide solution and alcohol is heated at 40 or 50° to form potassium osmate. A slight excess of dilute sulphuric acid is added and then 10 cc. more of alcohol in order to prevent reoxidation. After ten or twelve hours, a bluish-black deposit settles, while the supernatant liquid is colorless and free from osmium. The precipitate is filtered, washed with aqueous alcohol, and converted into metallic osmium by reduction in a current of hydrogen.

4. The residue containing osmium is fused with five grams KOH and one gram KNO₃ in a silver crucible as explained under ruthenium. Add HNO₃ slowly to the distilling flask which is connected to receivers containing NaOH solution and alcohol (10% NaOH and 10% C₆H₅OH). Draw the distillate over gently with the aid of the vacuum, the same as for the chlorine distillation under ruthenium. Continue the HNO₃ until strongly acid and then boil for a short time. Transfer the alkaline solution containing the OsO₄ distillate to a beaker and pass in hydrogen sulphide gas while the solution is heating until saturation; then add HCl until the solution is distinctly acid and continue to saturate the hot acid solution with hydrogen sulphide gas. Let stand over night, filter through a weighed Gooch crucible, washing well with hot water. Ignite in hydrogen, cool in CO₂ and weigh as metallic Os.

¹ “Select Methods of Chemical Analysis,” Sir Wm. Crookes.
ASSAY METHODS OF PLATINUM ORES, ETC.

Take from 10 to 30 grams of the material and place in a 2½- or 3-in. scoriifier with about 20 to 30 grams of test lead and cover with litharge. Fuse in a muffle for a half hour. When cool clean the lead button thoroughly and dissolve the lead with dilute nitric acid (1:5). When the lead is dissolved, filter, and wash the residue with hot water till free from lead. Dry the filter and transfer the bulk of the residue to a small glass beaker. Burn the filter, and add the ash to the main residue. This is treated with dilute aqua regia to remove any gold, platinum, etc., that may be present. Filter and wash thoroughly with hot water and ignite at a low temperature for a short time only, as osmium will volatilize. Weigh as osmiridium. (See Ir and Os.)

Take another portion of 10 to 30 grams of the material and treat with aqua regia two or three times. This will bring the platinum and the alloys (except osmiridium) into solution. After filtering make up the volume to 500 to 1000 cc., depending on the amount of platinum present. Take two or three portions of 25 to 50 cc. of the solution and evaporate to nearly dryness with additions of HCl to get rid of the HNO₃. Take up with a small amount of water and add ammonium chloride. Digest on the water bath and let cool overnight if convenient. Filter onto an ashless filter and wash with dilute ammonium chloride solution and alcohol. Ignite cautiously and weigh as platinum and iridium sponge. For the determination of iridium see under Iridium.

The filtrate from the platinum precipitation is treated with ferrous sulphate to precipitate the gold. Digest and filter out the gold. Ignite and alloy with silver and part for gold.

In the filtrate from the gold precipitation the palladium and rhodium are treated with zinc and HCl until the solution is colorless. Filter, wash well with hot water and dilute HCl.

Ignite, reduce in hydrogen, cool and weigh as Pd and Rh. Treat with HNO₃. Filter, wash well, ignite and reduce in hydrogen, cool and weigh as metallic rhodium. The difference is palladium, or determine this as described under palladium.

In the revision of the chapters on platinum, palladium and the other metals of the group a considerable number of suggestions by Dr. Edward Wichers of the U. S. Bureau of Standards, have been included by revising the statements of previous editions. The chemistry of the platinum metals is a field of much variance of opinion and the methods for isolation of these elements are far from perfect. We feel, however, that the chapters present the latest and best work on the subject.—Editor.
## Reactions of Salts of Platinum Metals

<table>
<thead>
<tr>
<th></th>
<th>Ruthenium (RuCl₂)</th>
<th>Rhodium (RhCl₃)</th>
<th>Palladium (PdCl₂)</th>
<th>Osmium (OsCl₆)</th>
<th>Iridium (IrCl₄)</th>
<th>Platinum (PtCl₄)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Colour</strong></td>
<td>Dark brown</td>
<td>Red</td>
<td>Brownish yellow</td>
<td>Yellow</td>
<td>Dark brown</td>
<td>Yellow</td>
</tr>
<tr>
<td><strong>Hydrogen sulphide at 30°C</strong></td>
<td>Azure-blue color on prolonged treatment</td>
<td>Brownish black ppté., Rh₃S₄</td>
<td>Brownish black ppté., PdS</td>
<td>Brownish black ppté., OsS₄</td>
<td>Brownish black ppté., Ir₃S₄</td>
<td>Brownish black ppté., PtS₂</td>
</tr>
<tr>
<td><strong>Ammonium sulphide</strong></td>
<td>Dark brown ppté., Ru, difficult soluble in excess</td>
<td>Dark brown ppté., Rh₃S₄, insoluble in excess</td>
<td>Black ppté., PdS, insoluble in excess</td>
<td>Dark ppté., insol. in excess</td>
<td>Brown ppté., Ir₃S₄, soluble in excess</td>
<td>Brown ppté., PtS₂, soluble in excess</td>
</tr>
<tr>
<td><strong>Caustic alkalies</strong></td>
<td>Black ppté. of hydrated oxide soluble in excess</td>
<td>Yellow-brown ppté., Rh(OH)₃, soluble in excess</td>
<td>Yellowish brown basic salts soluble in excess</td>
<td>Brownish red OsO₄·2H₂O</td>
<td>Green solution</td>
<td>Brownish black double chloride ppted.</td>
</tr>
<tr>
<td><strong>Ammonium hydroxide on warming</strong></td>
<td>Greenish coloring</td>
<td>Slow decolorization</td>
<td>Decolorized</td>
<td>Yellowish brown ppté.</td>
<td>Bright color</td>
<td>Slow decolorization</td>
</tr>
<tr>
<td><strong>Saturated NH₄Cl solution</strong></td>
<td>Brown ppté.</td>
<td>No ppté.</td>
<td>No ppté.</td>
<td>Red ppté.</td>
<td>Black ppté.</td>
<td>Yellow ppté. (NH₄)₂PtCl₆</td>
</tr>
<tr>
<td><strong>Saturated KCl solution</strong></td>
<td>Violet cryst. ppté. of K₂RuCl₆</td>
<td>Red cryst. ppté. of K₃RhCl₆</td>
<td>Red ppté. of K₃PdCl₆</td>
<td>Brown cryst. ppté. of K₃IrCl₆</td>
<td>Brownish red ppté. of K₃IrCl₆</td>
<td>Brownish red ppté. of K₃IrCl₆</td>
</tr>
<tr>
<td><strong>KI solution (1:1000)</strong></td>
<td>No change</td>
<td>No change</td>
<td>No change</td>
<td>No change</td>
<td>No change</td>
<td>No change</td>
</tr>
<tr>
<td><strong>Hg(CN)₂ solution</strong></td>
<td>No change</td>
<td>No change</td>
<td>No change</td>
<td>No change</td>
<td>No change</td>
<td>No change</td>
</tr>
<tr>
<td><strong>KCNS, 1 per cent. solution</strong></td>
<td>Dark violet color</td>
<td>Yellow color</td>
<td>Unchanged</td>
<td>Unchanged</td>
<td>Decolorized</td>
<td>Increased yellow color</td>
</tr>
<tr>
<td><strong>Hydrazine in hydrochloric acid solution</strong></td>
<td>Yellow color</td>
<td>Yellow color</td>
<td>Black ppté. of metallic Pd</td>
<td>No change</td>
<td>Yellow color</td>
<td>Black ppté., metallic Pt</td>
</tr>
<tr>
<td><strong>Dimethyl glyoxime</strong></td>
<td>Yellow ppté.</td>
<td>No change</td>
<td>No change</td>
<td>No change</td>
<td>No change</td>
<td>No change</td>
</tr>
<tr>
<td><strong>Metallic zinc</strong></td>
<td>Ppte., Ru</td>
<td>Ppte., Rh</td>
<td>Ppte., Rd</td>
<td>Ppte., Os</td>
<td>Ppte., Ir</td>
<td>Ppte., Pt</td>
</tr>
</tbody>
</table>

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2. With the platinum-metal salts in dilute solution. Based on the results of Mylius and Mazzucchelli, Zeitsch. anorg. Chem., 1914, 89, I.