POTASSIUM, SODIUM AND OTHER ALKALIES

Sodium, Na, at.wt. 23.00; sp.gr. 0.9735; m.p. 97.6°; b.p. 877.5° C.; oxides Na₂O, Na₂O₂.

Potassium, K, at.wt. 39.10; sp.gr. 0.875; m.p. 62.5°; b.p. 757.5° C.; oxides K₂O, K₂O₂.

Lithium, Li, at.wt. 6.94; sp.gr. 0.534; m.p. 186°; b.p. >1400° C.; oxide Li₂O.

Rubidium, Rb, at.wt. 85.44; sp.gr. 1.532; m.p. 38.5°; b.p. 696° C.; oxides Rb₂O, Rb₂O₂, Rb₂O₃, Rb₂O₄.

Caesium, Cs, at.wt. 132.81; sp.gr. 1.87; m.p. 26.37°; b.p. 670° C.; oxides Cs₂O, Cs₂O₂, Cs₂O₃, Cs₂O₄.

DETECTION

Detection of Sodium

Sodium is usually identified by the color which it imparts to the flame or by means of the spectroscope. The solution is prepared as directed under Preparation and Solution of Sample, and is freed from all constituents other than the chlorides of magnesium and the alkalies according to the methods given under Separations. With exceedingly small amounts of sodium, it may be necessary to remove the magnesium also. After acidifying with hydrochloric acid, a drop of the solution is brought into the flame by means of a loop of platinum wire. In the presence of sodium, the flame assumes an intense yellow color, which is usually sufficient to identify the element. The results may be confirmed by examining the flame in the spectroscope, when the characteristic yellow sodium line will be prominent even in the presence of traces of sodium. The spectrum of sodium is shown on Plate II. As a matter of fact, the ever-presence of the sodium line is a hindrance to the success of the method, but by observing the sudden change in the intensity of the line, little trouble will be experienced in detecting exceedingly small amounts of the metal.

Sodium may also be detected by precipitation as sodium pyroantimonate, H₃Na₂Sb₂O₇·H₂O, from a sufficiently concentrated neutral or weakly alkaline solution by means of a solution of acid potassium pyroantimonate. The precipitate comes down in granular or crystalline form, and its formation is hastened by rubbing the sides of the vessel with a glass rod. In making this test, magnesium must also be previously removed from the solution.

In waters and soluble salts, it is usually sufficient to test directly the concentrated solution in the flame or spectroscope.

Chapter contributed by W. B. Hicks.

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Detection of Potassium

For the detection of potassium in insoluble compounds, bring the sample into solution by one of the methods given under Preparation and Solution of Sample. In other cases, prepare a strong solution of the material to be tested. Where only very small amounts of potassium are present, remove all the constituents from the solution except the chlorides of magnesium and the alkalies as directed under Separations. In the presence of considerable amounts of potassium, small quantities of other constituents will not materially interfere with the flame and spectroscopic tests. After acidifying with hydrochloric acid, bring a drop of the solution to be tested into the non-luminous flame by means of a platinum wire and observe the color produced through a Merwin color screen.¹ In the presence of potassium, a distinct reddish-violet coloration will be apparent. This must not be confused with the color caused by large amounts of sodium, which appear bluish-violet through the screen. Comparison with the coloration produced by pure salts is advisable. If necessary, confirm the results by examining the flame in the spectroscope. In the presence of a moderate amount of a volatile potassium compound, a bright red line will be readily seen in the red portion of the spectrum, and a less distinct violet line will be visible far out in the violet rays.

Potassium may be identified by precipitation as cobaltic nitrite. For this purpose place a small quantity of the solution to be examined in a test tube, acidify slightly with acetic acid, add about an equal quantity of the sodium nitrite solution, prepared by dissolving 125 grams of sodium nitrite (NaNO₂) in 250 cubic centimeters of distilled water, and about half as much of cobalt nitrate solution, prepared by dissolving 25 grams of cobalt nitrate (Co(NO₃)₂·6H₂O) in 100 cubic centimeters of distilled water and adding 50 cubic centimeters of concentrated (glacial) acetic acid. Mix and allow the mixture to stand until effervescence ceases and the cherry-red solution is transparent. If an appreciable amount of potash is present a yellow precipitate will have settled to the bottom of the test tube. By comparing the volume of the precipitate with that produced when a known quantity of potassium chloride is used, an idea of the amount of potash present can be obtained. Ammonium salts produce a similar precipitate.

Potassium chloroplatinate, perchlorate, acid tartrate, picrate, silico-fluoride, and phospho-tungstate are all sparingly soluble in water while the corresponding sodium salts are readily soluble. Precipitation of these compounds from solution may be used in the identification of potassium.

Silicate rocks and minerals may be tested for potash by mixing the finely powdered material with an equal quantity of pure calcium carbonate, moistening with hydrochloric acid, and examining a small amount of the wet mixture on a platinum loop in the flame.

¹ The Merwin color screens are manufactured and sold by G. M. Flint, 84 Wendell Street, Cambridge, Mass., at 50 cents apiece, and are far superior to the ordinary cobalt glass.
Detection of Lithium

Bring the sample into solution as directed under Preparation and Solution of Sample, and separate the alkali chlorides from other constituents according to the methods under Separations. Digest the dry chlorides with amyl alcohol or with a mixture of absolute alcohol and ether, filter, and evaporate the filtrate to dryness. Moisten the residue with dilute hydrochloric acid and examine it in the spectroscope. A bright red band and a faint orange line make up the flame spectrum of lithium Plate II. These lie between the sodium line and the red potassium line and are easily recognized.

Lithium salts impart a carmine-red color to the flame, which is obscured by sodium, and by large amounts of potassium. But by the proper use of a color screen, the lithium flame may be recognized in the presence of large amounts of sodium.

Confirmation of the presence of lithium may be had by the formation of the sparingly soluble lithium phosphate or lithium fluoride.

Detection of Rubidium and Caesium

In the usual course of analysis, these rare elements are separated along with sodium, potassium, and lithium from all other bases. In order to detect rubidium and caesium, extract the dry chlorides of the alkali metals with a few drops of hydrochloric acid and 90% alcohol. This will dissolve most of the rare alkalies along with some sodium and potassium. Evaporate the solution to dryness, dissolve in a very small amount of water, and add chloroplatinic acid solution. Rubidium, caesium, and potassium chloroplatinates will be precipitated. Filter and wash the residue repeatedly with hot water to remove the potassium salt, which is much more soluble than rubidium and caesium chloroplatinates. During this treatment, examine the residue from time to time in the spectroscope. As the rubidium and caesium salts are concentrated through washing, their spectra will gradually become visible.

The flame spectrum of rubidium consists of two red lines at the extreme left end of the spectrum, 3 orange lines rather close together just to the left of the sodium line, and a narrow and a broad line between the violet and indigo portion of the spectrum.

Caesium has one narrow orange line, one broad yellow line just left of the sodium line, one green line, and two broad blue lines close together.

The spectra of rubidium and caesium are shown on Plate II.
ESTIMATION

The estimation of sodium and potassium is required in the analysis of rocks, clays, soils, ashes of plants, waters, brines, saline deposits, salts of the alkalies, many technical products, and in other cases. The determination of potassium is of special importance in the analysis of fertilizers. The estimation of lithium is desired in the analysis of lithium minerals, frequently in mineral waters, occasionally in rocks, and in certain other special cases. The estimation of rubidium and caesium is seldom required.

Preparation and Solution of Sample

Procedure for Rocks and Other Insoluble Mineral Products. For silicate rocks and other silicious material, bring the alkalies into solution, according to the J. Lawrence Smith or the hydrofluoric acid method, as directed on page 416. For products which are dissolved by hydrochloric acid, effect the solution by acid digestion, expel the excess of acid by evaporation, and remove other constituents as directed under Separations.

Procedure for Soils. 1 Digest 10 grams of moisture-free soil with 100 cc. of hydrochloric acid of a constant boiling-point (sp.gr. 1.115) in a 300-cc. Erlenmeyer flask fitted with a ground-glass or rubber stopper and a reflux condenser. Digest continuously for ten hours on the steam bath, shaking the flask every hour. After settling, decant the solution into a porcelain dish. Wash the insoluble residue onto a filter with hot water, and continue the washing until free from chlorides, adding the washings to the original solution for evaporation. Oxidize the organic matter present in the solution with a few drops of nitric acid and evaporate to dryness on a water bath. Moisten with hydrochloric acid and dissolve in hot water and evaporate a second time to complete dryness and until the excess of hydrochloric acid is completely removed. Moisten the cooled residue with strong hydrochloric acid and dissolve in hot water. Filter into a 250-cc. graduated flask, wash free from chlorides, and dilute to the mark. Use an aliquot of 100 cc. for the determination of the alkalies.

Procedure for Fertilizers. 2 Potash salts. Boil 10 grams of the sample with 300 cc. of water for thirty minutes, wash into a 500-cc. graduated flask, cool, dilute to the mark, mix and pass through a dry filter. Determine the potassium in a 25-cc. aliquot representing 0.5 gram of the original substance, according to either the modified chloroplatinate or the Lindo-Gladding method.

Mixed fertilizers. Boil 10 grams of the sample with 300 cc. of water for thirty minutes, and wash into a 500-cc. graduated flask. Add to the hot solution a slight excess of ammonia and sufficient ammonium oxalate to precipitate all the lime, cool, dilute to the mark, mix, and pass through a dry filter. Evaporate

POTASSIUM, SODIUM AND OTHER ALKALIES

50 cc. of the filtrate to dryness and ignite gently to remove ammonium salts. Dissolve in water, filter, and determine the potassium according to the modified chloroplatinate \(^1\) or the Lindo-Gladding method.

**Organic compounds.** When it is desired to determine the total potash in organic substances such as cottonseed meal, tobacco stems, etc., saturate 10 grams with strong sulphuric acid, and ignite in a muffle at low red heat to destroy organic matter. Add a little strong hydrochloric acid, warm slightly to loosen the mass from the dish, dissolve in water, filter, and determine the potassium according to the modified chloroplatinate or the Lindo-Gladding method.

If for any reason it is desired to use either the chloroplatinate or the perchlorate method in the determination of potassium, interfering substances, including sulphates, must first be removed from the solution.

**Procedure for Ashes of Plants.** Boil 20 grams of the sample with 300 cc. of water for thirty minutes, filter into a 500-cc. flask, and wash the residue thoroughly with hot water. Cool, dilute to the mark and mix. Take aliquots for the determination of the alkalies. The solution may also be prepared by digestion with hydrochloric acid.\(^2\) This treatment is preferable when all the constituents of the ash are to be determined.

**Procedure for Saline Residues, Soluble Salts, Brines, etc.** In the case of water-soluble products, the convenience of the analyst usually determines the manner of preparing the solution. Usually it is preferable to weigh out a convenient portion, to make up the solution to definite volume, and to take an aliquot for each determination. As a general rule, a sample should be taken sufficient to give about a half gram of solids. Strong brines should be weighed and not measured.

**SEPARATIONS**

Separation of the Alkali Metals from other Constituents

Separation from the Hydrogen Sulphide and Ammonium Sulphide Groups of Metals

The alkali metals are usually weighed as chlorides or sulphates, and in general before undertaking their determination, all other bases and acids must first be separated from them. The hydrogen sulphide and the ammonium sulphide groups of metals are seldom to be found in solutions in which the determination of the alkalies is desired. If these are present, however, they may be readily precipitated by means of hydrogen sulphide and ammonium sulphide as detailed on pages 168 and 292.

Separation from Silica

Acidify the solution with hydrochloric acid and evaporate it in a platinum or porcelain dish on the water bath until the odor of hydrochloric acid in the dry residue can no longer be detected. Break up the dry mass with a platinum or glass rod, cool, moisten with a minimum amount of concentrated hydrochloric

\(^1\) If this method is used, it will not be necessary to remove the calcium by addition of ammonia and ammonium oxalate.

Acid, dissolve in a small quantity of water, filter and wash the residue free from chlorides. In the presence of much silica, repeat the operation.

Separation from Iron, Aluminum, Chromium, Titanium, Uranium, Phosphoric Acid, etc.

If phosphoric acid is present in amounts insufficient to combine with all the iron, alumina, etc., or is absent altogether, heat the solution to boiling, add a few drops of nitric acid to oxidize the iron, add gradually an excess of ammonia, boil for a minute or so, allow the precipitate to settle, and filter. Wash the precipitate free from chlorides with hot water.

If phosphoric acid is present in the solution in excess of that required to combine with the iron, alumina, etc., heat the solution to boiling, oxidize with nitric acid, add a slight excess of ferric chloride solution, and precipitate with ammonia as described above.

When the precipitate is considerable, it should be dissolved in hydrochloric acid, and the precipitation repeated.

If chromates are present, these must first be reduced to the chronic salt. For this purpose, add 10 to 15 cc. of hydrochloric acid and a small amount of alcohol to the solution and heat on the water bath or hot plate for a few minutes. Heat to boiling and precipitate with ammonia as directed above. The reduction may also be done by boiling with sulphurous acid.

Separation from Sulphates

Precipitate the sulphate radical as $\text{BaSO}_4$ by the addition of a slight excess of barium chloride to the hot solution as directed on page 497 for the determination of $\text{SO}_4^2-$. Remove the excess of barium chloride by addition of ammonia and ammonium carbonate.

The two operations may be combined as follows: Add a slight excess of barium chloride to the hot solution and boil for a few minutes. Then, without filtering off the $\text{BaSO}_4$, add an excess of ammonia and ammonium carbonate, allow the precipitate to settle, filter, and wash free from chlorides.¹

Separation from Barium, Calcium and Strontium

To the not too concentrated solution, add a slight excess of ammonia and ammonium carbonate, heat to boiling, allow the precipitate to settle, filter and wash the residue a few times with hot water. Dissolve the precipitate, which is likely to contain small amounts of the alkalies, in a little dilute hydrochloric acid, and repeat the precipitation with ammonia and ammonium carbonate. Filter and wash the residue. Evaporate the combined filtrates to dryness in a platinum or porcelain dish and ignite cautiously at a very faint red heat to remove ammonium salts. Dissolve the residue in a little water, add a few drops of ammonia, ammonium carbonate, and ammonium oxalate, and allow to stand for several hours in order to precipitate the last traces of the alkaline earths. Filter and wash the residue free from chlorides.

¹ This procedure does not give faultless results as some of the potassium is carried down with the precipitate and lost.
POTASSIUM, SODIUM AND OTHER ALKALIES

Separation from Iron, Aluminum, Chromium, Barium, Calcium, Strontium, Phosphates, Sulphates, etc., in One Operation

To the hot solution add a slight excess of barium chloride and boil for a few minutes. Then, without filtering off the BaSO₄, add an excess of ammonia and ammonium carbonate, heat to boiling, and allow the precipitate to settle. Filter and wash free from chlorides with hot water. After evaporating the filtrate to dryness, removing the ammonium salts by ignition, and dissolving the residue in a little water, precipitate the last traces of barium and calcium by addition of a few drops of ammonia, ammonium carbonate, and ammonium oxalate. By this procedure a small portion of the alkalies is retained by the precipitate and lost.

Separation from Boric Acid

Acidify the solution strongly with hydrochloric acid and evaporate to dryness. Stir up the residue with 15 to 20 cc. of pure methyl alcohol and cautiously evaporate on a water bath at not too high a temperature. Moisten the residue with a drop or two of concentrated hydrochloric acid, add 15 cc. of methyl alcohol, and again take to dryness. Repeat the evaporation with methyl alcohol a third time. This should be ample for the complete removal of half a gram of B₂O₃.

Separation from Magnesium

Mercuric Oxide Method. After removing other bases and acids, evaporate the solution of the chlorides to dryness, expel ammonium chloride by gentle ignition, and dissolve the residue—except for the small amount of magnesium oxide present—by warming with a little water. Add an excess of mercuric oxide in the form of a thin paste prepared by shaking up freshly precipitated mercuric oxide in water. Evaporate the mixture to complete dryness on a water bath with frequent stirring, dry thoroughly and ignite gently at first and then more strongly until all the mercuric chloride present has been volatilized. Be careful not to inhale the fumes. The whole of the unchanged mercuric oxide need not be expelled by ignition. Digest the residue, composed of the excess of mercuric oxide, the precipitated magnesium oxide, and the alkali chlorides, with small amount of hot water, filter rapidly, and wash with successive portions of hot water, first by decantation and then on the filter, but do not prolong the operation unnecessarily. If desired, determine the magnesium in the residue by spilling the mercuric oxide by ignition and weighing the magnesium oxide. Acidify the filtrate, which contains the alkalies, with hydrochloric acid, evaporate to dryness, gently ignite, cool and weigh. If the residue contains a small amount of magnesium, as it usually does, determine the magnesium in an aliquot and apply the necessary correction. The mercuric oxide should be tested for alkalies by volatilizing a portion and testing the residue.

The Barium Hydroxide Method. Evaporate the solution, which may contain chlorides, sulphates or nitrates, to dryness and gently ignite to remove uranium salts. Warm the residue with a small amount of water and treat the hot neutral solution so obtained with baryta water until no more precipitate formed and barium hydroxide remains in slight excess. Boil, filter and wash

the precipitate with hot water. If desired, determine the magnesium in the residue. Treat the filtrate, which contains the alkalies, barium and a trace of magnesium, with an excess of ammonia and ammonium carbonate to remove the barium. Acidify the filtrate with hydrochloric acid and evaporate to dryness, ignite and weigh. This residue will contain a small amount of magnesium which may be determined in an aliquot and a correction applied.

Remark. The barium hydroxide method is applicable in the presence of lithium.

The Ammonium Phosphate Method. To the hot solution, add an excess of ammonia and ammonium chloride, and precipitate the magnesium by adding a slight excess of ammonium phosphate. Allow the mixture to stand an hour or so, filter and wash the residue with 2% ammonia solution. Expel most of the free ammonia from the filtrate by evaporation, acidify very slightly with hydrochloric acid, and add an excess of ferric chloride solution, which should color the solution slightly yellow. Neutralize the solution with ammonium carbonate, heat to boiling, and filter off the basic ferric phosphate, washing the residue with hot water. Evaporate the filtrate to dryness, ignite to expel ammonia salts, and determine the alkalies in the residue. Magnesium may also be separated by precipitation as magnesium ammonium arsenate or magnesium ammonium carbonate.

Separation of the Alkali Metals from One Another

Separation of Sodium from Potassium

After weighing the sodium and potassium together as chlorides, dissolve the residue in water and precipitate the potassium as chloroplatinate or perchlorate according to one of the methods detailed under Determination of Potassium.

Separation of Lithium from Sodium and Potassium

Extract the dry chlorides with amyl alcohol as prescribed under the Goedt method, or with alcohol saturated with hydrochloric acid gas as detailed under the Rammelsberg method.

Separation of Lithium and Sodium from Potassium, Rubidium, and Caesium

Precipitate the potassium, rubidium, and caesium as chloroplatinites as described under the chloroplatinate method for the estimation of potassium. Evaporate the filtrate to dryness and ignite gently with a little oxalic acid to reduce the platinum, or else dissolve the residue in water and pass a current of hydrogen through the hot solution to reduce the platinum. In any case, filter off the reduced platinum and determine lithium and sodium in the filtrate.

1 Fresenius, op. cit.
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METHODS FOR DETERMINATION OF SODIUM

Determination as Sodium Chloride

Sodium is commonly weighed as NaCl when it is already present as such or after conversion of other forms into the chloride. In the case of salts of volatile acids, such as nitrates for instance, the transformation is made by evaporating the solution to dryness with hydrochloric acid repeatedly or until only the chloride remains. When the sodium is present as a salt of a non-volatile acid, the latter is removed and the transformation effected according to the methods under Separations.

Usually the solution in which sodium chloride is to be determined will contain ammonium salts from some previous operation. In such cases, proceed as follows: Evaporate the sodium chloride solution, which must contain no other non-volatile substance, in a platinum dish to complete dryness on the water bath. Cover the dish with a watch-glass, and cautiously dry the residue in an air bath at 110 to 130° C. Make sure that no loss of sodium chloride is sustained by decrepitation during drying and subsequent ignition. Heat the dish and contents over a free flame held in the hand and moved back and forth under the dish in order to remove ammonium salts. But to avoid loss of sodium chloride by volatilization, take care not to heat the dish to more than a faint redness in any one spot and not to raise the temperature of the salt above incipient fusion. ‘Cool the residue, dissolve it in a little water, and filter from the carbonaceous matter into a weighed platinum dish. Acidify the filtrate with hydrochloric acid and evaporate it to dryness on the water bath. Dry the residue at 100 to 130° C; in an air bath, ignite cautiously over a free flame, taking the precautions mentioned above to prevent loss of sodium chloride, cool in a desiccator, and weigh.

Determination as Sodium Sulphate

Sodium is often determined by weighing as Na₂SO₄ when it is present as such or after conversion of other forms into the sulphate. In the case of salts of volatile acids, the change into the sulphate is made by simply evaporating the solution with a slight excess of sulphuric acid. With salts of non-volatile acids, the transformation is effected according to the methods under Separations. When the sodium is present as an organic salt, the substance is moistened with concentrated sulphuric acid and carefully heated over a free flame until fumes cease to come off. The residue is dissolved in water and filtered from the carbonaceous matter.

As a rule the solution in which sodium sulphate is to be determined will contain an excess of sulphuric acid. In such cases, evaporate the solution to dryness in a weighed platinum dish, and cautiously ignite the dry residue until fumes cease to come off. Cool, add a lump of ammonium carbonate to the contents of the dish, and ignite a second time at dull red heat until no more fumes are given off. Cool in a desiccator and weigh as Na₂SO₄. Repeat the ignition with the addition of ammonium carbonate until a constant weight is obtained.

In case an excess of sulphuric acid is not present, evaporate the solution to dryness in a weighed platinum dish, ignite, cool in a desiccator and weigh as Na₂SO₄.
Determination by Difference

Ordinarily sodium and potassium are weighed together as chlorides or sulphates as detailed above for sodium. Potassium is then determined by one of the methods given below, and the value for sodium obtained by difference.

METHODS FOR DETERMINATION OF POTASSIUM

Determination as Potassium Chloride or Potassium Sulphate

Potassium may be weighed as chloride or sulphate. The procedure is the same as that described for sodium. Observe, however, that the potassium salts are a little more volatile than the corresponding sodium salts, so that greater care must be taken not to lose potassium by volatilization.

The Chloroplatinate Method

Application. This method is applicable in the presence of the chlorides of sodium, lithium, magnesium, calcium, and strontium.

Principle. Potassium chloroplatinate is practically insoluble in strong alcohol while the other chloroplatinates are readily soluble.

Procedure. Treat the aqueous solution of the alkali chlorides contained in a small porcelain dish with slightly more than enough chloroplatinic acid to convert all the chlorides present into the corresponding chloroplatinates. The chloroplatinic acid solution should contain the equivalent of 1 gram of platinum in each 10 cc. Evaporate the solution on the steam bath to a syrupy consistency, i.e., until solidification occurs on cooling. Flood the cooled residue with a small quantity of alcohol of at least 80% strength, grind thoroughly with a pestle made by enlarging the end of a glass rod, and allow to stand one-half hour. Pour the liquid through a previously weighed Gooch crucible containing an asbestos mat, and before adding more alcohol, rub up the residue again with the glass pestle. Now continue the washing by decantation with small portions of alcohol until the wash liquid becomes colorless. Transfer the precipitate to the crucible and wash two or three times with alcohol. Dry at 130°C, cool in a desiccator, and weigh. Repeat the drying until a constant weight is obtained. Multiply the weight of $K_2PtCl_6$ by 0.161 to obtain the weight of K; by 0.194 to obtain $K_2O$; and by 0.307 to obtain KCl.

Remarks. This method is considered to be the most accurate known for the estimation of potassium. Care should be taken not to conduct the evaporation at too high a temperature nor let it go too far, as this may cause the formation of anhydrous sodium chloroplatinate, which dissolves slowly in alcohol. Too large a volume of alcohol for washing should be avoided, as $K_2PtCl_6$ is slightly soluble in alcohol, especially that of 80%. For this reason 95% alcohol is preferable for the washing.

Instead of using a Gooch crucible, the precipitate may be filtered on paper, dried, washed through the filter with hot water into a weighed platinum dish, evaporated to dryness, and heated at 130°C to constant weight.

POTASSIUM, SODIUM AND OTHER ALKALIES

The Modified Chloroplatinate Method

Application. The method is applicable in the presence of chlorides, sulphates, phosphates, nitrates, carbonates, borates and silicates, salts of sodium, barium, calcium, strontium, magnesium, iron and alumina, and is especially suited for the estimation of potassium in salines, potassium salts, and fertilizers in which only the potassium is desired.

Principle. On evaporating a solution containing potassium with a slight excess of chloroplatinic acid, the potassium is completely transformed into potassium chloroplatinate which is insoluble in strong alcohol, while any of the other chloroplatinates which may be formed are either dissolved or decomposed by alcohol, so that the excess of chloroplatinic acid may be readily removed. After dissolving the $\text{K}_2\text{PtCl}_4$ along with any other soluble salts contained in the residue in hot water, the platinum is precipitated from the solution by magnesium, and from the weight of platinum so obtained, the amount of potassium present is calculated.

Procedure. To the solution slightly acidified with hydrochloric acid, add chloroplatinic acid solution slightly in excess of that necessary for the complete precipitation of the potassium present and evaporate the solution on the steam bath to a syrupy consistency, i.e., until solidification occurs on cooling. Flood the cooled residue with a small quantity of alcohol of at least 80% strength, grind thoroughly with a pestle made by enlarging the end of a glass rod, and allow to stand one-half hour. The alcoholic solution should be colored if an excess of chloroplatinic acid has been used. Pour the liquid through a small filter, using suction if desired, and before adding more alcohol, rub up the residue again with the pestle. Now continue the washing by decantation with small portions of alcohol until the wash liquid becomes colorless. Three or four washings usually suffice. Transfer the precipitate to the filter and wash two or three times with alcohol.

Dissolve the precipitate of $\text{K}_2\text{PtCl}_4$ along with any other soluble salts present in hot water, washing it through the filter into a beaker of convenient size. To the hot solution add about 4 cc. of concentrated HCl and approximately 0.5 gram magnesium ribbon pressed into the form of a ball for every 0.2 gram potassium present, stirring the solution and holding the magnesium at the bottom of the beaker by means of a glass rod. A lump of stick magnesium weighing about 0.4 gram is preferable to the ribbon. When the action has practically ceased, add a few cc. of hydrochloric acid and allow the floeulent platinum to settle, preferably by allowing the beaker to set for an hour on the hot plate. The supernatant liquid should be perfectly clear and limpid like water if reduction is complete. To make sure, add more magnesium, in which case the solution will darken if reduction is incomplete. To the completely reduced solution, add concentrated hydrochloric acid, and boil to dissolve any basic salts, filter on paper or a Gooch, wash thoroughly with hot water, ignite in platinum or porcelain and weigh. $\text{Pt} \times 4006 = K$ or $\times 4826 = \text{K}_2\text{O}$.

Remarks. If the solution contains very large amounts of iron, alumina, or silica, it is preferable to remove the greater part of these before proceeding to the determination of potassium. Care should be taken to insure the complete removal of the soluble chloroplatinates from the residue without the use of air.

1 Hicks, J. Ind. Eng. Chem., 5, 650, 1913.
excessive amount of alcohol, and also that the subsequent reduction of the potassium chloroplatinate with magnesium be complete.

**Lindo-Gladding Method**

**Application.** This method is applicable in the presence of chlorides, sulphates, and phosphates of the alkalies and magnesium.

**Principle.** The potassium is precipitated as $K_2PtCl_6$, and the soluble chloroplatinates removed by washing with 80% alcohol. The impurities in the precipitate are then washed out by a strong solution of ammonium chloride saturated with $K_2PtCl_6$, and the wash solution is removed by again washing with alcohol. The purified $K_2PtCl_6$ is finally dried and weighed.

**Procedure.** To the solution, slightly acidified with hydrochloric acid, add an excess of chloroplatinic acid solution, and evaporate on the water bath to a thick paste. Treat the residue with 80% alcohol, avoiding the absorption of ammonia. Wash the precipitate thoroughly with 80% alcohol both by decantation and on the filter, continuing the washing after the filtrate is colorless. Wash finally with 10 cc. of ammonium chloride solution prepared as follows: Dissolve 100 grams of pure ammonium chloride in 500 cc. of water, add from 5 to 10 grams of potassium chloroplatinate, and shake at intervals of five to six hours. Allow the mixture to settle over night and filter. Repeat the washing with successive portions of the ammonium chloride solution five or six times in order to remove the impurities from the precipitate. Wash again thoroughly with 80% alcohol, dry for thirty minutes at 100° C. and weigh as $K_2PtCl_6$. The precipitate should be perfectly soluble in water. Multiply the weight of $K_2PtCl_6$ by 0.161 to obtain the weight of $K$; by 0.194 to obtain $K_2O$; and by 0.307 to obtain $KCl$.

**The Perchlorate Method**

**Application.** This method is applicable in the presence of chlorides and nitrates of barium, calcium, magnesium and the alkalies metals, and also in the presence of phosphates. Sulphates should not be present.

**Principle.** The separation depends on the insolubility of potassium perchlorate, and the solubility of sodium and other perchlorates in 97% alcohol.

**Procedure.** To the neutral or slightly acidified solution, add twice as much perchloric acid as is required to convert all the bases present into perchlorates and evaporate on the water bath with stirring to a syrupy consistency. Add a little hot water and continue the evaporation with constant stirring until all the hydrochloric acid is expelled and heavy fumes of perchloric acid are given off. Avoid excessive loss of perchloric acid. Stir up the cooled mass thoroughly with 20 cc. of 97% alcohol to which 0.2% perchloric acid has been added, but avoid breaking up the potassium perchlorate crystals too finely or else they may pass through the filter. Allow the mixture to settle, and decant the alcohol off through a Gooch crucible. Repeat the washing once by decantation and then warm to remove the alcohol. Dissolve the residue in hot water, add about a half gram of perchloric acid and evaporate again until fumes of perchloric acid are given off. Wash the residue once by decantation and then several times on the filter. Remove the adhering wash-liquid by washing with pure 97% alcohol, dry at 130° C., and weigh. Multiply the weight of $KClO_4$ by 0.2825 to obtain the weight of $K$; by 0.3402 to obtain $K_2O$.

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Other Methods

Among the more important of other methods which have been proposed and used for the determination of potassium, may be mentioned the cobaltinitrite method, which has been studied by the Association of Official Agricultural Chemists and considered to be unreliable; \(^1\) the bitartrate method; \(^2\) the colorimetric method; \(^3\) and the spectroscopic method. \(^4\)

Determination of Sodium and Potassium by Indirect Method

After removing all other constituents, weigh the sodium and potassium as chlorides. Dissolve the weighed residue in water and determine the chlorine gravimetrically by precipitation as AgCl or volumetrically by titration with standard silver nitrate (potassium chromate indicator). From the weight of the combined salts and the weight of the chlorine, calculate the amount of sodium and potassium as follows:

Let: \[ x = \text{weight of NaCl} + \text{KCl} \]

\[ y = \text{weight of Cl.} \]

Then: \[ \text{Na} = 3.004y - 1.428x; \]

\[ \text{K} = 2.428x - 4.004y. \]

The method is satisfactory when sodium and potassium are present in about equal quantities.

Determination of Magnesium, Sodium and Potassium in the Presence of One Another

In the usual course of analysis, magnesium, sodium and potassium are separated as chlorides from all other constituents. Instead of going through the tedious process of separating the magnesia from the alkali, the magnesium, sodium, and potassium may be accurately determined in the presence of each other as follows:

Treat the solution containing these constituents with slightly more than enough sulphuric acid to convert all three bases into sulphates, evaporate it to dryness on the water bath, and ignite gently at first and then at dull red heat to break up bisulphates and expel the excess of sulphuric acid. To hasten the decomposition of the bisulphates, cool, add a lump of ammonium carbonate, and heat a second time. Cool in a desiccator and weigh. Repeat the heating with the addition of ammonium carbonate until a constant weight is obtained. Dissolve the residue in water and dilute to definite volume. Determine the potassium in one portion according to one of the methods described above, and the magnesium in a second portion as described on page 293. Deduct the weight of magnesium and potassium sulphates from the weight of the combined sulphates to obtain the amount of sodium sulphate.

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\(^3\) Bayer, Chem. Zeit., 17, 686, 1893.


\(^5\) Gooch and Hart, Am. J. Sci. (3), 34, 448, 1891.
METHODS FOR DETERMINATION OF LITHIUM

Determination as Lithium Chloride

Lithium may be weighed as LiCl. The procedure is practically the same as that described for sodium, but since lithium chloride is very hygroscopic, this salt must be weighed out of contact with the air. For this purpose the lithium chloride is ignited in a platinum crucible, cooled in desiccator, and the crucible and contents weighed in a glass-stoppered weighing bottle.

Determination as Lithium Sulphate

Lithium is weighed preferably as LiSO₄. The procedure is the same as that described for sodium, but since lithium bisulphate is easily broken up on heating, it is not necessary to ignite with ammonium carbonate.

The Gooch Method

Principle. Lithium chloride is readily soluble in amyl alcohol, while sodium and potassium chlorides are not.

Procedure. Concentrate the solution as far as possible by evaporation, transfer it to a 50-cc. Erlenmeyer flask, add a small amount of amyl alcohol and heat cautiously on an asbestos plate until the water has been expelled and the boiling-point of the solution rises to about that of pure amyl alcohol (132° C.). To prevent bumping during this treatment, pass a current of dry air through the solution. When all the water has been removed, the sodium and potassium chlorides, together with some LiOH will separate from the solution. Decant the solution through a filter and wash the residue several times with hot amyl alcohol. Moisten the residue with dilute hydrochloric acid, dissolve in a little water and repeat the extraction with amyl alcohol. If much lithium chloride is present, it will be necessary to repeat the extraction with amyl alcohol three or four times. Evaporate the combined filtrates and washings to dryness and dissolve in a little dilute sulphuric acid. Filter from the carbonaceous matter into a weighed platinum dish, evaporate to dryness, and remove the excess of sulphuric acid by gentle heating. Ignite the residue at dull redness, cool in a desiccator, and weigh as Li₂SO₄.

Remarks. For very accurate work, account must be taken of the fact that the lithium sulphate obtained according to the procedure just described always contains small amounts of potassium and sodium sulphates, if these metals were originally present. To correct for this, deduct 0.00041 gram for every 10 cc. of the filtrate exclusive of the washings in case only sodium chloride was present, or 0.00051 if only potassium chloride was present, and 0.00092 if both sodium and potassium chlorides were present.

POTASSIUM, SODIUM AND OTHER ALKALIES 415

The Rammelsberg Method

Principle. Anhydrous lithium chloride is soluble in equal parts of alcohol and ether which have been saturated with hydrochloric acid gas, while the chlorides of sodium and potassium are practically insoluble in this mixture.

Procedure. Evaporate the solution of the chlorides to dryness in a small flask provided with a two-hole stopper. During the evaporation, pass a current of dry air through the flask. Place the flask containing the dry residue in an oil or air bath and heat for half an hour at 140 to 150° C., during which time pass dry hydrochloric acid gas through the flask. Cool in a current of hydrochloric acid gas, treat the residue with a few cc. of absolute alcohol which has been saturated with hydrochloric acid gas, and add an equal volume of absolute ether. Close the flask tightly and allow it to stand with frequent shaking for twelve hours. Pour the solution through a filter, wet with the alcohol-ether mixture and wash the residue three times by decantation with the alcohol-ether mixture. Add a few more cc. of the alcohol-ether saturated with hydrochloric acid gas to the contents of the flask and allow to stand again for twelve hours. Pour the liquid through a filter, and wash the residue by decantation with the alcohol-ether mixture until the residue tested in the spectroscope shows the complete absence of lithium. Carefully evaporate the combined alcohol-ether extract to dryness on a lukewarm water bath. Dissolve the residue in sufficient dilute sulphuric acid to convert all the lithium into the sulphate, transfer the solution to a weighed platinum dish, evaporate to dryness on the water bath, and finally ignite gently. Cool the residue in a desiccator and weigh as lithium sulphate.

Note. Lithium may also be precipitated and weighed as LiP2O7 or it may be precipitated as LiF and then changed into the sulphate and weighed.

Spectroscopic Method

Dissolve the lithium salt containing small amounts of sodium and potassium resulting from the separation by the Gooch or Rammelsberg methods in 5 or 10 cc. of water, depending on the amount of lithium present. Gradually add measured amounts of this solution to a known volume of water—testing the solution from time to time in the spectroscope—until the lithium line appears. When only traces of lithium are present, it is better to dissolve the lithium salt in a little water and dilute to the vanishing point of the lithium line. Make the spectroscopic examination as follows: Prepare a loop by winding a platinum wire four times around a No. 10 wire. Plunge the loop into the solution, and remove with the axis parallel to the surface of the water. Evaporate the drop to dryness carefully, ignite in the Bunsen flame, and observe through a good spectroscope.

Before undertaking the determination, standardize the instrument and platinum loop by carrying out the determination with known amounts of lithium.

The method gives satisfactory results when only an approximation is desired. For weighable amounts of lithium, the Gooch method is preferable.

3 Carnot, 3 Anal. Chem., 29, 332, 1890.
Determination of Sodium, Potassium, and Lithium in the Presence of One Another

Weigh the combined bases as sulphates, observing the precautions detailed under Determination of Sodium, dissolve in water and dilute to definite volume. In one portion determine the potassium and in a second portion determine the lithium by the Gooch or Rammelsberg method. Obtain the value for the sodium by difference.

Determination of the Alkalies in Silicates

J. Lawrence Smith method

Principle. By heating the substance with 1 part ammonium chloride and 8 parts calcium carbonate, and leaching the sintered mass with water, the alkalies are obtained in solution in the form of chlorides along with some calcium, while the remaining metals are for the most part left behind as insoluble oxides, and the silica is changed to calcium silicate.

Procedure. Triturate 0.5 gram of the finely powdered mineral with an equal quantity of pure ammonium chloride in an agate mortar, add 3 grams of precipitated calcium carbonate \(^1\) and mix intimately with the former. Transfer the mixture to a platinum crucible (preferably the J. Lawrence Smith alkali crucible), rinse the mortar with 1 gram of calcium carbonate and add to the contents of the crucible. Place the covered crucible in a slightly inclined position with the top protected from the heat of the flame. This can be done by setting the crucible in a hole in a cylinder of fire clay, as shown in Fig. 56. Gradually heat the crucible over a small flame until no more ammonia is evolved, but avoid heating sufficiently to cause the evolution of ammonium chloride. This should require about fifteen minutes. Then raise the temperature until finally the lower three-fourths (and no more) of the crucible is brought to a red heat, and maintain this temperature for one hour. Allow the crucible to cool and remove the sintered cake by gently tapping the inverted crucible. Should this not be possible, digest the mass a few minutes with water to soften the cake, and then wash it into a large porcelain or platinum dish. Heat the covered dish with 50 to 75 cc. of water for half an hour, reduce the large particles to a fine powder by rubbing


\(^2\) Blank determinations should be run on the calcium carbonate, and corrections made for its alkali content.
with a pestle in the dish, and decant the clear solution through a filter. Wash the residue four times by decantation, transfer it to a filter, and wash with hot water until a few cc. of the washings give only a slight turbidity with silver nitrate. To make sure the decomposition of the mineral has been complete, treat the residue with hydrochloric acid. No trace of undecomposed mineral should remain undissolved.

The aqueous extract obtained in the above operation contains the chlorides of calcium and the alkalies. To remove the calcium, treat the solution with ammonia and ammonium carbonate, heat to boiling, filter and wash the residue. As this precipitate invariably retains some alkali salts, it should be dissolved in hydrochloric acid and the precipitation repeated. Evaporate the filtrate to dryness in a platinum or porcelain dish, and expel the ammonium salts by gentle ignition over a moving flame. After cooling, dissolve the residue in a little water, and add a few drops of ammonia and ammonium oxalate to remove the last trace of calcium. After standing several hours, filter off the calcium oxalate, receive the filtrate in a weighed platinum dish, evaporate to dryness and ignite gently to remove ammonium salts. Moisten the cooled mass with hydrochloric acid to transform any carbonate into chloride, and again evaporate to dryness and ignite. Cool in a desiccator and weigh the combined chlorides. Dissolve in water, and if an insoluble residue remains, filter off, weigh and deduct from the weight of the chlorides. Determine the potassium by one of the methods already described, and obtain the value for sodium by difference.

The Hydrofluoric Acid Method

Procedure. Weigh out a half-gram sample of the finely powdered mineral, place in a small platinum dish or a large platinum crucible, moisten with a few drops of water, and add about 10 cubic centimeters of hydrofluoric acid and about 2 cubic centimeters of dilute sulphuric acid. Hold the dish with the tongs and heat it and its contents cautiously over the free flame for a few minutes. Evaporate the solution on the steam bath to complete dryness, and during this evaporation agitate the solution occasionally by giving the dish a gyratory motion with the tongs. This treatment is nearly always sufficient to decompose the mineral, but if decomposition seems incomplete add more hydrofluoric acid and evaporate a second time, agitating the mixture frequently. With refractory silicates it may be desirable to digest the mineral with the acid mixture in a covered crucible for an hour or so. Heat the dish and its contents on a radiator to expel the excess of hydrofluoric and sulphuric acids. Cover the residue with dilute hydrochloric acid and digest on a steam-bath until solution is complete, adding more water and acid if necessary. Flakes of organic matter which remain undissolved may be neglected. Remove the iron, alumina, calcium, etc., by the methods described under "Separations." Finally weigh the magnesium, sodium, and potassium as sulphates as described on page 413 and determine the potassium according to the modified chloroplatinate or Lindo-Gladding method. An alternative procedure is to remove sulphates and magnesium also as described under "Separations," weigh the alkalies as chlorides, and determine the potash by any of the methods already described. It should be noted however that potash is carried down with barium sulphate, and the loss thus occasioned may be appreciable.

Test for Hydroxide. A small amount of the material dissolved in CO₂ free water is treated with an excess of BaCl₂ solution and filtered. Phenolphthalein added to the filtrate will produce the characteristic red color if an alkali hydroxide is present in the sample.

Sodium Chloride, Table Salt

U. S. Standard Specifications. Table salt must contain not over

<table>
<thead>
<tr>
<th>Impurity</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Barium chloride</td>
<td>0.05%</td>
</tr>
<tr>
<td>Calcium and magnesium chlorides</td>
<td>0.5%</td>
</tr>
<tr>
<td>Calcium sulphate</td>
<td>1.4%</td>
</tr>
<tr>
<td>Water insoluble matter</td>
<td>0.1%</td>
</tr>
</tbody>
</table>

In addition to these impurities, salt frequently contains combined Fe₂O₃, Al₂O₃, K₂O, P₂O₅, CO₂.

Outline of Method for Examination

Moisture. A 10 gram sample is dried to constant weight at 100° C. and the loss of weight noted.

Insolubles in Water. A fifty gram sample is dissolved in 200 cc. of water and filtered on a weighed, dry filter paper. The residue is washed five times with small portions of water and then dried at 100° C. for an hour. The increased weight = water insolubles. It is advisable to run side by side a second filter, which is washed and also dried in the same way, the paper being used as a tare weight.

The filtrate from the insoluble matter is diluted to exactly 500 cc. in a volumetric flask and used for the following tests.

Sulphur Trioxide. 100 cc. of the above solution equivalent to 10 grams of sample is examined for SO₃ by addition of BaCl₂ sol. and the BaSO₄ filtered off and weighed.

Barium. If SO₃ is present above, Ba will not be found in the solution. If SO₃ is absent, test for Ba by addition of H₂SO₄ to 100 cc. of the solution, by the standard procedure. BaSO₄ x 0.8923 = BaCl₂.

Lime. After removal of Fe₂O₃ and Al₂O₃ by addition of NH₄OH (100 cc. solution) CaO is determined by precipitation as oxalate by regular method.

Magnesia. MgO is determined in the filtrate from CaO by concentrating this and precipitating phosphate salt as usual.

P₂O₅. This is determined by precipitation as ammonium phosphomolybdate according to the standard procedure. (NH₄)₂HPO₄.12MoO₃ x 0.038 = P₂O₅.

Fe₂O₃ and Al₂O₃. Determined on a 10-gram sample. See page 69. If Fe₂O₃ alone is desired determine colorimetrically. (See page 258.)

Alkalies in Alunite. The ore is mixed with pure silica and is run by the J. L. Smith method.

RADIUM

Ra, at.wt.225.95; m.p. about 700 degrees C.; half period 1580 yr.; chloride RaCl₂.

In 1895 Roentgen discovered X-rays. In the following year Becquerel, while studying the phosphorescent properties of some potassium uranium salt which he had prepared about fifteen years before, noticed that it was capable of producing an effect on a photographic plate without exposure to light. The plate was wrapped in several thicknesses of black paper, being perfectly opaque to ordinary light, and then placed with the uranium salt in a dark chamber. Pictures of coins and other articles were made in this way. These effects were found to be due to radiations from the disintegration products of ordinary uranium. Uranium decomposes in succession into the following products: Uranium X₁, Uranium X₂, Uranium II, Ionium, Radium, Emanation, Radium A, Radium B, Radium C, Radium D, Radium E, Radium F (polonium), Radium G (lead). There are about thirty-five members in the three radioactive families—uranium, thorium, and actinium. Uranium and thorium are the only ordinary elements that are strongly radioactive. Potassium and rubidium give off some beta radiation. The actinium series seems to be a side chain of the uranium family.

The Curies discovered radium in 1898. It is the most important of the radioactive elements.

Kinds of Radiation. Three kinds of radiation are emitted by the various radioactive substances: alpha (α) particles, beta (β) particles, and gamma (γ) rays. Rutherford showed that the alpha particles are doubly positively charged helium atoms. They have an initial velocity of from 1/20 to 1/15 that of light. The beta particles are singly charged atoms of negative electricity, commonly known as electrons. They have an initial velocity from some substances approaching that of light. The gamma rays are very short waves in ether, and therefore have the general properties of light. They resemble X-rays but are much shorter than any X-rays that have yet been produced. They also have a much higher penetrating power. On account of the very high electrical effects of these radiations and also on account of the extremely small quantities of some of the radioactive substances it is necessary to depend for their detection and determination on the electroscope. The rays ionize the air and this discharges the electroscope.

The Lind instruments, made by the Sachs-Lawlor Company of Denver, Colorado, and distributed by the Denver Fire Clay Company of Denver, are very satisfactory for radium determinations. These instruments may be obtained from any laboratory supply house. Methods for the determination of radium are found in the second volume.

Chapter contributed by L. D. Roberts.

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Detection

Radium discharges the electroscope of the alpha ray instrument. However, other radioactive elements do also. There are only three elements that give a gas called emanation as a product. These elements are actinium, radium and thorium. They can all be distinguished by collecting the gas and observing its rate of decay. The time required for one half of the gas to decay is known as the half-period. The half-period of actinium emanation is 3.9 sec., radium emanation 3.85 days, thorium emanation 54 sec. In preparing samples for the alpha ray test they should be ground to about the same mesh. If the sample causes the leaf to move faster than it moves when the chamber is empty, the specimen is radioactive. The time is taken with a stop-watch.

![Diagram of Radium Instrument](image)

Fig. 56a.

Estimation

Radium is determined by the following methods: I, Alpha Ray; II, Emanation; III, Gamma Ray. The determination with the alpha ray instrument is only approximate and depends on having the samples in the same physical condition as much as possible. The discharge of the leaf is influenced by the fineness of the sample. Also the compound that the element is found in makes a difference. The emanating power of radium chloride is greater than that of radium sulfate, or oxalate. This method is used in the mining camps because it is simple and requires very little equipment. The emanation method is more accurate and is usually used at the plant and laboratory. The
The gamma ray method is used when the sample cannot be removed from its container, and also for very high grade material. Tubes of emanation prepared for therapeutic use are determined in this way.

The Alpha Ray Method

The alpha ray instrument consists of an electroscope head $A$ (Fig. 56a) and the chamber $B$. Head $A$ contains an aluminum or gold leaf attached to a metal rod and a reading telescope so placed as to read the deflection of the leaf when charged. $B$ is the chamber to receive the sample. A spring from the metal rod in $A$ connects this with a rod which extends into $B$. On the end of the latter is placed a disk. The rays discharge the leaf through this disk and rod. The rod in the chamber is insulated from the case with amberoid, made by subjecting amber powder to great pressure. $A$ is charged by means of a battery, or an ebonite rod can be used. The battery is made by connecting seventy-five to a hundred French cells (or Eveready Tungsten No. 703) of about five volts each in series. It is best to ground the negative end and connect $A$ by a floating wire to the positive pole of the cell which will give the desired deflection of the leaf. The case of the chamber is connected to the ground wire. A tube of distilled water is placed in the circuit to prevent the shorting of the batteries. Care should be taken not to charge the leaf enough to throw it against the case. The "natural Leak" is found by taking the time for the leaf to move over forty divisions, and calculating the divisions per second. Less than forty divisions may be taken if the time for forty divisions is quite long. If the leaf moves at the same rate over the whole scale, any part may be taken. The sample is placed in the plate for solids, and this is made exactly level full. The plate containing the sample is placed in a pan to protect the instrument from receiving active matter. The pan with its contents is now placed in the chamber $B$. As the charged leaf passes $8$ (or some other chosen starting place) the stop watch is started. The watch is stopped at $4$. The rate of discharge is calculated in divisions per second, and the natural leak is subtracted. A standard is run in exactly the same way. Since the rate of discharge is directly proportional to the amount of radium present, the amount of radium in the sample may be found by comparing its rate of discharge with that of the standard. This method gives approximate results. If the samples are of the same general character, the results may be in very good agreement, checking those obtained by the emanation method very closely.

Emanation Method

I. Carbonate Fusion. About 2 grams of a mixture of sodium and potassium carbonates are placed in a platinum boat about 2 in. long, $\frac{1}{2}$ in. wide and $\frac{1}{2}$ in. deep. Larger boats may be used for low grade samples where large amounts are taken for analysis. From 0.05 to 1 gram of the sample should be weighed in the boat. The boat is now filled level full of the fusion mixture. The fusion is made over flame, or better, in an electric furnace at about 1000° C.
The boat should be put in the furnace while the furnace is cool. This will allow the fusion to dry and melt slowly, thus tending to prevent "boiling" over. The analyst will learn by practice how fast to heat up the furnace. When thoroughly fused and while still at the highest temperature, suddenly chill the fusion by dipping the boat in water, being careful not to allow water to run into the boat and wet the fusion. This chilling causes the mass to draw away from the boat and in the acid treatment slip out of the boat. The mass is also made more porous so that the acid attacks it much better. If very little silica is present, the chilling is not necessary. However, it does no harm. The boat with the fusion is sealed in a glass tube as shown in Fig. 56b. The tube should be no larger than necessary. A number of tubes should be prepared in advance by having one end sealed. After standing from one to five or more
days (this time depends on the amount of radium present and on the time the result is demanded, the fourth day is usually about right; this gives a little more than a 50 per cent. recovery of the emanation), the emanation surrounding the boat is drawn into an evacuated chamber. The chamber may be evacuated by means of an aspirator on the water faucet or by a pump. To draw the emanation from the tube to the evacuated chamber a rubber tube

![Diagram](image)

**Fig. 56d.**

is placed on one end of the sealed tube and connected to the chamber with a capillary tube intervening to prevent broken glass from being drawn into the chamber, and a glass stopcock is connected by a rubber tube on the other end. The tip of the sealed tube next to the chamber is broken with a pair of pliers and the stopcock of the chamber opened for an instant. The other tip is broken and the glass stopcock opened for an instant. The stopcock of the chamber is opened again and closed after an instant. Air is let in through the glass stopcock again. After air is taken through about three times the chamber is ready to receive the emanation from the burette. It is necessary to use only a small part of the vacuum to draw the emanation from the sealed tube. The tube is broken and the boat is folded in a filter paper in such a manner that the paper will hold the boat in the neck of the flask until the flask is connected
with the apparatus as shown in Fig. 56c. About 4 in. of a stick of sodium hydroxide is placed in the leveling bulb D. Boiling water is poured on this and the solution is raised in the burette about three-fourths of its height, having stopcock E closed and F open. F is now closed and the leveling bulb hung on hook C. Flask C contains 1–1 HNO₃; or if the fusion is hard to disintegrate 3 parts of acid to 2 of water is used. The boat is shaken into the nitric acid and stopcock E opened immediately. A bunsen burner flame is applied to the flask and the acid brought to boiling. The boiling is continued for 10 to 30 minutes according to the nature of the fusion. The heating must be regulated so that the solution in the burette is not driven too low. If the flask is heated too strongly the gas may be prevented from escaping through tube H by raising leveling bulb D. The burette is now connected to the chamber by means of a micro-drying bulb A containing sulfuric acid. The stopcock of the chamber is opened very slightly. Then the stopcock of the burette is opened slowly but fully. The stopcock of the chamber is now regulated till the flow of gas is such that the liquid in the burette rises steadily but not too fast. When the liquid rises to the stopcock the stopcock is turned and air let in till the level is about one-fourth down the tube. The air is drawn into the chamber till the liquid again reaches the stopcock. The air is again let in as before. The stopcock is opened into the chamber again and the liquid poured out of the leveling bulb. Air is drawn through the column till the chamber is full. The burette is disconnected, and the chamber set away to be read at the end of three hours. Just before time to make the reading the electroscope head is placed on the chamber and charged for fifteen minutes, and the chamber is opened to atmospheric pressure by opening the stopcock for only an instant, Fig. 56d. From three to ten readings with the stop watch are taken over forty small divisions, say from 8 to 4. The temperature and pressure are noted. If these vary greatly from the conditions at which the instrument was standardized, the correction of the discharge must be made. The rate of discharge will be proportional to the pressure and inversely proportional to the temperature. The discharge is calculated in divisions per second. The natural leak, or still better, the blank is subtracted from this. This discharge is compared with that of a standard.

Example of a Determination and Calculation.

0.5 g. of sample sealed Oct. 1 at 5:00 P.M.
Boiled off Oct. 5 at 8:30 A.M.
Time of recovery 3 days, 15½ hours
Recovery factor for 3 days, 15 hr. 0.47926 See table.
½ hr. 0.00193

| 0.4812 |
| log. of 0.4812 | -1.6822 |
| colog. of 0.4812 | .3178 |

A–II Time of discharge over 40 divisions of head A on chamber II. 92.5 sec
B–II Time of discharge over 40 divisions of head B on chamber II. 100 sec.
1.6021 log. of 40
1.9661 log. of 92.5

\[
\begin{align*}
-1.6360 & \quad -1.6330 \log \text{ of } 0.4295 \\
0.4325 & \quad -9.9450 \text{ standardization of instrument} \\
0.0030 \text{ blank} & \quad 0.3178 \\
 & \quad 0.3010 \text{ to change } \frac{1}{2} \text{ g. to gram.} \\
0.4295 & \quad 2.6567 \text{ to change grams to pounds} \\
 & \quad 3.3010 \text{ to change pounds to tons} \\
 & \quad -2.1545 \\
14.3 \text{ mg. of radium per ton.}
\end{align*}
\]

B–II is calculated in the same way. The standardization of this particular instrument was \(-9.9825\). The last four numbers are the same in the two cases. The number for the standardization of the instrument is the log of the number of grams of radium necessary to discharge the leaf one division per second. This is obtained by running through the instrument pitchblende or a radium solution the radium content of which is accurately known. In all cases the natural leak or a blank must be subtracted.

The instrument is charged 15 minutes before the readings are made in order to allow the active deposits of Radium A, B and C to collect on the wall of the chamber. The leaf system should be charged positively. The readings are taken at the end of three hours after the emanation is drawn into the chamber because the activity increases to a maximum at that time. For the first part of the period the increase is very rapid. The maximum is actually reached at the end of four hours, but between three and five hours the change is very slow.

![Diagram](image.png)
As soon as the readings are made the instruments must be freed from emanation by drawing dry air through them, the air being dried by sulfuric acid.

II. Bisulfate Fusion. A pyrex test tube 1.1/8 in. in diameter and 8 in. long is filled about 1/4 full of fused potassium bisulfate. Sodium bisulfate or a mixture of both potassium and sodium bisulfates may be used. From 0.05 to 5 grams of the finely ground sample should be added, the amount depending on the radium content of the sample. The tube is filled about 3/4 full of potassium bisulfate. In adding the last bisulfate care should be taken to carry down any of the sample adhering on the side of the tube. The mixture is now thoroughly fused, continuing till reaction is complete. The test tube is removed from the flame and held in a nearly horizontal position and slowly turned while the melt solidifies. A very small amount of barium carbonate is dropped into the tube. About 1/4 of a gram is sufficient. In cases of carnotite ores, slimes, and tails the fusion will be yellow. As soon as the tube is cool enough to be handled a rubber stopper carrying two outlet tubes drawn out to rather fine tips (see figure) is inserted. If this is done as soon as possible there will be a partial vacuum in the tube when it cools and this will indicate when the emanation is taken off that there has been no leak. One of the outlet tubes should extend about one fourth way down the test tube and the other just through the stopper. After emanation has recovered at least one day the tube is connected to an evacuated chamber as shown in Fig. 56c. Micro-drying bulb A contains water or sulfuric acid and acts as an indicator to show when the current of air into the chamber is correctly regulated. B contains the fusion; C sodium hydroxide solution; D sulfuric acid. The tip near A is broken with a pair of pliers. On account of the vacuum in B air rushes through A. Immediately after breaking the first tip the second should be broken. The stopcock of the chamber is slowly opened till air bubbles rather slowly through A. The tube containing the fusion is carefully heated until all the fusion is melted. It is boiled for at least five minutes, or till the chamber is about to atmospheric pressure. During the heating, a steady current is maintained throughout the heating by regulating the stopcock of the chamber. The chamber is disconnected and set away to be read at the end of three hours. The procedure is the same from this point as in the carbonate fusion method.

The Gamma Ray Method

The sample is placed in the holder at such a distance as will cause a reasonable rate of discharge—about one division per second. A standard is then placed at the same distance and the two rates of discharge compared. The natural leak should be subtracted from each reading. The quantities of radium are proportional to the rates of discharge.

In the gamma ray instrument the lead plate and the brass case of the chamber stop all the radiation except the gamma rays.

See Fig. 56f.

Method for Solutions

A measured volume of the solution is placed in a 150 cc. pyrex flask and dilute nitric acid added, filling the flask about one-half full. A little barium nitrate should be added to prevent the precipitation of radium sulfate. The solution is boiled to expel all the emanation. In the Colorado Sc hool of Mines
a special flask with a long $\frac{1}{2}$ in. neck is used. This is sealed off in the flame while the solution is nearly boiling. The ordinary flask may be used by inserting a rubber stopper carrying a tube which can be sealed. Or the neck of a pyrex flask can be drawn out and sealed. With the rubber stopper the emanation sometimes leaks. The special flasks are made by the Denver Fire Clay Company. After the emanation has recovered for one or more days the flask is connected to the burette by a light-walled rubber tube as in Fig. 56c. The tip is broken and heat is applied to the flask. On breaking the tip the rubber tube collapses if the flask has not leaked. When the pressure in the tube is about atmospheric the stopcock is opened slightly from time to time until the gas goes into the burette, and then opened wide. The solution is boiled for about ten minutes. The gas is then drawn into an evacuated chamber, as described in the other methods. The calculation may be made in milligrams per liter.

**Notes**

The carbonate method is similar to that given in bulletin 104, U. S. Bureau of Mines.

The bisulfate method of which the method here given is a modification was first published by Howard H. Barker in the Journal of Industrial and Engineering Chemistry for July, 1918, and improved by the Radium Company of Colorado.

Radium is found principally in carnotite and pitchblende. The largest carnotite deposits in the world are in southwestern Colorado and southeastern Utah. Uranium ores contain radium; the ratio of radium to that of uranium is $3.4 \times 10^{-7}$; or, there are 3.4 parts of radium to 10,000,000 of uranium.

Radium salts correspond chemically to those of barium. In water barium sulfate is 100 times as soluble as radium sulfate.

Radium is used in the treatment of certain malignant growths and in luminous paints. Some of the radioactive elements have furnished the means of studying atomic structure.

Emanation should not be allowed to remain in the chambers any longer than is necessary. Air dried by sulfuric acid should be drawn through them.
The percent of $\text{U}_3\text{O}_8$ multiplied by 2.6 gives the milligrams of radium per ton in ores. This holds good unless the ratio has been disturbed by leaching or some other cause.

References.

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Figures 232, 233 and 235 were drawn by M. Ettington.

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SELENIUM AND TELLURIUM

DETECTION

Se, at.wt. 79.2; sp.gr. (Cryst. 4.82; Amorp. 4.26; m.p. 217°C) b.p. 690°C; oxide, SeO₂.
Te at.wt. 127.5; sp.gr. 6.27; m.p. 452; b.p. 1390°C; oxides, TeO₂, TeO₃.

Selenium and tellurium are commonly detected by precipitation with sulphur dioxide in hydrochloric acid solution. A selenium solution containing strong hydrochloric acid in the cold gives with either sulphur dioxide gas or the aqueous solution the amorphous red variety which, on warming, goes to the gray crystalline form. Tellurium solutions in presence of dilute hydrochloric acid with sulphur dioxide yield black elementary tellurium.

Hydrogen sulphide gives with selenious acid solutions a precipitate which is at first lemon yellow but on standing changes over to a red, due to the dissociation of yellow sulphide of selenium into sulphur and amorphous red selenium. Tellurious solutions with hydrogen sulphide give at first a red brown precipitate which rapidly darkens due to dissociation into elementary tellurium and sulphur. Both of the sulphides are soluble in alkaline sulphide solutions.

Stannous chloride, ferrous sulphate, hydroxylamine hydrochloride, hydrazine hydrochloride, phosphorous acid, or hypophosphorous acid added in the cold to selenious solutions gives red elementary selenium, which goes over to the black variety on warming. Potassium iodide added in excess to a hydrochloric acid solution of either a selenite or selenate gives, in the cold, red selenium together with iodine. On warming the iodine distils and the red selenium goes over into the gray form.

A tellurium solution yields black elementary tellurium when treated with stannous chloride, hypophosphorous acid, hydrazine hydrochloride or with metals like zinc, aluminum, and magnesium.

Neutral selenious solutions with barium chloride give a precipitate of barium selenite which is soluble in hydrochloric acid. Neutral selenites with barium chloride yield insoluble barium selenate, which, like all selenates, is decomposed with the evolution of chlorine and subsequent reduction to the selenite which dissolves in the hydrochloric acid.

The few soluble alkaline tellurites give with barium chloride a white precipitate of barium tellurite which is soluble in hydrochloric acid. Barium tellurate is precipitated when a tellurate solution is treated with barium chloride. It is decomposed by hydrochloric acid, yielding chlorine and forming barium tellurite which dissolves in hydrochloric acid.

Sulphuric Acid Test. Selenium or a selenide with concentrated sulphuric, gently warmed or fuming sulphuric acid, in the cold, gives a green color, the intensity of which varies from a light green to an almost opaque greenish black, depending on the amount of selenium present. When the green solution is added to water, red elementary selenium is precipitated. This red selenium when boiled in the diluted acid changes into the gray crystalline form.

Chapter contributed by Victor Lenher.

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green color in the strong sulphuric acid is destroyed by warming the solution a few minutes. This test is not applicable to an oxidized selenium compound. Tellurium or a telluride, but not oxidized tellurium compounds, gives in the cold with fuming sulphuric acid or with warm concentrated sulphuric acid a red color, the intensity of which depends on the amount of tellurium present. When the red solution is poured into water, black elementary tellurium is precipitated. When the red solution is warmed, sulphur dioxide is evolved, the red color disappears and if much tellurium is present, white crystals of the basic sulphate of tellurium separate.

The sulphuric acid test is frequently of no value when both of the elements are present, since the red of the tellurium may obscure the green of the selenium.

Qualitative Detection of Selenium and Tellurium in Complex Mixtures

**First Method.** The substance is treated with aqua regia or with a mixture of hydrochloric acid and potassium chlorate, and the free chlorine is expelled by warming at a temperature below boiling in order to avoid loss of volatile chlorides. The solution is then diluted and filtered to remove insoluble matter. Should tellurous acid precipitate on diluting with water, it can be redissolved by hydrochloric acid. The acid solution is treated with sulphur dioxide gas, or sodium acid sulphide. The formation of a precipitate indicates the possible presence of selenium, tellurium, or gold. (1) If the precipitate is allowed to settle, the liquid poured off, and the precipitate warmed with strong nitric acid, selenium and tellurium will dissolve leaving the gold insoluble. The nitric acid solution can be evaporated with hydrochloric acid to destroy the nitric acid and then treated in concentrated hydrochloric acid solution with sulphur dioxide gas. If selenium is present, it will appear as a red precipitate which on warming goes to the gray crystalline. The selenium precipitate can be filtered off through an asbestos filter and the solution when diluted with water and more sulphur dioxide added gives a black precipitate of elementary tellurium. (2) The sulphur dioxide precipitate containing possible selenium, tellurium, and gold can after washing be treated directly with hot concentrated sulphuric acid in order to get if possible the characteristic selenium or tellurium colors.

**Second Method.** Crude selenium or tellurium containing material from any source whether oxidized or non-oxidized can be fused with five to six times its weight of potassium cyanide. Tellurium forms potassium telluride, selenium forms selenocyanate and sulphur, which is invariably present, gives sulphocyanate. Extraction of the fused mass with water gives a purple solution if tellurium is present, the selenocyanate and sulphocyanate being colorless. The heavy metals remain insoluble, and can be removed by filtration. When a current of air is bubbled through the solution, the purple color is discharged and black elementary tellurium is precipitated. This tellurium can be filtered off and verified by the sulphuric acid test.

The selenocyanate and sulphocyanate from the air oxidation of the potassium telluride solution can be treated under a good hood with hydrochloric acid, when hydrocyanic acid is set free and red selenium is precipitated. The selenium can be confirmed by conversion to the black variety by heat or the sulphuric acid test can be applied.
SELENIUM AND TELLURIUM

SEPARATIONS

Separations of selenium and tellurium from other elements can be readily accomplished. Heating of the selenide and telluride combinations or mixtures in chlorine gas affords a separation from the metals whose chlorides are non-volatile.

Heating of selenites or tellurites in a current of hydrochloric acid gas forms volatile SeO₂·2HCl or TeO₂·2HCl, while the selenates or tellurates give chlorine in addition. This treatment with hydrochloric acid gas, when applied to the oxidized selenium and tellurium compounds, is an excellent method of separation from the metals whose chlorides are non-volatile.

Both of these elements can be separated from most of the more common elements by the general principle of reducing their compounds and precipitating them in elementary form by means of sulphur dioxide, hydrazine or hydroxylamine. Gold is precipitated at the same time but can be separated by treating the well-washed precipitate with nitric acid, sp.gr. 1.25, which will dissolve the selenium and tellurium but not the gold. The nitric acid solution can then be carefully evaporated with hydrochloric acid to destroy the nitric, and convert to chloride solution.

Separations of Selenium and Tellurium

Koller's method is to separate the selenium and tellurium from each other by making use of the principle that selenium is completely precipitated by sulphur dioxide from strong hydrochloric acid solution while tellurium is not.

Procedure. The two elements are separated from the other elements by sulphur dioxide in dilute hydrochloric acid solution. The washed precipitate is dissolved in nitric acid and the solution evaporated to dryness on the water bath. The residue is dissolved in 200 cc. of hydrochloric acid, sp.gr. 1.175, and the solution warmed to expel all free nitric acid. The solution is then saturated with sulphur dioxide gas at 15-22°C. The precipitated selenium is allowed to settle, washed first by decantation with cold hydrochloric acid, sp.gr. 1.175, then with cold water to displace the acid and finally treated in the beaker with boiling water which transforms the red selenium into the black granular variety. The selenium is brought on a Gooch crucible washed with alcohol and dried at 105°C. The tellurium is precipitated in the filtrate by diluting with water, adding more sulphur dioxide and hydrazine hydrochloride as in the gravimetric method for tellurium. The tellurium is finally washed with water, then alcohol, dried at 105°C and weighed.

Separation of Selenium and Tellurium. Distillation Method

The following method is excellent for determining selenium and tellurium in alloys.

Procedure. The apparatus having been set up as is shown in the cut, Fig. 57, 0.5 gram of the alloy containing selenium and tellurium is placed in the distilling flask D and 30 cc. of H₂SO₄ (sp.gr. 1.84) added. All connections are made tight.

A current of dry HCl gas is allowed to flow into the distilling flask and the contents of the flask heated to 300°C. (The H₂SO₄ should not fume and the temperature should be kept below the boiling point of this acid, otherwise the
 Selenium and Tellurium

Acid distilling into the reservoir $R$ would interfere with the precipitation of selenium by $\text{SO}_2$. Selenium distills as selenium chloride into $R$, while tellurium remains in the distillation flask. During the distillation, $\text{SO}_2$ gas is passed into $R$, to reduce the selenic salt in solution and precipitate metallic selenium.

The distillation is continued for two or three hours, keeping the temperature of the distillation flask at about 300° C. (i.e., below the boiling-point of $\text{H}_2\text{SO}_4$). The contents of the receiver $R$ is transferred to a 400-cc. beaker, and the distillation continued into fresh $\text{HCl}$ to assure complete volatilization of selenium from the flask $D$. The contents of the receiver and any of the metal adhering to the glass wool, or the glass of the vessel, are combined. (The adhering selenium is dissolved off with a little Bromine-Potassium Bromide solution.)

**Fig. 57. Apparatus for Determining Selenium and Tellurium.**

Fig. 57 shows a convenient apparatus for routine determinations of selenium and tellurium in alloys. Hydrochloric acid gas is generated by allowing strong hydrochloric acid to flow into concentrated sulphuric acid (see $A$ and $B$ in drawing Fig. 57). The gas is dried by passing it through strong sulphuric acid ($C$ in figure). A mercury pressure gauge, arranged to allow gas to blow out at a pressure of 3 or 4 pounds, prevents accident occurring due to stoppage in the system.

**Determination of Selenium.** The solution in the beaker is saturated with $\text{SO}_2$, then heated to boiling and the precipitated selenium allowed to settle several hours, or overnight. The precipitate is filtered into a weighed Gooch crucible, then washed with hot water and finally with alcohol. The residue is dried for an hour at 100° C. and weighed.

$$\frac{\text{Weight of } \text{Se} \times 100}{0.5} = \% \text{ Se}.$$
Determination of Tellurium. The residue in the distilling flask is transferred to a 600-cc. beaker containing 150 cc. of cold water. Ten cc. of 3% Fe(NO₃)₃ solution is added, and made ammoniacal, and then heated to boiling; the precipitate filtered off on a large filter and washed with hot water. The precipitate is dissolved in hot dilute HCl and the solution nearly neutralized with NH₄OH. The slightly acid solution is saturated with H₂S, the precipitated tellurium filtered off on an S. and S. No. 589, 12½ cm. filter, and washed with H₂S water.

The precipitate is dissolved off the paper into a small beaker with a mixture of equal parts of HCl and bromine-potassium bromide solution. The paper is washed with water keeping the volume of the solution as small as possible. The filtrate should contain 20% HCl.

Tellurium is precipitated by saturating the solution with SO₂. The precipitate, after heating to boiling, is allowed to settle for several hours and filtered onto a weighed Gooch. It is washed with hot water and then with alcohol and dried for an hour at 100° C., cooled in a desiccator and weighed.

\[
\frac{\text{Weight of Te} \times 100}{0.5} = \% \text{Te.}
\]

ESTIMATION

Selenium and tellurium closely resemble sulphur in chemical properties. They have crystalline and amorphous forms. The elements occur in nature frequently associated with sulphur. Selenium is frequently present in iron pyrites, hence is found in the flue dust of lead chambers of the sulphuric acid plant, and as an impurity in sulphuric acid, prepared from pyrites containing selenium.

Ores—Selenium. In copper and iron pyrites; meteoric iron. In the rare minerals clausthalite, PbSe; lehrbachite, PbSe·HgSe; omorith, HgSe·4HgS; eucairite, CuSe·Ag₃Se; crookesite, (CuTlAg)Se₂₁.

Tellurium. Occurs in tellurides and arsenical iron pyrites. Frequently associated with gold, silver, lead, bismuth and iron. In the minerals—altsait, PbTe; calaverite, Au₃Te₅; coloradolite, HgTe; nagyagite, (AuPb)₃(To₃Sb)₄; petaite, Ag₃Au₃Te₅; sylvanite, AuAgTe₃; telluride, TeO₃ (tellurium ochre); tetradynte, Bi₂Te₅.ⁱ

¹ Thorpe, "Dictionary of Applied Chemistry."
SELENIUM AND TELLURIUM

QUANTITATIVE METHODS FOR SELENIUM

Selenium is most commonly precipitated as element by either sulphur dioxide, hydroxylamine or hydrazine. This reduction to element at the same time separates the selenium from most of the elements except tellurium and gold. When hydroxylamine hydrochloride or hydrazine hydrochloride is the precipitating agent, the material is usually most conveniently brought into hydrochloric acid solution and converted if necessary into the selenious state. From this selenious solution, which may be acid, neutral or ammoniacal, these reducing agents on boiling precipitate elementary selenium which can be brought on a Gooch crucible, washed with hot water, dried at 105°C, and weighed.

Sulphur Dioxide Method

The addition of sulphur dioxide to a solution of selenious acid or a selenite which is strongly acid with hydrochloric acid is one of the oldest and best methods of precipitating elementary selenium. A selenate or selenic acid must first be reduced to a selenite or selenious acid by warming with hydrochloric acid, after which sulphur dioxide can be introduced.

It is sometimes convenient to produce the sulphur dioxide by the addition of sodium acid sulphite or of sodium sulphite. This procedure is satisfactory but should be accompanied by a blank test on the sulphite with hydrochloric acid, since the sulphites, on standing, not uncommonly give a precipitate of sulphur on acidification.

The best procedure in the precipitation of selenium by sulphur dioxide is to pass the gas slowly through the selenious containing solution which is strongly acid with hydrochloric acid. The gas should be passed into the solution at a temperature of 15–22°C. When the solution smells strongly of sulphur dioxide gas, the beaker is removed and allowed to stand for a half hour, in order that the selenium may settle. The supernatant liquor is decanted through a previously weighed Gooch crucible, and the selenium washed first by decantation with strong hydrochloric acid, after which one treatment with cold water is used to wash the precipitate in the beaker. After again decanting, hot water is poured into the beaker containing the precipitate when the flocculent red selenium turns black and granular. It is then filtered, washed with hot water, followed by alcohol and dried at 105°C to constant weight.

If the temperature in the solution during the precipitation of the selenium rises above 22°C, the selenium agglomerates and occludes impurities which cannot be washed out. If the temperature is below 15°C, the precipitation is either incomplete or very much delayed.

Evaporation of selenious acid should be made on the water bath rather than at a higher temperature since there is an appreciable loss of selenium dioxide when heated above 100°C. In the reduction of selenates or selenic acid to the selenious condition by means of hydrochloric acid, the temperature must never exceed that of the steam bath or considerable selenium may be lost.
SELENIUM AND TELLURIUM

Potassium Iodide Method

Potassium iodide added to a selenious solution containing free hydrochloric acid gives a precipitate of elementary selenium, iodine being liberated simultaneously.

$$\text{SeO}_3 + 4\text{HI} = \text{Se} + 2\text{H}_2\text{O} + 2\text{I}_2.$$  

With samples containing less than 0.1 gram selenium satisfactory results are obtained but with larger amounts iodine is likely to be occluded.

Procedure. The sample containing selenious acid or a selenite in a dilution of 400 cc. is acidified with hydrochloric acid, 3–4 grams of potassium iodide are added and the iodine liberated is boiled off. The selenium is brought on a Gooch crucible washed with hot water, dried and weighed. Gooch and Pierce ¹ suggest the use of sodium arsenite and iodide solutions in carrying out the method volumetrically.

The thiosulphate method of Norris and Fay ² consists in treating a hydrochloric acid solution of selenious acid with a measured excess of standard sodium thiosulphate solution and then titrating the excess of thiosulphate with an iodine solution.

$$\text{H}_2\text{SeO}_3 + 4\text{Na}_2\text{S}_2\text{O}_3 + 4\text{HCl} = 4\text{NaCl} + \text{Na}_2\text{SeO}_4 + \text{Na}_2\text{S}_4\text{O}_6 + 3\text{H}_2\text{O}.$$  

Selenates or selenic acid can be analyzed by boiling with hydrochloric acid when chlorine is evolved which can be collected and titrated.

QUANTITATIVE METHODS FOR TELLURIUM

Tellurium can be determined gravimetrically and separated from most of the elements except selenium and gold by a number of reducing agents. The oldest method, that of Berzelius, is the use of sulphur dioxide in slightly acid solution. Black elementary tellurium is precipitated but complete precipitation is much delayed even when the solution is warm. The hydrochloric acid solution of the tellurium should always be allowed to stand twenty-four hours. The tellurium is then conveniently brought on a Gooch crucible and the filtrate further digested after the addition of more sulphur dioxide. Very frequently more tellurium settles out on standing twenty-four hours longer. After all of the tellurium is collected on a Gooch crucible, it is washed and dried at 105° C. as quickly as possible in order to avoid the slight superficial oxidation which always takes place with tellurium which has been precipitated in this manner.

Hydrazine hydrochloride used as a reducing agent for the precipitation of elementary tellurium gives fairly good results but complete precipitation as with sulphur dioxide is somewhat delayed.

The use of sulphur dioxide and hydrazine hydrochloride together is the most accurate as well as the most rapid method for the determination and is applicable to both tellurites and tellurates, as well as to the free acids.

Hydrazine Hydrochloride-Sulphur Dioxide Method

The tellurium, either as a derivative of the dioxide or as a tellurate, should be present in a solution which has an acidity of approximately ten per cent free hydrochloric acid, and it is preferable that the solution be concentrated, for otherwise the precipitate will be so finely divided that it will be difficult to wash. The solution is heated to boiling, 15 cc. of a saturated solution of sulphur dioxide is added, then 10 cc. of a fifteen per cent solution of hydrazine hydrochloride followed by 25 cc. of sulphur dioxide solution. The boiling is continued until the precipitate settles in such a way that it can be easily washed, which should not take more than five minutes. The precipitated tellurium is brought on a previously weighed Gooch crucible washed with hot water until all of the chlorides are removed, after which the water is displaced by alcohol, and the crucible and contents dried at 105° C.

Tellurates or telluric acid can be analyzed by boiling with hydrochloric acid when chlorine is given off.

\[ \text{H}_2\text{TeO}_4 + 2\text{HCl} = \text{H}_2\text{TeO}_3 + \text{Cl}_2. \]

The chlorine evolved may be passed into potassium iodide solution and the liberated iodine titrated by sodium thiosulphate or an arsenite solution.

Selenium and Tellurium

Precipitation as Tellurium Dioxide

Browning and Flint \(^1\) utilize the insolubility of tellurium dioxide as a means of separation from the readily soluble selenious acid. Selenium and tellurium are precipitated by sulphur dioxide from a hydrochloric acid solution. The elements are filtered, washed and dissolved in hydrochloric acid containing sufficient nitric acid to effect solution and then evaporated to dryness on the water bath.

Procedure. The material is dissolved in hydrochloric acid or in a ten per cent solution of potassium hydroxide, using 2 cc. per 0.2 gram of oxide. The solution, if alkaline, is slightly acidified with hydrochloric acid and then diluted to 200 cc. with boiling water. Dilute ammonium hydroxide is now added in slight excess, and is followed by the faintest excess of acetic acid. Crystalline tellurium dioxide separates out completely on cooling and can be brought on a Gooch crucible dried at 105\(^\circ\) C. and weighed.

Notes

Tellurium. The element dissolves in hot concentrated hydrochloric acid. On dilution of the solution a precipitation of H\(_2\)TeO occurs. Treated with concentrated nitric acid or aqua regia H\(_2\)TeO\(_4\) forms. With sulphuric acid the compound H\(_2\)TeO\(_4\) forms and SO\(_3\) is evolved. Tellurium is insoluble in carbon disulphide. The oxides TeO and TeO\(_2\) are soluble in acids, TeO\(_2\) being not readily soluble. All the oxides dissolve in hot potassium hydroxide solutions.

Care must be exercised to avoid overheating acid extracts in the preparation of the sample, since loss by volatilization is apt to occur; this is especially true of the halogen compounds of selenium and tellurium, the former being more volatile than the latter.

Fusion Method. The finely powdered substance is intimately mixed with about five times its weight of a flux of sodium carbonate and nitrate (4 : 1) and heated gently in a nickel crucible, gradually increasing the heat, until the charge has fused. When the molten mass appears homogeneous, it is cooled and extracted with water. Sodium selenate and tellurate pass into solution and are separated from most of the heavy metals. The water extract is acidified with hydrochloric acid and boiled until no more free chlorine is evolved. (Test with starch iodide paper. Cl = blue color.) \(^2\) Metallic selenium and tellurium may be precipitated by passing sulphur dioxide into the hydrochloric acid solution.

Keller has shown that tellurium is not precipitated by SO\(_3\) in strong hydrochloric acid solutions (sp.gr. 1.175), whereas selenium is precipitated. Diluted with an equal volume of water (acidity 12 to 20\% of above) both tellurium and selenium are precipitated by SO\(_3\).

\(^1\) Amer. Jr. Sci. (4), 1909, 28, 112.
SELENIUM AND TELLURIUM

METHODS AT REFINERIES

Commercial Selenium

A half-gram portion of the material ground to 100 mesh is placed in a 150-cc. beaker, and 10 cc. of water are added, followed by 15 cc. conc. nitric acid. After the sample has dissolved in the beaker, which is covered with a watch glass, it is evaporated to dryness on the water bath, and taken up in 10 cc. conc. hydrochloric acid and 20 cc. of water in the cold. The insoluble matter is filtered off and the solution received in a 400-cc. beaker. Sufficient conc. hydrochloric acid is added to make the solution 70 per cent conc. hydrochloric acid.

The selenium is precipitated at room temperature by passing a slow current of sulphur dioxide gas through the solution at the rate of two small bubbles per second, stirring frequently, to granulate the selenium. It is recommended that the temperature of the solution be maintained at 60 to 70° F. by placing the beaker in a vessel of running water.

When complete precipitation has been effected and the solution smells strongly of sulphur dioxide, the beaker is removed and allowed to settle for a half hour. The supernatant liquor is decanted through a previously weighed Gooch crucible; the precipitated selenium in the beaker is washed three times with conc. hydrochloric acid and once with cold water, decanting each time through the crucible. To the precipitate in the beaker 25 cc. of cold water are added, followed by hot water and vigorous stirring until the selenium turns black and granular. It is then filtered, washed with hot water followed by alcohol, and dried at 105° to constant weight. After weighing, the crucible can be gently heated to expel the selenium, in order to obtain a check on its purity. A residue may consist of silica or gold.

Tellurium in the filtrate is recovered by adding three gm. of powdered tartaric acid, diluting with four times its bulk of hot water, then adding 25 cc. ammonium hydroxide and saturating with sulphur dioxide gas. After the sulphur dioxide treatment, which takes but a few minutes, the solution is brought to boiling and allowed to stand for two hours on a hot plate. The granular elementary tellurium is brought on a previously weighed Gooch crucible, washed with hot water, dried at 105° and weighed.

The important laboratory details suggested by Greenwood are:

1. Evaporation of the selenious acid should be made on the water bath rather than on a hot stove in order to avoid loss by volatilization. There is an appreciable loss of selenium dioxide when heated above 100° C. even in the presence of sodium and potassium chlorides. This fact has been verified in Lenher's laboratory.

2. If the temperature of the solution during the precipitation of selenium is above 70° F., the selenium agglomerates and oculudes impurities, which cannot be washed out. If the temperature is below 60° F., the precipitation is either incomplete or very much delayed.

3. If the precipitated selenium is not granular, it cakes during the drying and retains moisture even at 110°.

Lead, copper and iron in selenium are determined in a sample of from 10 to 25 gm. which is dissolved in 50 to 75 cc. conc. nitric acid in a 375-cc. casserole and evaporated to dryness. The volatile selenium dioxide is expelled

1 Eng. and Min. Jr. (1915), 100, 1012.
by carefully raising the temperature. The non-volatile residue is dissolved in 10 cc. conc. nitric acid and 5 cc. conc. hydrochloric acid, evaporated to 5 cc., when 5 cc. concentrated sulphuric acid are added and evaporated to fumes; it is allowed to cool, 75 cc. of water are added and allowed to stand over night, when the lead sulphate is filtered off and weighed as usual. The filtrate from the lead is treated with hydrogen sulphide, the precipitate is ignited to burn off selenium, tellurium and arsenic, the residue dissolved in nitric acid and the copper determined volumetrically. The filtrate from the precipitation of the copper is boiled to expel the hydrogen sulphide, oxidized by a few crystals of potassium chlorate, and the iron precipitated in the usual manner by ammonia.

An alternate method for the determination of iron in selenium is to weigh 10 gm. of the sample into a porcelain dish, ignite at a red heat until the selenium appears to be completely driven off. The residue is sometimes weighed and reported as "non-volatile matter." This residue is fused with sodium carbonate, treated with dilute sulphuric acid, the solution reduced with zinc, and the iron titrated with a weak solution of permanganate.

**Insoluble in commercial selenium.** 10 to 25 grams are dissolved in a 375-cc. casserole, in conc. nitric acid, and evaporated to dryness; conc. hydrochloric acid is added and the silica dehydrated. The insoluble is taken up in hydrochloric acid and water, filtered off, ignited and weighed.

**Selenium and tellurium in metallic tellurium.** A 0.5-gram sample of the finely powdered metal is treated with 10 cc. of conc. sulphuric acid and fumed until all the tellurium has dissolved; after which it is cooled and 20 cc. water and 50 cc. conc. hydrochloric acid are added.

Selenium is precipitated from the cold solution by passing in sulphur dioxide gas for 3 to 4 minutes, after which it is filtered through a Gooch crucible, washed three times with hydrochloric acid (2 parts conc. acid to 1 water), then with hot water and finally with alcohol, dried and weighed. To obtain a check on the purity of the selenium the Gooch crucible is ignited and reweighed.

The tellurium-containing filtrate is diluted to about 700 cc., heated to nearly boiling, a few grams of hydrazine hydrochloride added and a rapid current of sulphur dioxide gas is passed in for 15 minutes, or until the tellurium separates readily; it is then brought on to a Gooch filter, washed with hot water, finally with alcohol. The elementary tellurium is dried for one hour at 105° and weighed.

**A selenium and tellurium** procedure used for a number of years in one of the refineries consists in dissolving in nitric acid, adding a pinch of salt, evaporating to dryness, taking up in 25 cc. hydrochloric acid (1:1) and bringing to boiling. The insoluble matter is filtered off, the solution diluted to 150 cc. and sulphur dioxide passed through the boiling solution. A few grams of hydrazine hydrochloride are added and sulphur dioxide again passed in after which the solution is boiled a few minutes. The precipitated selenium and tellurium are filtered off, dissolved in nitric acid with the addition of a pinch of salt, and the solution evaporated. The residue is taken up in about 200 cc. conc. hydrochloric acid, the solution boiled about ten minutes and the selenium brought on a Gooch crucible where it is washed with hot water, then alcohol, dried and weighed.

The tellurium-containing filtrate is diluted with water to three times its volume and saturated with sulphur dioxide; a few grams of hydrazine hydro-
chloride are added, boiled a few minutes, the tellurium is brought on a Gooch crucible, washed with hot water, then with alcohol, dried and weighed.

**Selenium and tellurium in blister or pig copper** are commonly determined by the method of Keller, using samples of 50 grams or less.

**Selenium and tellurium in electrolytic copper slimes** are determined by treating a 0.5-gram sample of the slime in a 250-cc. beaker with 10 cc. conc. sulphuric acid, heating until the sample is decomposed and nothing remains but a white residue. After cooling, 20 cc. of water are added, followed by 2 cc. conc. hydrochloric acid, the solution is agitated to coagulate the silver chloride which is then filtered off. The acidity of the filtrate is brought up to about 32 per cent by adding conc. hydrochloric acid and the selenium and tellurium separated by sulphur dioxide, following the customary procedure.

**Selenium in lead slimes.** A 2-gram sample is fused with a mixture of 8 grams sodium carbonate and 2 grams nitrate in a nickel crucible. The cold fusion is extracted with water and filtered. The filtrate is acidified with hydrochloric acid and heated until chlorine is expelled. To the solution is added an equal volume of hydrochloric acid, and sulphur dioxide gas is added until the red precipitate becomes granular. The selenium can be brought on an asbestos filter, washed with hydrochloric acid, redissolved in hydrochloric acid and potassium chloride and reprecipitated by sulphur dioxide.

**Tellurium in lead slimes.** 1 gram of slimes is treated with a mixture of 10 cc. conc. sulphuric acid, 10 cc. conc. nitric acid, and 20 cc. water, and evaporated to fumes. After cooling, 40 cc. water and about 2 grams tartaric acid are added. The solution is boiled and filtered. The residue is washed back into the original beaker, 5 to 10 cc. conc. sulphuric acid are added, and again evaporated to fumes; 40 cc. of water are added and the solution boiled and filtered. The two filtrates are united and treated with hydrogen sulphide gas. The sulphides are filtered on paper washed with hydrogen sulphide water, washed back into the beaker, and a little sodium bicarbonate added followed by about 4 cc. of 10 per cent sodium sulphide solution. The solution is brought to boiling, digested for 12 hours, and filtered through the filter previously used. The sulphide-containing filtrate is acidified with dilute sulphuric acid and treated with hydrogen sulphide gas to render it granular. The sulphide precipitate, after filtration, is dissolved in nitric acid with the addition of 10 cc. conc. sulphuric acid and evaporated to fumes of sulphuric acid. It is then diluted with water and boiled after adding about 2 grams of tartaric acid. The solution is cooled, diluted to about 60 cc. with water, and after adding 40 cc. conc. hydrochloric acid, is again treated with hydrogen sulphide. The precipitate is filtered off, washed with 1:1 hydrochloric acid, dissolved in hydrochloric acid and potassium chlorate, warmed gently to expel the excess of chlorine, tartaric acid is again added, any residue filtered off, and the filtrate made strongly acid with hydrochloric acid. The selenium is then precipitated by sulphur dioxide.

The filtrate containing the tellurium is diluted with warm water, and the tellurium precipitated and weighed as usual.

**Selenium and tellurium in flue dust.** 2 grams are dissolved in hydrochloric acid and potassium chlorate on a water bath, and the excess of chlorine expelled by gentle heat. The insoluble matter is filtered off and washed with concentrated hydrochloric acid, and the filtrate is treated with sulphur dioxide gas. The selenium and tellurium are brought on a Gooch crucible, washed,
then dissolved in hydrochloric acid and potassium chlorate, about 2 grams of tartaric acid are added, followed by conc. hydrochloric acid, and the selenium is precipitated by sulphur dioxide, filtered off and weighed. The filtrate is diluted to three times its volume with warm water, and the tellurium is precipitated by sulphur dioxide, collected and weighed.

**Flue Dust and Niter Slag**

Flue dust or niter slag from Doré furnaces can be analyzed for water-soluble selenium and tellurium by boiling a 1-gram sample with water, filtering and washing with hot water, keeping the volume down to 20 cc. To this filtrate are added 200 cc. conc. hydrochloric acid; the solution is chilled with iced water; and sulphur dioxide is passed in, the selenium and tellurium being separated by the method of Keller.

The insoluble selenium and tellurium are transferred from the filter to a 50-cc. beaker, conc. nitric acid and conc. hydrochloric acid are added, and the solution evaporated at 50° C. or below. It is recommended to evaporate twice more with hydrochloric acid, keeping the temperature at 50° C. or below. The residue is taken up in hydrochloric acid (1 : 2) and filtered, after which 100 cc. conc. hydrochloric acid are added and the selenium and tellurium in the filtrate are separated by the Keller method.

**Commercial Sodium Selenite**

To 1 gram of the sample in a 50-cc. beaker are added 10 cc. of water and 5 drops of hydrochloric acid and shaken gently until solution is complete. After filtering out the insoluble matter, a large excess of conc. hydrochloric acid is added to the filtrate and selenium is precipitated by sulphur dioxide. In the filtrate from the selenium, the tellurium can be recovered by diluting with warm water and passing in more sulphur dioxide.

**Selenic Acid**

20 grams of the sample are quickly transferred to a tightly stoppered weighing bottle. After weighing, the acid is put into a liter flask, dissolved in water, and made up to the mark. A 25-cc. portion is measured out and treated with an excess of conc. hydrochloric acid and the selenium precipitated by sulphur dioxide. If tellurium is present, it can be recovered in the filtrate.

**Selenium in Glass**

In ruby glass where selenium is present in quantities of about 0.25%, a two-gram sample is evaporated with hydrofluoric and nitric acids. This evaporation is repeated several times without ignition. The nitrates are then transferred to a small Erlenmeyer flask and the nitric acid destroyed by adding hydrochloric acid. Care must be taken not to boil the solution or selenium will volatilize. A high concentration of the hydrochloric acid must be maintained in order to hold the tellurium in solution. Sulphur dioxide is next passed into the solution when elementary selenium is precipitated, washed, dried and weighed as usual.

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¹ Method furnished by the Corning Glass Works.
In glasses where selenium is used as a decolorizer and in which the selenium is present to the extent of less than .0025%, Cousen recommends dissolving the glass in nitric and hydrofluoric acids and determining the selenium colorimetrically by phenyl hydrazine hydrochloride, keeping the selenium from precipitating by adding gum arabic. A yellow to a yellowish red solution is obtained which is compared with a color standard containing a known amount of sodium selenite.

Selenium and Tellurium in Refined Copper

The success and accuracy of determining small amounts of impurities, is to collect these impurities from a large sample, and to do the necessary chemical work in a small volume of solution.

Ferric hydroxide when precipitated from a copper solution has the peculiar property of forming insoluble compounds with As, Sb, Se and Te.

For complete precipitation, the iron contents must be at least thirty times the combined As, Sb, Se and Te and must be entirely precipitated from the solution.

The iron is best added by means of the ferrous salt (FeSO₄+7H₂O) dissolved in water and oxidized to the ferric salt with HNO₃. Roughly the iron content of FeSO₄+7H₂O is 20%, or one-fifth of the weight of ferrous sulphate.

Weigh 100 grams of drillings into a 1300 cc. beaker, cover with water and add gradually 350 cc. HNO₃ (1.42). When the copper is in solution, boil out all red fumes, dilute to 700 cc. with warm water and neutralize with NH₄OH until just enough copper hydroxide has been formed to cover the bottom of the beaker; then add the required amount of oxidized ferrous sulphate in solution. Stir well, dilute to 900 cc. and boil for at least one hour, settling on the warm plate over night. Filter on a 15 cm. filter.

Treat the filtrate with ammonia until a precipitate of copper hydroxide has formed to cover the bottom of the beaker and half the quantity of oxidized FeSO₄+7H₂O added previously, is again added and the solution boiled for one hour, allowing to settle over night on the warm plate. Filter on a 15 cm. filter. It is absolutely necessary that no iron salts be left in this filtrate, either in solution, or as hydrate, therefore, this filtrate had best be tested with ammonia and refiltered on a 15 cm. filter. The three precipitates on the 15 cm. papers are treated as one, dissolved in the least quantity of warm H₂SO₄ (1-1), the papers washed well with hot dil. H₂SO₄ (1-20) and filtered into a 600 cc. beaker. Make strongly amoniacal, boil well and filter, washing the precipitate well and free from the folds into the apex of the filter. Refilter the filtrate to catch any iron that has washed through. The papers are spread open and the precipitates dissolved in 25 cc. warm HCl (1-1) in a 250 cc. beaker, using as little hot water as possible to remove the yellow stains.

Filter the solution into a 400 cc. beaker, washing with as little hot water as possible. To the filtrate add four times its volume of conc. HCl and cool.

Pass SO₂ gas through this liquid at the rate of one bubble per second, keeping the solution cool.

Filter off the precipitated Se on a tared Gooch crucible wash with cold water and alcohol, dry at 60° C. for two hours, then at 105° C. to constant weight.

Weigh as metallic Se.

Expel the Se from the crucible and reweigh as a check on the weight and the purity of the precipitate.
SELENIUM AND TELLURIUM

Tellurium

To the filtrate from the precipitated Se, add 2 grams of tartaric acid in order to keep the Sb in solution, dilute to 600 cc. with hot water, add 50 cc.\(^1\) conc. \(\text{NH}_4\text{OH}\), and saturate the solution with \(\text{SO}_2\) gas. Boil for two minutes and allow to settle 4-6 hours.

Filter the Te on a tared Gooch crucible, wash with hot water and finally with alcohol, dry at \(115^\circ\) C. to constant weight.

Weigh as metallic Te.

VOLUMETRIC DETERMINATION OF SELENIUM AND TELLURIUM

Iodometric Determination of Selenic, or Telluric Acid—Reduction with Hydrochloric Acid and Distillation

The method depends upon the reduction of selenic or telluric acid to selenious or tellurous acid by heating with hydrochloric acid, the evolved chlorine being a measure of the acids in question. The chlorine absorbed in potassium iodide solution liberates its equivalent of iodine, which may readily be determined by titration with standard thiosulphate. The following reactions illustrate the change that takes place:

\[
\begin{align*}
\text{K}_2\text{SeO}_4 + 4\text{HCl} &= 2\text{KCl} + \text{H}_2\text{SeO}_3 + \text{H}_2\text{O} + \text{Cl}_2, \\
\text{K}_2\text{TeO}_3 + 4\text{HCl} &= 2\text{KCl} + \text{H}_2\text{TeO}_3 + \text{H}_2\text{O} + \text{Cl}_2,
\end{align*}
\]

\(1\ \text{Cl} = 1\ \text{I} = \frac{\text{Se}}{2}\) or \(\frac{\text{Te}}{2}\) = 63.75 grams Te or 39.6 grams Se per liter normal solution.

According to Gooch and Evans over 30% of strong hydrochloric acid (sp.gr. 1.20) should be present. Dilute hydrochloric acid having a strength of 10% of \(\text{HCl}\), sp.gr. 1.2, does not react with liberation of chlorine. Care must be taken not to prolong the boiling after the solution reaches a concentration of half strength, since over reduction may take place and the metals be liberated.

Procedure. The sample containing the selenate or tellurate is treated with 75 cc. of hydrochloric acid, containing 25 cc. of strong \(\text{HCl}\), sp.gr. 1.20, per 0.2 gram of the oxides, in a distillation flask connected with a Drexel wash bottle receiver, water cooled, and charged with potassium iodide solution. A current of \(\text{CO}_2\) is passed into the flask to sweep the liberated chlorine into the iodide solution. The sample is boiled until nearly one-third its volume has distilled into the receiver. The liberated iodine is titrated with standard thiosulphate. One cc. \(\text{N}/10\ \text{Na}_2\text{S}_2\text{O}_3 = 0.00396\) gram Se or 0.006375 gram Te.

\(1\) Te is best precipitated by \(\text{SO}_2\) gas in a 20-30% HCl solution and the strong (80%) HCl solution from the Se precipitation is best neutralized to 25-30%, by the use of ammonia.
SILICON

Si, at. wt. 28.06; sp. gr. amor. 2.00.; crys. 2.49; m.p. 1420° C.; oxides SiO₂, SiO₃

DETECTION

The finely ground sample together with a small quantity of powdered calcium fluoride is placed in a small lead cup 1 cm. in diameter and depth (see Fig. 58), and a few drops of concentrated sulphuric acid added. A lead cover, with a small aperture, is placed on the cup, and the opening covered with a piece of moistened black filter paper. Upon this paper is placed a moistened pad of ordinary filter paper. The cup is now gently heated on the steam bath. At the end of about ten minutes a white deposit will be found on the under side of the black paper, at the opening in the cover, if an appreciable amount of silica is present in the material tested.

A silicate, fused with sodium carbonate or bicarbonate in a platinum dish and the carbonate decomposed by addition of hydrochloric acid with subsequent evaporation to dryness, will liberate silicon as silicic anhydride, SiO₂. The silica placed in a platinum dish is volatilized by addition of hydrofluoric acid, the gaseous silicon fluoride being formed. A drop of water placed in a platinum loop, held in the fumes of SiF₄, will become cloudy owing to the formation of gelatinous silicic acid and fluosilicic acid,

\[ 3\text{SiF}_4 + 3\text{H}_2\text{O} = \text{H}_2\text{SiO}_3 + 2\text{H}_2\text{SiF}_6. \]

If a silicate is fused in a platinum loop with microcosmic salt, the silica floats around in the bead, producing an opaque bead with weblike structure upon cooling.

ESTIMATION

The gravimetric procedure is the only satisfactory method for the estimation of silica. The substance in which the element is combined as an oxide or as a silicate is decomposed by acid treatment or by fusion with an alkali carbonate or bicarbonate, the material taken to dryness with addition of hydrochloric acid, whereby the compound silica is liberated. If other elements are present the silica is volatilized by addition of hydrofluoric acid and estimated by the loss of weight of the residue.

The element silicon has no important application. Its use for electrical resistance has been suggested. A rod 10 cm. long with cross section of 40 sq.mm. has a resistance of 200 ohms against a carbon rod of the same dimensions of 0.15

Chapter contributed by Wilfred W. Scott.
SILICON

Impure silica finds use in fluxes in manufacture of glass; pure silica for manufacture of silica ware. With caustic it forms an adherent sodium e. Silicon carbide, carborundum, is used for refractory purposes, fire zinc muffles, coke ovens. Crystolon, the crystalline form, is used as anive, in making grinding wheels, sharpening stones, etc.
ombined as SiO₂ and in silicates the element is very widely distributed in and is a required constituent in practically every complete analysis of minerals, soils, etc. It is present in certain alloys, ferro-silicon, silicon le, etc.

Element is scarcely attacked by single acids, but is acted upon by nitric-fluoric acid mixture. It dissolves in strong alkali solutions. Silica is posed by hydrofluoric acid and by fusion with the fixed alkali carbonates froydes.

Preparation and Solution of the Sample

Meral Considerations. The natural and artificially prepared silicates may ofed under two classes: 1. Those which are decomposed by acids. 2. es not decomposed by acids. The minerals datolite, natrolite, olivine many basic slags are representative of the first class, and feldspar, ortho-pumice and serpentine are representative of silicates not decomposed by

(See more complete list under List of More Important Silicates, page 433.)

First division simply require an acid treatment to isolate the silica, the latter equire fusion with a suitable flux.

technical analysis, in cases where great accuracy is not required, the residue igning, after certain conventional treatments with acids, is classed as silica.
ay consist of fairly pure silica or a mixture of silica, undecomposed sili-barium sulphate and certain acid insoluble compounds. For accurate ses this insoluble residue is not accepted as pure silica, unless impurities, are apt to be found with the silica residue, are known to be absent from the al under examination.

though the procedure for isolation of silica is comparatively simple, errors rise from the following causes:

Imperfect decomposition of the silicate.
Loss of the silica by spouting when acid is added to the carbonate fusion.
Slight solubility of silica, even after dehydration, especially in presence um chloride and magnesia.
Loss due to imperfect transfer of the residue to the filter paper.
Mechanical loss during ignition of the filter and during the blasting, due draft whirling out the fine, light silica powder from the crucible.
Error due to additional silica from contaminated reagents or from the porse-nes or glassware in which the solution was evaporated. A blank of 0.01% me sodium carbonate will make an error of 0.1% per gram sample in an ery fusion where 10 grams of the flux are required.
Error due to loss of weight of the platinum crucible during the blasting.
Incomplete removal of water, which is held tenaciously by the silica.
more, weighing of the residue should be done quickly, as the finely divided tens to absorb moisture.

general procedures will be given for treatment of the acid decomposa-
d undecomposable silicates. It is frequently advisable to use these two
lures in conjunction, extracting the material first with acid, and then fusing
the insoluble residue with sodium carbonate; this procedure is used when a gritty residue remains after the acid extraction. Following the general procedures for decomposition of silicates, certain special methods will be given.

**List of Most Important Silicates.** Silicates decomposed by acids. Allanite; allopaine; analcite; botryolite; brewsterite; calamine; chabasite; croustedtite; datolite (hydrated silicate and borate of Ca with Al and Mg); diopside; eulytite; gadolinite; gehlenite; ilvaite (silicate ferrous and ferric iron with Al₂O₃, CaO and MgO); laumontite; melilite; natrolite (hydrated silicate of Al and Na with Fe and CaO); okenite; olivine (silicate of Fe and Mg); pectolite; prehenite (hydrated Al and Ca silicate with Fe, Mn, K, Na, etc.); teproite; wernerite; woolastonite; zalkite.

Silicates undecomposed by acids. Albite; aludalusite; augite; axinite; beryl; carpholite; cyanite; diabase; epidote (silicate of Fe, Al and Ca with FeO, Mn, Mg, K, Na); euclase; feldspar (silicate of K, Na, Al, Fe, Ca and Mg); garnet; iolite; labradorite; micas of K and Mg; orthoclase; petalite; pinite, procholrite; pumice; serpentinite; sillimanite, talc, topaz, tourmaline (Fe₅O₈, FeO, Mn, Al, Ca, Mg, K, Na, Li, SiO₂, BeO, P₂O₅, F); vesuvianite.

**Preparation of the Substance for Decomposition**

If the material is an ore or mineral it is placed on a steel plate within a steel ring and broken down by means of a hardened hammer to small lumps and finally to a coarse powder. A quartered portion of this is air dried and ground as fine as possible in an agate mortar and preserved in a glass-stoppered bottle for analysis.

Analyses are based on this air-dried sample. If moisture is desired it may be determined on a large sample of the original material. Hygroscopic moisture is determined on the ground, air-dried sample, by heating for an hour at 105 to 107°C.

**Decomposition of the Material, General Procedures**

Silicates Decomposed by Acids

*Acid extraction of the silicates.* 0.5 to 1 gram of the finely pulverized material placed in a beaker or casserole is treated with 10 to 15 cc. of water and stirred thoroughly to wet the powder.¹ It is now treated with 50 to 100 cc. of strong hydrochloric acid and digested on the water bath for fifteen or twenty minutes with the beaker or casserole covered by a watch-glass. If there is evidence of sulphides (pyrites), etc., 10 to 15 cc. of concentrated nitric acid are now added and the containing vessel again covered. After the reaction has subsided, the glass cover is raised by means of riders and the mixture evaporated to dryness on the water bath. (This evaporation may be hastened by using a sand bath, boiling down to small bulk at comparatively high temperature, then to dryness on the water bath. Decomposition is complete if no gritty particles remain. A flocculent residue will often separate out during the digestion, due to partially dehydrated silicic acid, hydrated silicic acid, Si(OH)₄, is held in solution.) The silicic acid is converted to silica, SiO₂, the residue taken up with dilute hydrochloric acid, silica filtered off, washed with water acidified with hydrochloric acid, and estimated according to the procedure given later.

¹Water is added to the sample and then acid, as strong acid added directly would cause partial separation of gelatinous silicic acid, which would form a covering on the undecomposed particles, protecting them from the action of the acid.
Silicates Not Decomposed by Acids

**Fusion with Sodium Carbonate or Sodium Bicarbonate.** 0.5 to 1 gram of the air-dried, pulverized sample is placed in a large platinum crucible or dish in which has been placed about 5 grams of anhydrous sodium carbonate. The sample is thoroughly mixed with the carbonate by stirring with a dry glass rod, from which the adhering particles are brushed into the crucible. A little carbonate is sprinkled on the top of the mixture and the receptacle covered. It is heated to dull redness for five minutes and then gradually heated up to the full capacity of a Meker burner. When the mix has melted to a quite clear liquid, which generally is accomplished with twenty minutes of strong heating, a platinum wire with a coil on the immersed end is inserted in the molten mass, and this allowed to cool. The fusion is removed by gently heating the crucible until the outside of the mass has melted, when the charge is lifted out on the wire, and after cooling disintegrated by placing it in a beaker containing about 75 cc. dilute HCl (1 part HCl to 2 parts H₂O), covering the beaker to prevent loss by spattering. The crucible and lid are cleaned with dilute hydrochloric acid, adding this acid to the main solution. When the disintegration is complete, the solution is evaporated to dryness and silica is estimated according to directions given later.

If decomposition is incomplete, gritty material will be found in the beaker upon treatment of the fusion with dilute acid. If this is the case, it should be filtered off and fused with a second portion of sodium carbonate, and the fusion treated as directed above.

**Notes.** Fusions with soluble carbonates are generally best effected with the sodium salt, except in fusions of niobates, tantalates, tungstates, where the potassium salt is preferred on account of the greater solubility of the potassium compounds. Sodium alone has an advantage over the mixed carbonates, Na₂CO₃ + K₂CO₃, as silica has a high melting-point and a flux, which fuses at 810° C., is more apt to cause disintegration of the silicate than the mixture, which melts at 690° C.

Prolonged blasting is undesirable, as it renders the fusion less soluble. Aluminum and iron are also rendered difficultly soluble, when their oxides are heated to a high temperature for some time.

If the melt is green, it is best to dissolve out the adhering melt from the crucible with dilute nitric acid, as a manganate (indicated by the color), if present, will evolve free chlorine by its action on HCl and this would attack the platinum.

**Fluorides.** In presence of fluorides the melt is extracted with water (an acid extraction would volatilize some of the silica), and the extract filtered off from the insoluble carbonates. To the filtrate is added about 5 grams of solid ammonium carbonate, and the mix warmed to 40° C. and allowed to stand for several hours. The greater part of the silica is precipitated. This is filtered off and washed with water containing ammonium carbonate. Preserve this with the insoluble carbonate for later treatment. The filtrate, containing small amounts of silicic acid, is treated with 1 to 2 cc. of ammoniacal zinc oxide solution (made by dissolving C.P. moist zinc oxide in ammonia water). The mixture is boiled to expel ammonia and the precipitate of zinc silicate filtered off. The precipitate is washed into a beaker through a hole made in the filter, and the adhering material dissolved off with dilute HCl, enough being added to dissolve the remaining residue. This is evaporated to dryness and silica separated as usual. Meantime the insoluble carbonate is dissolved with HCl, evaporated to

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1 Sodium bicarbonate may be used in place of the carbonate with excellent results.
dryness and any silica it contains recovered. Finally all three portions of silica are combined, ignited and silica estimated as usual.

Special Procedures for Decomposing the Sample

Treatment of Iron and Steel for Silica. One gram of pig-iron castings, or 5 grams of steel are taken for analysis, both the fine and coarse drillings being taken in equal proportion. (Fine particles contain more silicon than the coarse chips.) Twenty to 50 cc. of dilute nitric acid (sp.gr. 1.135) are added to the sample in a 250-cc. beaker or small casserole, and this covered. If the action is violent, cooling, by placing the beaker in cold water until the violent action has subsided, is advisable. Twenty cc. of 50% sulphuric acid are added and the solution evaporated on the hot plate to SO₂ fumes. After cooling, 150 cc. of water are added and 2 to 5 cc. dilute sulphuric acid. The mixture is heated until the iron completely dissolves and the silica is filtered off on an ashless filter, washed with hot dilute hydrochloric acid (sp.gr. 1.1), and with hot water until free from iron. The residue is ignited and the silica estimated according to the procedure given later.

Pig iron and cast iron may be decomposed by digestion with a mixture of 8 parts by volume of HNO₃ (sp.gr. 1.42), 5 parts of H₂SO₄ (sp.gr. 1.84), and 17 parts of water.

Steel and wrought iron may be disintegrated by a mixture of 8 parts by volume of HNO₃ (sp.gr. 1.42), 4 parts H₂SO₄ (1.84), and 15 volumes of water.

Ferro Silicons. Dilute hydrochloric acid, 1 volume of acid (sp.gr. 1.19), with 2 volumes of water is a better solvent than the strong acid.

Steels Containing Tungsten, Chromium, Vanadium and Molybdenum. Fusion with potassium acid sulphate, KH₂SO₄, in a platinum dish, or sodium peroxide in a nickel crucible will generally decompose the material. Sodium peroxide is of special value in decomposing chromium alloys.

Silicon Carbide, Carborundum. This is best brought into solution by fusion with potassium hydroxide in a nickel crucible. Sulphuric, hydrochloric, nitric acids, or aqua regia have no effect upon this refractory material.

Sulphides, Iron Pyrites, etc. These require oxidation with strong nitric acid or a mixture of bromine and carbon tetrachloride, followed by nitric, exactly according to the procedure given for solution of pyrites in the determination of sulphur. The sample is taken to dryness and then hydrochloric acid added and the solution again evaporated. The residue is dehydrated and silica determined as usual.

Slags and Roasted Ores. Digestion with hydrochloric acid according to the first general procedure is best. The addition of nitric acid to decompose sulphides may be necessary.

Decomposition of silicates by fusion with lead oxide (method of Jannasch), and calcium carbonate and ammonium chloride (method of Hillebrand), are of value when sodium is desired on the same sample. The procedures are given under chapters on Sodium and Potassium.

Note. K₂CO₃ is preferred to Na₂CO₃ for fusion of tungstates, niobates and tantalates on account of the greater solubility of the potassium salts. For corundum and alumina silicates Na₂CO₃ is preferred as double salt of potassium and aluminum are less soluble than the sodium salt.¹ Fluorides of silicon are fused with boric acid, BF₃ is volatilized, SiF₄ is not formed.

P. Jannasch.²

²Ber., 28, 2822, 1896.
PROCEDURE FOR THE DETERMINATION OF SILICON AND SILICA

As has been stated, the gravimetric method for determination of silica is the only satisfactory procedure for estimation of this substance. The oxidation of the element and its isolation have been dealt with in the section Preparation and Solution of the Sample. The following directions are for purification and final weighing of the element in the form of its oxide, silica, SiO₂.

**Extraction of the Residue—First Evaporation.** The residue, obtained by evaporation of the material after decomposition of the silicate, by acids or by fusion, as the case required, is treated with 15-25 cc. of hydrochloric acid (sp.gr. 1.1) covered and heated on the water bath 10 minutes. After diluting with an equal volume of water, filtration is proceeded with immediately, and the silica is washed with a hot solution consisting of 5 cc. hydrochloric acid (sp.gr. 1.2) to 95 cc. of water and finally with water. This filtration may be performed with suction. The filtrate and washings are evaporated to small volume on a sand bath and then to dryness. This contains the silica that dissolved in the first extraction.

**Second Evaporation.** The residue obtained from evaporation of the filtrate is dehydrated for 2 hours at 105-110° C.¹ and extracted with 10 cc. of hydrochloric acid (sp.gr. 1.1) covered and heated on the water bath for ten minutes diluted to 50 cc. with cold water and filtered immediately, without suction. The residue is washed with cold water containing 1 cc. concentrated hydrochloric acid to 99 cc. water, the washed residue containing practically all² the silica, that went into solution in the first extraction, is combined with the main silica residue. This is gently heated in a platinum crucible until the filters are thoroughly charred, and then ignited more strongly to destroy the filter carbon and finally blasted over a Meker burner for at least thirty minutes, or to constant weight, the crucible being covered. After cooling the silica is weighed. For many practical purposes this residue is accepted as silica, unless it is highly colored. For more accurate work, especially where contamination is suspected (silica should be white), this residue is treated further.

**Estimation of True Silica.** Silica may be contaminated with BaSO₄, TiO₂, Al₂O₃, Fe₂O₃, P₂O₅ combined (traces of certain rare elements may be present). The weighed residue is treated with 3 cc. of water, followed by several drops of concentrated sulphuric acid and 5 cc. of hydrofluoric acid, HF (hood). After evaporation to dryness, the crucible is heated to redness and again cooled and weighed. The loss of weight represents silica, SiO₂.³

¹ Dehydration of silica is aided by the presence of lime and retarded by magnesia. In presence of the latter a soluble magnesia silicate will form if the dehydration is conducted at a temperature much above 110° C., hence it is better to avoid this by taking more time and heating to 100 or 105° as recommended.

² Sodium chloride has a solvent action on silica, the reaction of HCl on sodium silicate being reversible: 2HCl + Na₂SiO₃ ⇌ 2NaCl + H₂SiO₄. An evaporation of the filtrate to dryness will recover the greater part of the silica thus dissolved.

³ Not more than 0.1% of the original SiO₂ may still be in solution.

⁴ Silicic acid cannot be completely dehydrated by a single evaporation and heating, nor by several such treatments, unless an intermediate filtration of silica is made. If, however, silica is removed and the filtrate again evaporated to dryness and the residue heated, the amount of silica remaining in the acid extract is negligible. (See Article by Dr. W. F. Hillebrand, Jour. Am. Soc., 24.)
SILICON

NOTES. Lenher and Truog make the following observations for determining silica:

1. In the sodium carbonate fusion method with silicates, there is always a non-volatile residue when the silica is volatilized with hydrofluoric and sulphuric acids.

2. The non-volatile residue contains the various bases, and should be fused with sodium carbonate and added to the filtrate from the silica when the bases are to be determined.

3. In the dehydration of the silica from the hydrochloric acid treatment of the fusion, the temperature should never be allowed to go above 110°.

4. Dehydrated silica is appreciably soluble in hydrochloric acid of all strengths. With the dilute acid used, this error is almost negligible.

5. Dehydrated silica is slightly soluble in solutions of the alkaline chlorides. As sodium chloride is always present from the sodium carbonate fusion, an inherent error is obviously thus introduced.

6. The dehydrated silica along with the mass of anhydrous chlorides must not be treated first with water, since hydrolysis causes the formation of insoluble basic chlorides of iron and aluminum, which do not dissolve completely in hydrochloric acid.

7. Hydrochloric acid (sp.gr. 1.1) in minimum amount should be used first to wet the dehydrated chlorides and should be followed by water to bring the volume to about 50 cc., after which the silica should be filtered off as quickly as possible.

8. Pure silica comes quickly to constant weight on ignition. Slightly impure silica frequently requires long heating with the blast flame in order to attain constant weight, and is then common'ly hygroscopic.

9. Evaporations of the acidulated fusion in porcelain give practically as good results as when platinum is used.

10. Filtration of the main bulk of the silica after one evaporation is desirable, inasmuch as the silica is removed at once from the solutions which act as solvents.

11. Dehydration of the silica under reduced pressure has no advantages over the common evaporation at ordinary atmospheric pressure.

12. Excessive time of dehydration, viz., four hours, possesses no advantages.

13. Excessive amounts of sodium carbonate should be avoided, since the sodium chloride subsequently formed exerts a solvent action on the silica. The best proportions are 4–5 sodium carbonate to 1 of silicate. Less than 4 parts of sodium carbonate is frequently insufficient completely to decompose many silicates.

14. The non-volatile residue has been found to be invariably free from sodium. Pure silica, on fusion with sodium carbonate, subsequently gives no non-volatile residue.

ANALYSIS OF SILICATE OF SODA

Determination of Na₂O

Five grams of the sample are dissolved in about 150 cc. of water and heated; 1 cc. of phenolphthalein is added and then an excess of standard sulphuric acid from a burette. The excess acid is titrated with standard sodium hydroxide to a permanent pink.

\[ H_2SO_4 \times 0.6321 = Na_2O. \]

Silica. Ten grams of the sample are acidified with hydrochloric acid and evaporated to dryness on the steam bath. The treatment is repeated with additional hydrochloric acid and then the residue taken up with 5 cc. of the acid and 200 cc. of water. The residue is digested to dissolve the soluble salts, filtered, washed and ignited. Silica is determined by loss of weight by volatilization of the silica with hydrofluoric and sulphuric acids. The filtrate is made to 1 liter.

Iron and Alumina. Five hundred cc. (5 grams) of the filtrate from the silica determination are oxidized with HNO₃ and the iron and alumina precipitated with ammonium, washed, ignited and weighed as Al₂O₃ and Fe₂O₃. The residue is dissolved by digestion with hydrochloric acid or by fusion with sodium acid.

sulphate, and subsequent solution in hydrochloric acid. Iron is determined by
titration in a hot hydrochloric acid solution with standard stannous chloride,
SnCl₂, solution as usual. If only a small amount of precipitate of iron and
alumina is present, as is generally the case, solution by hydrochloric acid is preferable
to the fusion with the acid sulphate. The latter is used with larger amounts of
the oxides.

**Lime, CaO.** This is determined in the filtrate from iron and alumina by
precipitation as the oxalate and ignition to CaO.

**Magnesia, MgO.** This is determined in the filtrate from lime by precipita-
tion with sodium ammonium phosphate. The precipitate is ignited and weighed
as Mg₃P₂O₇ and calculated to MgO. Precipitate × 0.3621 = MgO.

**Combined Sulphuric Acid.** One hundred cc. of the filtrate from the silica
determination (= 1 gram) is treated with BaCl₂ solution and sulphuric acid
precipitated as BaSO₄.

\[
\text{BaSO}_4 \times 0.4202 = \text{H}_2\text{SO}_4 \quad \text{or} \quad \times 0.3430 = \text{SO}_3.
\]

**Sodium Chloride.** Ten grams of the silicate of soda are dissolved in 100 cc.
of water and made acid with HNO₃ in slight excess and then alkaline with MgO.
Cl is titrated with standard AgNO₃ solution.

**Water.** This is determined either by difference or by taking 10 grams to
dryness and then heating over a flame and blasting to constant weight.

**Note.** For detailed procedures for each of the above see special subject.

**ANALYSIS OF SAND, COMMERCIAL VALUATION**

**Silica.** Two grams of the finely ground material are fused in a platinum cru-
cible with 10 grams of fusion mixture (K₂CO₃ + Na₂CO₃) by heating first over a
low flame and gradually increasing the heat to the full blast of a Meker blast
lamp. When the fusion has become clear it is cooled by pouring on a large platin-
num cover. The fused mass on the cover and that remaining in the platinum:
crucible are digested in a covered beaker with hot hydrochloric acid on the steam
bath. The solution is now evaporated to dryness, taken up with a little water
and 25 cc. of concentrated HCl and again taken to dryness. Silica is now deter-
mined by the procedure outlined under the general method on page 436.

**Ferric Oxide and Alumina.** The filtrate is oxidized with crystals of solid
potassium chlorate, KClO₃, and iron and aluminum hydroxides precipitated
with ammonia. The precipitate is filtered, washed, ignited and weighed as
Al₂O₃ + Fe₂O₃.

**Calcium Oxide.** To the ammoniacal filtrate 10 cc. of ammonium oxalate
solution are added, the solution heated to boiling and the precipitate allowed
to settle until cold. The solution should not be over 200 cc. The calcium
oxalate is filtered off, washed and ignited. The residue is weighed as CaO.

**Magnesium Oxide.** The filtrate from the lime is made strongly ammoniacal and
10 cc. of sodium ammonium phosphate added. The solution during the
addition is allowed to stand cold for some time, three to four hours. The pre-
cipitate is filtered and washed with dilute ammonia (1 of reagent to 3 parts of
water), then ignited and weighed as Mg₃P₂O₇. This weight multiplied by
0.3621 = MgO.

For more detailed directions see the individual subjects under the chapters
devoted to the element.
Silicon in Cast Iron and Steel

One gram of pig iron, cast iron, and high silicon iron, or 5 grams of steel, wrought iron, and low silicon iron are taken for analysis. (By taking multiples of the factor weight 0.4693, SiO₂ to Si, the final calculation is simplified.) The sample is placed in a 250-cc. beaker and 20 to 50 cc. of dilute nitric acid added. If the action is violent, cooling the beaker in water is advisable. When the reaction subsides, 20 cc. of dilute sulphuric acid, 1:1, are added, the mixture placed on the hot plate and evaporated to dense white fumes. The residue is taken up with 150 cc. of water containing 2 to 5 cc. of sulphuric acid and heated until the iron completely dissolves.

The solution is filtered and the silica residue washed first with hot dilute hydrochloric acid, sp.gr. 1.1, and then with hot water added in small portions to remove the iron sulphate. The residue is now ignited and weighed as silica.

Note. If the ash is colored by iron oxide, silica is determined by difference, after expelling the silica by adding 4 to 5 cc. of hydrofluoric acid and a few drops of sulphuric, taking to dryness and igniting the residue.

The following acid mixtures are recommended by the U. P. Ry. For steel, wrought iron and low silicon iron, 8 parts by volume of HNO₃, sp.gr. 1.42; 4 parts of cone. H₂SO₄, sp.gr. 1.84; 6 parts HCl, sp.gr. 1.2 and 15 parts by volume of water.

Silicon in Ferro Silicon

Decompose the alloy with Eschka's mixture (Na₂CO₃-MgO) fusing in a platinum (or nickel) crucible. Dissolve the fusion in HCl and evaporate to dryness. Bake the residue at 135° and take up with HCl and water. Filter, wash and ignite to SiO₂. If titanium is present make a cold acid extraction and digest for one hour with dilute HCl. Take to fumes with 2 cc. H₂SO₄. Take up with water, filter, wash and ignite residue to SiO₂.

\[ \text{SiO}_2 \times 0.4693 = \text{Si} \]

Causes of Error in Silica Determinations

F. G. Hawley (Min. Eng. Jour., March 31, 1917) states the following:

It has been shown that there are three main sources of error in the method commonly used for the determination of silica: A plus error from the small amount of SiO₂ from the flux; another plus error due to impurities retained by the SiO₂; and a minus error due to the solubility of SiO₂ in HCl.

By far the largest and most troublesome error is the one due to the solubility of the SiO₂ in the HCl. This error is much greater than most chemists realize.

The amount of freshly precipitated SiO₂ that dissolves in HCl, depends on the following conditions: First, the amount of acid present; second, the strength of the acid; third, the temperature; and fourth, the length of time the silica is in contact with the acid. There may be other conditions governing the solubility of SiO₂ in HCl, but these seem to be the principal ones. By far the most important is the amount of acid used.

Most chemists use acid of about the same strength to treat the dehydrated silica, and the assays are brought to a boil, insuring the same temperature, and are boiled for a fairly uniform length of time. Few, however, consider the importance of using a definite amount of acid. It seems to be a prevalent idea that the amount of silica dissolved by the acid solution is proportional to the amount of SiO₂ in the sample. When a small bulk of acid is used, this is certainly not the case. Experiments prove clearly that when a small amount of SiO₂ is present, the amount dissolved is proportional to the quantity of acid solution present and not to the amount of SiO₂ in the sample.
Recommended Procedure for Silica (Hawley's Method)

A modification of the peroxide method, as used for routine work, is as follows:

Weigh 0.5 gram of pulp into a 30 cc. nickell crucible and add one scoopful (about 4 grams) of flux composed of equal parts of sodium peroxide and sodium hydroxide. Mix the pulp and flux, and if the sample is known to contain over 50% of SiO₂ put on a cover to prevent loss. Fuse at a low temperature, beginning much below redness and increasing very slowly until a dull red is reached.

When the fusions are made as described the nickel crucibles can be used from 20 to 40 times, but if the temperature is too high, or if there is too much sodium peroxide in the flux, they will burn out much quicker.

Remove the crucibles and partly cool; place in 4-in. casserole, and cover the crucibles with 2-in. watch glasses so placed that a slight opening is left on one side. Through this opening squirt in 2 or 3 cc. of warm distilled water from a wash bottle. This should start a vigorous reaction between the water and the flux. As soon as the action has somewhat diminished add 3 or 4 cc. more water and continue to do this until the fused mass is disintegrated. Toward the end the water should be added with enough force to thoroughly stir the contents. If the crucible gets too cold or the water is not hot enough, the action may cease before the melt is loosened from the crucible; and if too hot the contents may boil over. With a little practice the right conditions are readily found. As soon as the action ceases and the crucible is a little over half full, rinse off the watch glass and from a large burette add about 10 cc. of 60% HCl in small portions so as to avoid too violent reaction; then add 90% HCl until it is in excess. The crucible should now be about full and everything in solution except possibly a little gelatinous silica.

With the fingers or platinum-tipped tongs, remove the crucible, rinse, and place the casserole on the hot plate to evaporate. No harm is done if it boils gently at first. When about half evaporated, place the casserole on an iron or aluminum ring so made that the bottom of the casserole is kept about one-quarter inch above the hot plate. These rings are very beneficial in preventing spitting. When the residue has become dry, cover with a watch glass and bake at about 125° C. for 30 min.; remove and when cool add 15 cc. of 60% HCl and turn about so as to moisten all parts of the residue. Allow to stand a short time and then put on the hot plate, and with cover still on, boil for 3 min. Remove and allow to cool, rinse the sides down with the minimum amount of warm distilled water, and swirl around to loosen any crust still adhering to the sides. The NaCl does not all dissolve, but will readily do so in the wash water.

It is very necessary that the casserole should not be heated after rinsing down the sides with water. After standing a few minutes, transfer the contents to a filter and wash twice with warm water; then once with hot dilute HCl and add a little to the casserole. Rub the sides and bottom of the casserole to loosen any adhering SiO₂ and rinse into the filter. This SiO₂ is ground rather fine by the rubbing and has a tendency to clog the filter, hence it is better to add this after the main portion has been partly washed. Wash the filter twice again with water, place in a crucible, partly dry, and ignite strongly for ten minutes. Weigh the SiO₂ as soon as cool, for it is hygroscopic. A correction is now made for the SiO₂ lost in solution, which under these conditions will amount to about 0.4%. A deduction is made for impurities in the SiO₂ and the SiO₂ from the flux. These gains about balance the solubility loss. Occasional tests should be made to check these losses and gains.
SILVER

Ag, at.wt. 107.88; sp. gr. 10.50-10.57; m.p. 960.5° C.; b.p. about 1950° C.; oxides, Ag₂O, Ag₂O₂, Ag₂O₃

DETECTION

A trace of silver in most substances is detected with greatest certainty by furnace assay methods.

The wet method of detection of silver most commonly practiced, depends upon observation of the properties of the precipitate formed by the addition of a not excessive amount of alkaline chloride to a cold nitric or sulphuric acid solution of the substance undergoing examination. One-tenth milligram of silver precipitated as silver chloride in a cold 200-cc. acid solution gives a very perceptible opalescence to the liquid.

Silver chloride is white when freshly precipitated, tinted pink when palladium is present; in colorless liquids on exposure to light turns brown, violet, blue or black. By agitation, heating or long standing the precipitate becomes coagulated or granular and in such a state is retained by an ordinary filter. The presence of some forms of organic matter prevents coagulation.

Silver chloride is dissolved by concentrated hydrochloric acid; raising the temperature of the acid assists the action. It is dissolved by sodium thiosulphate, alkali cyanides, mercuric nitrate, and alkaline chlorides.

From mercurous chloride, silver chloride, except when constituting a small proportion of the precipitate, is distinguished by its solubility without decomposition in ammonia. Precipitation from its ammoniacal solution is accomplished by acidifying. Lead chloride, precipitable also by hydrochloric acid, is not floeculent, does not coagulate, but dissolves quite freely by heating. Addition of hydrochloric acid to a solution of silicon, tellurium, thallium, tungsten or molybdenum may produce a precipitate, in each case, easily distinguishable from that of silver chloride, but may mask traces of the salt.

Silver, in a cold solution containing free nitric acid, only a small amount of colored salts and no mercury, may be detected through the formation of a white precipitate, similar in appearance to silver chloride, by addition of a slight excess of an alkaline thiocyanate.

When a solution of silver salt is added to a mixture of 20 cc. ammonium salicylate (20 gr. ms. salicylic acid neutralized with ammonia, a slight excess added and the whole made up to 1000 cc.) and 20 cc. of a 5% solution of ammonium persulphate added, an intense brown color is produced, which will detect the presence of a 0.01 milligram of silver. Lead does not affect the test.

When it appears that the chloride or thiocyanate test for silver is not positive on account of the presence of other precipitable elements, the precipitate, after it

Chapter contributed by W. G. Derby.
settles, is filtered through the finest quality of paper, and the mixture of the ash of the incinerated filter with dry potassium carbonate heated on charcoal with a mouth blowpipe. If silver is present and not associated with a large amount of palladium, there will be found on the charcoal pellicles of the color characteristic of silver, which have no white or yellow sublimate when melted in the oxidizing flame of the blowpipe. The pink palladium salts of silver precipitated by a chloride or thiocyanate before the blowpipe produces metal which is dull in appearance and not readily melted.

Notes. Silver may be recognized in a solution of concentration 1 to 240,000 by the reduction of its salts with alkaline formaldehyde. Whithby's\(^1\) method of detection and estimation of small amounts of silver depends upon the formation of a yellow color through addition of sucrose and sodium hydrate. Ammonium hydrate interferes, but bismuth, cadmium, copper, mercury of either valence, lead or zinc, in amounts equal to that of the silver, do not.\(^2\) Maletesta and DeNola add to the solution to be tested a few drops of a solution of nitrate of chromium and then potassium hydrate to alkalinity. A brownish turbidity or black precipitate of silver oxide forms. The limit of sensitiveness is 0.5 milligram in 100 cc.

ESTIMATION

Silver is determined in copper, lead, silver, sulphur or other ores, in copper and lead furnace by-products, and in lead by furnace assay methods, in which a preliminary acid treatment of the sample is rarely employed; in native copper ore, in copper, copper alloys, gold, gold alloys and in the slime from the electrolytic refining of copper or lead by furnace methods, in which a preliminary acid treatment of the sample is employed, in silver alloys by volumetric or gravimetric methods; in mercury by a gravimetric method; in cyanide mill solution or solutions containing much organic matter by furnace process on the residue obtained by evaporation or precipitation; in silver plating electrolyte by electrolysis.

Solubility. Nitric acid, dilute or concentrated, attacks silver rapidly when hot. The presence of a soluble chloride, iodide or bromide in the solvent or substance will retard and may prevent solution. Unless oxidizing agents are present, dilute sulphuric acid has practically no action on massive silver, but hot, strong acid commences to be an active solvent at a concentration of 75% H\(_2\)SO\(_4\). Hydrochloric acid attacks silver superficially. The action of alkaline hydrates or carbonates in solution is inappreciable; in a state of fusion, slight.

Furnace Assay Methods. These will be described in the chapter devoted to that subject.

\(^1\) Armani and Barbuni, Zeit. Chem. Ind. Kolloide, 6, 290.
\(^3\) Bull. Chim. Farm., 52, 533.
SILVER

GRAVIMETRIC METHODS FOR THE DETERMINATION OF SILVER

Precipitation as Silver Chloride

**Introductory.** Although silver might be determined as an iodide or bromide, the fact that these halides are more sensitive to light than the chloride, and decompose more readily, with liberation of the halide and the formation of sub-halides, has led to the precipitation of silver as the chloride.

**Reaction.** \( \text{AgNO}_3 + \text{HCl} = \text{HNO}_3 + \text{AgCl} \).

**Reagents. Hydrochloric Acid.** One volume of strong HCl (sp.gr. 1.19) diluted with five volumes of water (sp.gr. of dilute HCl 1.035); 1 cc. contains 0.074 g. of HCl, equivalent to 0.219 g. of Ag.

**Nitric Acid.** One volume of strong HNO₃ diluted with 1.6 volumes of water (sp.gr. of acid is 1.2); 1 cc. contains 0.38 g. of HNO₃, which would dissolve 0.64 g. of Ag.

1. **Preparation of the Sample. Solution. Silver Alloys.** Place 0.5–1.0 gram of the alloy in an Erlenmeyer flask and add 5 cc. of the dilute nitric acid. Heat gently until the alloy is dissolved and the brown fumes are expelled. The solution is now diluted to about 100 cc. and the silver precipitated as stated below.

**Soluble Silver Salts.** The salt is weighed into a weighing bottle; 1.0–2.0 grams are sufficient for a determination. The solution is now diluted to about 100 cc. and the silver precipitated as stated below.

**The Halides of Silver.** These are best brought into solution by fusion with about six times the weight of the sample of sodium carbonate. This converts the silver into the carbonate and the halide combines with sodium and is dissolved out in water. The silver carbonate is washed free of the halide and then dissolved out in dilute nitric acid.

**Ores of Silver.** These may be brought into solution by digestion with nitric acid, the residue remaining is treated as stated above under halides of silver. Unless the ore is very high in silver, it is preferable to make the analysis by Fire Assay.

2. **Precipitation of Silver Chloride.** Heat the solution to boiling and add from a burette, drop by drop, 5 cc. of dilute hydrochloric acid. This is sufficient to precipitate over 1 gram of silver. The excess of acid is desired as the chloride is less soluble in free hydrochloric acid.

**Note.** The chloride is soluble in strong hydrochloric acid, hence a large excess is undesirable. Shaking or vigorously stirring the mixture will clear a cloudy solution. This is necessary to coagulate the silver chloride, as the fine suspended silver chloride will pass through the filter paper.

3. **Filtration: (Procedure if Filter Paper is Used).** Decant the clear solution into the filter. Test the filtrate with a drop of dilute HCl to make sure all the silver is precipitated. Now wash two or three times by decantation, using hot water containing 1 cc. of HNO₃ per 100 cc. of distilled water. Transfer the silver salt to the filter and continue washing until free from chlorides. Six to eight additional washings should be sufficient.

4. **Dry** the filter and silver salt in the oven at 100–110 degrees C.

5. **Remove** as much of the silver chloride as possible from the paper, placing the salt on a glazed sheet of paper, covering it with a watch glass.

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1 Contributed by Wilfred W. Scott.
6. **Ignite** the filter in a crucible (whose weight has been ascertained), then add to the ash a drop of nitric acid and a drop of hydrochloric acid. **Heat gently** to expel the acids. (Handle the crucible with tongs. Do not place on the table.)

7. **Transfer** the chloride from the glazed paper to the crucible and heat gently until the salt just begins to fuse on the sides of the crucible.

8. **Cool** in a desiccator for fifteen to twenty minutes.

9. **Weigh** as AgCl, making an allowance for the weight of the crucible. AgCl $\times 0.7526$ gives the weight of Ag in the salt.

10. Calculate the per cent silver from the weight of sample taken.

3a. **Procedure if a Gooch Crucible is Used.** Prepare a Gooch crucible with a fairly thick pad of asbestos fibre (1/8 in. thick). Wash once with alcohol and dry to constant weight at 110 degrees C. Keep a record of the weight.

4a. **Wash** the precipitate by decantation, pouring the washings through the Gooch, with application of suction. Transfer the chloride to the crucible and wash free of chlorides.

5a. **Finally** wash once with alcohol and dry at 110 degrees C. to constant weight.

6a. **Calculate** the percentage of silver as directed in the first method.

**Notes.** **Solubility** of the silver halides. Milligrams of salt per 100 cc. of water. AgCl 0.00017; AgBr 0.00004; AgI 0.00001.

**Interferences.** Antimony, mercury, and lead interfere and should be removed if present.

**Paper** is separated in the first procedure as the carbon reduces the salt to metallic silver, causing low results.

**Gooch.** If the asbestos fibre is poor, a loss of the fibre will occur during washing of the precipitate, causing low results.

**Light.** Strong light will affect the salt causing the formation of the subhalide of silver and the liberation of chlorine. A drop of nitric followed by a drop of hydrochloric acid will restore the original form. This treatment is necessary only when a dark-colored salt is obtained by light action.

**Large Samples.** It is frequently advisable to dissolve larger samples than stated. The solution is made to 500 cc. and a portion taken for analysis.

**Solubility.** Nitric acid, dilute or concentrated, attacks silver rapidly when hot. The presence of a soluble chloride, iodide or bromide in the solvent or substance will retard and may prevent solution. Unless oxidizing agents are present, dilute sulphuric acid has practically no action on massive silver, but hot, strong acid commences to be an active solvent at a concentration of 75% H$_2$SO$_4$. Hydrochloric acid attacks silver superficially. The action of alkaline hydrates or carbonates in solution is inappreciable; in a state of fusion, slight.
Determination as Silver Cyanide

In the analysis of mercury, the nitric acid solution of the metal is nearly neutralized with a solution of sodium carbonate. Potassium cyanide solution is then added until the precipitate, which first forms, is dissolved. Then under a hood with strong draft, dilute nitric acid is added in slight excess of the quantity required to combine with the base in the amount of potassium cyanide present. The precipitate of silver cyanide, practically insoluble in dilute nitric or hydrocyanic acid, is coagulated by stirring or long standing and filtered from the cold solution of mercuric nitrate by use of a tared paper-bottomed Gooch crucible. The precipitate is washed with cold dilute nitric acid (1–10) until a test of the washings with hydrogen sulphide shows the absence of mercury. The crucible is dried at 100° to constant weight.

\[ \text{AgCN} \times 0.8057 = \text{Ag}. \]

**NOTES.** Determination of silver as metal through precipitation with hypophosphorous acid \(^1\) as silver sulphide or as silver chromate \(^1\) are methods of doubtful technical application.

Exner,\(^4\) using a platinum dish as the cathode and a 2-in. diameter bowl-shaped spiral anode revolving 700 R.P.M., deposited 0.4930 gram from about 125 cc. of a hot electrolyte containing 2 grams potassium cyanide in ten minutes at N.D.\(_{100}\) 2 amps. The above methods presume the absence of other metals precipitable under the conditions mentioned.

**Electrolytic Method\(^5\)**

According to the strength of the silver bath 10 or 20 cc. are filtered into a tared 200-cc. platinum dish and according to the greater or smaller excess of cyanide present, \(\frac{1}{4}\) to 1 gram of potassium cyanide in solution is added. The electrolyte diluted to about a half inch from the edge of the dish is kept, by a flame underneath, at a temperature of 60°–65° C. during the period of electrolysis at N.D._{100} = 0.08 amp.

Complete precipitation, which requires three to three and a half hours, is recognized by test with ammonium sulphide. Without interruption of the current, by use of a siphon, displacement of the electrolyte with water is accomplished. The dish is rinsed with alcohol and ether, dried at 100°, weighed and silver obtained calculated to grams per liter or cubic foot.

**NOTES.** Benner and Rose\(^6\) deposit 0.15 gram in twenty minutes with a current of 3 amperes from 50 cc. of electrolyte containing 8 grams potassium cyanide and 2 grams potassium hydrate on a 9-gram platinum gauze cathode.


\(^3\) Gooch and Bosworth, Am. J. Sci., 27, 241.


\(^5\) J. A. C. S., July, 1911, 1106.
VOLUMETRIC METHODS FOR DETERMINATION OF SILVER

Volhard’s Thiocyanate Method

This method is especially adapted to the determination of silver in cold dilute nitric acid solution. The method is based on the greater affinity of silver ions than ferric for thiocyanate ions. When the silver has been precipitated as thiocyanate, the ferric indicator reacts with the thiocyanate producing the characteristic red color.

Reactions: \[ \text{AgNO}_3 + \text{KCNS} = \text{KNO}_3 + \text{AgCN} \text{S ppt.} \]
\[ \text{Fe(NO}_3)_3 + 3\text{KCNS} = 3\text{KNO}_3 + \text{Fe(CNS)}_3 \text{ red} \]

Note. Mercury and palladium, highly colored salts of cobalt and nickel, copper if over 60% in the sample, nitrous acid and chlorine interfere and should be absent.

Ferric Indicator. Saturated Solution. Make 100 cc. of a saturated solution of ferric ammonium sulphate or ferric sulphate. Add sufficient HNO₃ (freed from nitrous acid by heating) to clear up the solution and produce a pale yellow color. .5 cc. of this reagent is used in a test. Ferric nitrate may be used in place of sulphate.

Standard Silver Solution. A N/10 solution contains per liter 10.788 grams of silver, or 16.989 grams of AgNO₃. A solution containing 0.005 gram of Ag per cc. is a convenient strength.

Dissolve 1.0 gram of pure silver foil in 10 cc. of dilute HNO₃, 1 : 1.6 (sp.gr. 1.2). Boil to expel the nitrous oxides and dilute to 200 cc. 1 cc. will contain 0.005 gram of silver.

Thiocyanate Reagent. Dissolve 7.4 grams NH₄CNS or 9.2 grams of KCNS in water and dilute to 1000 cc. Standardize the solution against the standard silver solution. Half this strength is used for the weaker silver solution above.

Standardization. Measure 50 cc. of the standard silver solution into a beaker or an Erlenmeyer flask and dilute to 100 cc.

Add .5 cc. of the ferric indicator.

Titrate with the thiocyanate reagent until a permanent red tint is obtained. Each addition of the reagent will produce a temporary red color which fades immediately as any silver remains uncombined with the thiocyanate. A trace of excess of the reagent produces a permanent faint red color.

Note the cc. required and calculate the value of 1 cc. in terms of silver. 50 cc. of the standard silver solution contains 0.25 g. of Ag.

Some prefer to have the thiocyanate exactly equal in strength to the silver solution. Should this be desired, dilute to the necessary volume and again standardize against the silver solution.

The value of 1 cc. should be recorded on the container.

Determination of Silver in the Unknown

Weigh 0.25–0.3 gram of the alloy and dissolve in an Erlenmeyer flask by addition of 5 cc. of dilute HNO₃ (sp.gr. 1.2). Heat to expel lower oxides.

Cool, dilute to about 100 cc. and add 5 cc. of the ferric indicator.

Titrate with the standard thiocyanate reagent to a permanent faint red color.

From the cc. of the reagent used, calculate the amount of silver present in the sample taken.

Divide the result by the amount of sample taken and multiply by 100 = percent Ag in the alloy.

†Contributed by Wilfred W. Scott.
SILVER

GAY–LUSSAC METHOD

This very accurate method is especially adapted to the valuation of silver bullion, but may be applied in principle to the determination of silver in a nitric acid solution which contains as little as 100 milligrams of the metal, providing the volume of the solution is not so large or color so deep as to make a precipitate of silver chloride equivalent to 0.1 milligram of silver indistinguishable. Metals that interfere are mercury and tin.

The method is founded upon the almost absolute insolubility of silver chloride or bromide in cold dilute nitric acid and the property of the precipitate becoming so completely coagulated through agitation that it settles speedily, leaving a liquid sufficiently clear to permit of observance of any precipitate produced by further addition of precipitant.

Reactions:  \[ \text{AgNO}_3 + \text{NaCl} = \text{NaNO}_3 + \text{AgCl} \downarrow \]
\[ \text{AgNO}_3 + \text{NaBr} = \text{NaNO}_3 + \text{AgBr} \downarrow \]

The use of a bromide is preferable to a chloride salt as a reagent, chiefly because on account of the greater insolubility of silver bromide, the end-point of the operation of titration is more sharply defined.

The presence of free sulphuric acid is prejudicial to a very close determination, because of the volume of liquid required to keep silver sulphate in solution, and also because the result of agitation after addition of precipitant is apt to be a fine precipitate which does not readily settle.

The factor of volume change per degree change of temperature from 15 to 21°C. is approximately 0.00012; from 20 to 26°C., 0.00019; from 25 to 31°C., 0.00024.

Although the approximate precipitating value should be known by previous test, it is the better practice to determine the exact value by running two or more checks of pure silver simultaneously with each batch of assays than to apply the temperature correction factor.

Apparatus. The apparatus required consists of a pipette which will deliver approximately 100 cc. with an accuracy of not over 5 milligrams variation in weight of the standard solution at constant temperature between successive deliveries, 10 cc. burettes with glass stopcocks; and 8-oz. narrow mouth, round, flint-glass bottles with high, tightly fitting stoppers; the assay bottles should be of a quality which will endure heating in a steam bath or on a hot plate.

Since the end-point by the Gay-Lussac method depends upon the observance of cessation of precipitation, it is evident, in order to avoid undue tediousness in its operation, that the silver content of the amount of sample taken for assay should be known within a few milligrams.
METHOD OF U. S. MINTS

U. S. Mint Modification of the Gay-Lussac Method for Silver

This method is used in all three of the United States Mints and the U. S. Assay Office, New York City, for determining silver in ingots and fine silver has been found very satisfactory both as regards speed and accuracy.

Standard Solutions. Two standard salt solutions are regularly used in the determinations. The first is called a "normal" and the second a "decimal" solution.

The first or "normal" solution is made of such concentration that 100 cc. of it will precipitate exactly 1002 milligrams of silver. 5.43 grams of C. P. sodium chloride are dissolved in water and diluted to make one liter of solution. It is kept in a large 40-liter carboy and is siphoned off as needed.²

The decimal solution is made by diluting 100 cc. of the "normal" solution to a liter.

Standardization

The normal solution must be standardized at frequent intervals because of temperature changes which affect the concentration of the solution. The factor of volume change per degree change of temperature from 15 to 21 degrees C. is approximately 0.00012; from 20 to 26 degrees, 0.00019; from 25 to 31 degrees, 0.00024.

The standardization is carried out as follows:

Solution and Precipitation. A "proof" of 1004 milligrams of fine silver is carefully weighed out, placed in a glass-stoppered 8-oz. bottle and dissolved in 10 cc. of 1:1 nitric acid on a hot plate. Then 100 cc. of "normal" salt solution, sufficient to precipitate 1002 grams of silver, are added from an upright stationary pipette. The pipette is filled by means of a siphon controlled by a stopcock convenient to the right hand. After filling, the left forefinger is placed over the pipette, the rubber hose connection removed from the bottom, and the bottle containing the dissolved proof placed underneath, when the forefinger is removed, allowing the contents to drain into the bottle, shaking the bottle once or twice to mix the solution. Then 2 cc. of the decimal solution are added by means of a small pipette graduated in cc. and held in the hand, and the stoppered bottle is placed in the shaker.

The shaker violently agitates the solution and causes the precipitate to coagulate and settle. The bottle is removed after four minutes.

More agitation than is absolutely necessary should be avoided, due to the increasing tendency of the precipitate to become granular and settle slowly.

¹ Communicated to W. W. Scott by F. C. Bond, Humid Assayer, Denver Mint, Colorado.
² 40 liters are made up at one time by the Denver Mint. The strength of the solution may be regulated by the size of the pipette used. At the Denver Mint 4.83608 grams per liter are taken of the C. P. NaCl, since the pipette delivers more than 100 cc.
Titration. The bottle containing the coagulated precipitate is best placed upon a shelf in a window through which only reflected light enters, at such a height that the top of the solution is upon a level with or slightly above the eye. The shelf is backed by a blackened board which covers the window under the shelf and extends nearly to the top of the bottle.

The bottle stands a moment to allow the precipitate to settle and 1 cc. of the decimal salt solution is added from the hand pipette. The solution is shaken by moving the top of the bottle through a small arc once or twice and the reading is taken after 10 seconds. A slight white cloud forming at the top of the solution and more pronounced when viewed from below constitutes a "show" and indicates that only a small portion of the cc. added was needed to precipitate the remaining silver. This is the desired condition for a proof.

The reading is taken as a "show," "quarter," "half," "three quarters," and "one"; according to the portion of the cc. of salt solution necessary to precipitate the remaining silver. If the cloud is deep enough to indicate that all of the cc. has been used, the bottle should be placed in the shaker and the precipitate coagulated, after which another cc. is added and the reading taken as before with the addition of one cc.

The assignment of the proper value to the precipitate is difficult for the novice and experience in comparison is of much more value than any description could be. However it may be stated that a slight precipitate extending through the upper half of the solution after a slight uniform shake should be called a "quarter," a precipitate of the same appearance throughout the solution is a "half," a heavier precipitate throughout is called "three quarters," while a still denser precipitate is read "one" and should be confirmed by shaking and adding another cc., which should yield a "show," a very faint cloudiness.

The "show" of the proof influences the reading of the determinations and its appearance should be kept constantly in mind, since a "quarter" on a determination means that one quarter of a cc. more of the decimal salt solution was used in precipitating silver than was used in the proof. Thus the proof reading or "show" is taken as zero and the concentration of the "normal" solution should be adjusted so that the proof gives as light a show as possible.

Procedure. In the following determinations it is advisable to run a standard of proof silver side by side with the sample bullion for comparative purposes.

Fine Silver. For silver bullion 998 parts fine or above a sample of 1005 milligrams is weighed out, dissolved, precipitated and titrated as described under Standardization.

In case 1 cc. was added, gave a heavy precipitate, was agitated and a second cc. added which gave a "half," the reading would be $1\frac{1}{2}$ and the silver would be

$$\frac{1002 + 1\frac{1}{2}}{1005} = \frac{1003.5}{1005} = 998.5 \text{ fine.}$$

In case a large number of samples are to be run, tables may be prepared for each fourth of a cc. which will make the above calculation unnecessary.

Coin Ingots. In determining the silver in silver coins or in silver coin
ingots as they come from the melting room, which are usually within 1½ points of 900 fine, the sample weighed is 1115 milligrams. The color given to the solution by the copper base need not interfere with the titration.

Notes on the Method

Determinations may be made on silver bullion of almost any grade if the approximate fineness is previously determined by fire assay or the Volhard method. It is ordinary practice to weigh up the sample at the next figure even five milligrams above that calculated. Thus if it is found from preliminary assay that 1082 milligrams of bullion will contain approximately 1002 milligrams of silver, 1085 milligrams will be weighed out for a sample.

Interfering Elements. There are very few substances which will be found in bullion in sufficient quantity to interfere with the process. The presence of free sulphuric acid is detrimental to a very close determination.

The use of a bromide is considered as preferable to a chloride as a reagent but the chloride is commonly used.

An eyeshade assists in making the readings accurately.

The chloride precipitate is reduced to a blue subchloride on standing in the sunlight so that the bottle should be exposed to the light as little as possible.

A set of twelve samples, with the bottles transported in a suitable wire frame, is usually run at one time.

A decimal solution of silver nitrate of equal strength with the decimal salt solution may be used for back titration, however the end-point is less distinct and it is advisable to weigh out a larger sample.

Duplicates are commonly run.

Tables giving the fineness for different classes of materials examined for each reading facilitate calculations and are recommended for use.

To determine the 1/2, 1/4 and 1/8, a beginner should have a pipette, graduated in 1 cc., holding 5 to 7 cc. length for hand use with one cc. divided in the 1/2, 1/4 and he should use the same until he is familiar with the density of precipitates produced by one cc. with silver equivalent to the above fractions.

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No pipette is of use in the practice of the Gay-Lussac method which shows any tendency to spatter at the beginning or ending, or yields a quickly following or clinging drop at the completion of discharge. The film of liquid adherent to the inner surface of the body of a good pipette will drain without sign of rivulet effect and be retained by the capillary of the discharge tube for at least a minute.
In the following table the left hand column represents the milligrams of bullion to be taken, the top line indicates the cc. of decimal solution required in addition to the 100 cc. of normal solution, the figures at the intersecting lines give the fineness of the bullion.

Ascertain the approximate fineness by a preliminary assay, consult the 0 column for the nearest corresponding figure slightly higher, the figure on the left of this is the weight of bullion to be taken. Now if the test required, in addition to the 100-cc. normal solution, 4 cc. decimal solution and 115 milligrams of bullion were taken, the fineness of the bullion would be 900.4. See table under Silver Coin Bullion.

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### Recovery of Silver from Silver Residues

Convert the residues to silver chloride by treating with hydrochloric acid and filtering off the chloride and washing. Dissolve the chloride in ammonium hydroxide added in slight excess. Add sodium hyposulphite, Na₂S₂O₃ (not thiosulphate, Na₂S₄O₆). Metallic silver is formed. Thiosulphate gives silver sulphide. Photographers' residues containing “hypo” yield silver sulphide.
Combination Methods

Combination of the operations of the Gay-Lussac and Volhard methods have been devised to avoid the tediousness incident to the performance of the Gay-Lussac method by the unexperienced. By the modified methods the amount of sample to be weighed out is determined by preliminary assay, and is dissolved in the same manner as in the practice of the Gay-Lussac method, but with the added precaution to decompose nitrous acid in the silver solution by gentle boiling when completion of the titration is to be accomplished by the Volhard method.

The operation of the combination methods consists briefly of precipitation of all but a few milligrams of silver by a standard solution of alkali thiocyanate, chloride or bromide added from the Stas pipette and estimation of the excess of silver with a decimal solution of thiocyanate or by a colorimetric or nephelometric method.

The procedure favored by the writer is to use a standard solution of potassium bromide as the pipette precipitant. After the liquid is cleared by shaking, it is decanted as completely as possible into a 500-cc. Erlenmeyer flask. The precipitate is washed by five 30-cc. portions of water containing a little nitrous-free nitric acid, each portion being shaken before decanting. Using the same amount of ferric indicator as in the check assays, decimal thiocyanate solution is added until not a very deep tint remains permanent after vigorous agitation. Decinormal silver solution is then added until the tint is discharged. When the assay is sufficiently free of copper or other colored salts to permit accurate matching of tints, the decanted liquid, which may contain particles of silver bromide without interference, is titrated with decimal thiocyanate to the appearance of a tint which will match that of the check assays. Except when colored salts are present in such quantity as to make recognition of the point of bleaching of the ferric thiocyanate coloration uncertain, the extreme range of error is 0.3 part per 1000.

For colorimetric method, see Smith, I.M.M Bull. No. 28. Determination of the residual silver in the filtrate from the thoroughly washed silver bromide precipitate is practicable by use of a suitable nephelometric apparatus.¹

Denigé’s Cyanide Method ²

Silver which has been precipitated as chloride may be determined volumetrically by dissolving the precipitate with a measured quantity of a standard solution of potassium cyanide of about decinormal strength.

\[ \text{AgCl} + 2\text{KCN} = \text{KAg(CN)}_2 + \text{KCl}. \]

Potassium iodide is then added and the excess of standard potassium cyanide solution determined by addition of potassium iodide and titration to the first appearance of a permanent precipitate with decinormal silver nitrate.

\[ \text{AgNO}_3 + \text{KI} = \text{AgI} + \text{KNO}_3; \ \text{AgI} + 2\text{KCN} = \text{KAg(CN)}_2 + \text{KI}. \]

Note: If the last portion of the precipitate of silver chloride dissolves with difficulty in the potassium cyanide, the liquid may be decanted into another beaker and solution completed with ammonia. The solutions are combined.

SILVER

Miscellaneous Volumetric Methods

Silver may be determined by addition from a burette of a portion of a known volume of its neutral or slightly acid solution to a standard solution of sodium chloride which contains a little potassium chromate or bichromate and sufficient chlorine-free magnesium oxide emulsion to neutralize free acid. The end-point is indicated by the formation of a reddish or brown precipitate.

By Pisani's Method: a standard solution of iodide of starch is added to a very dilute neutral solution of nitrate of silver until the fluid becomes permanently blue.

By Vogel's Modification of Pisani's Method: the silver solution, which may contain free acid, is titrated with standard starch iodide solution after addition of nitric acid containing nitrous acid.

By Andrews' Modification: the standard solution of starch iodide is added to a solution of silver nitrate which contains so much ferrous nitrate or sulphate that iron will be in excess of the silver present.

\[ 2\text{AgNO}_3 + 2\text{Fe(NO}_3)_2 + \text{I}_2 = 2\text{AgI} + 2\text{Fe(NO}_3)_3 \]

By Gooch and Bosworth's Method: silver is determined by precipitating with an excess of potassium chromate, dissolving the precipitate in ammonia, reprecipitating by boiling to low volume and determining iodometrically either the chromate ion combined with the silver, or that remaining after precipitating the silver with a known amount of standard potassium chromate.

Nephelometric Method

This method is practicable for the determination of a small concentration of silver in a clear and colorless liquid. Less than 2 miligrams of silver can be estimated with considerable accuracy by matching the opalescence produced by a drop of hydrochloric acid with that from a known quantity in a liquid of the same volume, depth and temperature. Intensity of opalescence attains the maximum in about five minutes after precipitation. Standard silver solution is made by dissolving 500 milligrams standard silver (see Preparation at close of chapter) with several cc. of dilute nitric in a liter flask and making the solution up to the mark. For most technical determinations the apparatus may consist of clear glass cylinders (color tubes) of suitable size. More accuracy can be arrived at by use of a nephelometer of refined construction, for example the combination of a projection lantern and a Duboseq colorimeter.

Preparation of Pure Silver. The volumetric methods used for the determination of high percentages of silver, employ solutions which should be standardized by metal of the highest purity. For the preparation of this metal, the electrolytic method as described below is preferred by laboratories which are suitably equipped.

2 Freseinus, "Quantitative Analysis."
For the manufacture of a large quantity—several pounds—a basket-like support for the anode is made of several glass rods bent so that they will hang from the rim of a tall 1000-cc. or larger beaker or battery jar and dip into the receptacle about an inch. Smaller anodes may be supported by the positive wire or by a cloth bag fixed in place by a string under the flare of the rim of the beaker. In any arrangement for the support of the anode, allowance of room should be made for the introduction and free movement of an L-shaped stirring rod.

The cathode may consist of sheet silver or of platinum foil, and lies flat on the bottom of the beaker. The immersed length of the silver or platinum wire leading from the cathode should be covered with rubber tubing.

Commercial silver, usually about 999 fine, may be used for the anode, but by retreatment of the deposit, very impure silver may be used, providing that the quantity of tellurium present is very low. The presence of tellurium will exhibit itself in the impossibility of obtaining the desired coarsely crystalline deposit.

Tellurium in moderate quantities may be removed by melting the silver in a crucible or scorifier, adding niter, permitting the silver to nearly freeze, raising the temperature and pouring into a hot crucible or scorifier in which the operation is repeated, preferably in a muffle furnace, until the surface of the silver is without streaks or spots when cooled to near freezing. An oxidizing atmosphere about the molten metal should be maintained. On the basis of 172 grams silver per cubic inch an anode mould for any convenient amount of silver may be shaped from 4-in. pieces of 1-in. square rod on a smooth iron plate. Just before the anode bar sets in the mould, a silver terminal strip or wire is plunged into it.

After coating the contact wire or strip and the surface of the anode about it with sealing wax, the anode is wrapped with filter paper, held firmly in place by string or rubber bands. If the anode weighs half a pound or more, the anode is also wrapped with cotton flannel which has been washed with water until free of chloride. A porous dish, cylinder or filter cone can be used instead of filter paper and cloth.

The electrolyte contains about 4% of C.P. silver nitrate and half a per cent of chlorine-free nitric acid in distilled water, and fills the beaker or jar so it wets only the lower surface of the anode.

The current, of about 0.1 ampere per square inch of cathode surface at the start, is raised after deposition has proceeded for a few minutes to the limit at which a coarsely crystalline deposit can be maintained.

Inasmuch as the electrolysis proceeds at a rate of 4 grams per ampere-hour, some attention is required to break up short circuits and to pack down the rather bulky deposit. The deposit, if coarse, can be washed very easily free of electrolyte, and after heating to near redness is in the form preferred for use by many assayers.

Other methods which may be employed consist of dissolving the crude silver with nitric acid about 1.20 m. p. gr. or with hot concentrated sulphuric acid, if platinum is present, separating the gold and platinum by filtration, precipitating AgCl with not too large an excess of HCl, stirring the precipitate until it coagulates, washing repeatedly with hot water until a washing is obtained which shows no precipitate with H₂S, reducing the silver chloride by contact with pure zinc, wrought iron or the silver terminal of a carbon-silver couple aluminum foil, and washing with hot dilute HCl until a test of the decanted liquid indicates absence of the precipitating element. The dried silver, mixed with about 1% of dry sodium carbonate, is packed into a clay crucible, the inside of which has been glazed with borax glass and covered with a layer of crushed charcoal.

The sodium carbonate is omitted in case it is desired to melt silver refined by electrolysis.

The silver melted in the tightly covered crucible is poured into an iron mould which has been chalked or black leaded.

By Knorr's method, a solution of silver nitrate from which excess of nitric acid has been removed by evaporation is freed of metallic impurities by adding enough sodium carbonate to precipitate one-tenth of the silver, boiling and filtering. The silver in the filtrate is precipitated by sodium carbonate and the precipitate decomposed without addition of reducing reagent, by melting in a crucible. Excess sodium carbonate carried down with the precipitate of silver carbonate will cover the fusion and such as adheres tightly to the metal is readily removed by hydrochloric acid. The metal should be smelted under charcoal.

1 Liddell, "Metallurgists and Chemists' Handbook."
If the cover of the charcoal is omitted or burned away during the fusion, the molten metal is capable of absorbing oxygen from the atmosphere to the extent of about 0.25% of its weight. This gas is expelled during the passage of the metal into the solid state and produces a casting which cannot be rolled into smooth sheets.

The most convenient size and shape of castings for rolling is but little larger than a lead pencil. Before rolling, the casting is cleaned of particles of the mould wash. After rolling to about cardboard thickness, the sheets may be cut up into strips of convenient size and length, then digested with dilute hydrochloric acid (1 to 5 of water) washed with ammonia and finally with pure water.

The silver then should be dried and annealed by heating to redness. It is best preserved in a glass-stoppered, salt-mouth bottle and should be exposed to laboratory atmosphere as little as possible.

The purity of each batch of silver made should be compared by use of the Gay-Lussac method with standard silver, the purity of which has been determined by analysis of a 50- or 100-gm. portion for Se and Te, As, Sb, Pb, Cu, Au, and the element employed in reducing silver chloride, if the reduction method was followed in the manufacture of the metal.
THE FIRE ASSAY FOR GOLD AND SILVER

Definitions. Fire assaying is a branch of quantitative chemical analysis in which metals are determined in ores and metallurgical products by extracting and weighing them in the metallic state. The methods employed involve slag-melting temperatures and the use of reducing, oxidizing and fluxing reagents, and are in principle the same as those used in metallurgy.

The metals ordinarily determined by fire assaying are gold, silver and platinum. Antimony, bismuth, lead and tin can be determined in this way also, but the results are usually more or less inaccurate.

An ore is a mineral aggregate from which one or more metals can be extracted at a profit.

Metallurgical products include a large number of metal-bearing mixtures and compounds, ranging from high grade gold and silver bullion to very weak cyanide and sulphate solutions.

The constituents of an ore are usually divided into two general classes, the valuable minerals containing the metals, and the non-valuable minerals or gangue. A similar classification can be made in the case of many metallurgical products. In gold and silver bullion and other alloys all of the components are metallic, and the assaying problems involve simply the separation of metals.

General Outline

With ores and metallurgical products containing non-metallic elements the process consists, briefly, in the production of two liquids, liquid lead containing the valuable metals, and liquid slag containing the waste matter or gangue. The two liquids separate from each other by reason of the great difference in specific gravity. The valuable metals are separated from the lead and from each other by taking advantage of differences in chemical properties. The slag is discarded.

In the operation of the process the gold and silver, and platinum, if present, are collected from the metal-bearing portion of the ore or metallurgical product by means of molten lead reduced from litharge or lead oxide. The gangue is converted into a fusible slag by means of reagents known as fluxes.

The effectiveness of the fire assay in separating gold, silver and platinum from ores and metallurgical products depends upon two properties of these metals: first, their weak affinity for non-metallic elements, especially at high temperatures, and second, their very great affinity for molten lead. The collection of the precious metals in the lead, therefore, is the simplest part of the process. The fluxing of the gangue is much more difficult, and requires considerable knowledge and skill. If the fluxing is properly performed, the collection of the valuable metals usually takes care of itself.

Reagents. A flux is a substance which when heated in contact with some difficulty fusible compound either combines with it or takes it into solution,

1 By Irving A. Palmer, Professor of Metallurgy, Colorado School of Mines.
in each case producing a compound or mixture which is easily fusible at ordinary furnace temperatures. The principal fluxes and other reagents used in fire assaying are described in the following paragraphs.

**Litharge** or oxide of lead, PbO, melting point 883° C., has several important uses. It furnishes the lead which collects the precious metals; it readily combines with silica, producing easily fusible silicates; and it acts as an oxidizing and desulphurizing agent. It is a very strong basic flux.

**Sodium carbonate**, Na₂CO₃, melting point 852° C., is a powerful basic flux. It combines with silica and alumina, producing fusible silicates and aluminates. When molten it has the property of dissolving or holding in suspension a number of refractory gangue materials. To some extent, also, it acts as an oxidizing and desulphurizing agent. Potassium carbonate, K₂CO₃, melting point 894° C., is rarely used in fire assaying because of its greater cost.

**Borax glass**, Na₄B₂O₇, melting point 742° C., is an acid flux used for combining with or dissolving the basic and some acid constituents of the gangue, producing easily fusible complex borates and mixtures of borates and other compounds. Even silica dissolves to some extent in molten borax glass.

**Silica**, SiO₂, melting point 1755° C., is a strong acid flux. It combines with metallic oxides and produces silicates which in many cases are considerably more fusible than silica itself.

**Granulated lead** or **test lead** is used in the scorification assay, which is conducted under oxidizing conditions, and in which, therefore, litharge could not be employed as a source of lead.

**Lead foil** or **sheet lead** is used in the assay of gold and silver bullion. It, as well as the granulated lead, should be free from silver and bismuth.

**Flour** is known as a reducing agent. It contains carbon, which reduces lead from litharge. Charcoal was formerly used for this purpose, but it is not so convenient.

**Argo** or **crude cream of tartar**, KHC₄H₄O₆, is both a basic flux and a reducing agent. On being heated it decomposes as follows:

\[ 2\text{KHC}_4\text{H}_4\text{O}_6 + \text{heat} \rightarrow \text{K}_2\text{O} + 5\text{H}_2\text{O} + 6\text{CO} + 2\text{C}. \]

It is effective in assays requiring strong reducing action and low temperatures.

**Iron** is sometimes used as a desulphurizing and reducing agent. It decomposes most of the heavy sulphides, yielding the metals and iron sulphide.

**Potassium nitrate**, KNO₃, melting point 339° C., is a powerful oxidizing agent. It is used to neutralize the effect of an excess of reducing substances in the material to be assayed. High sulphur ores, if assayed without previous roasting, require the addition of nitre to the charge. In contact with a reducing agent two molecules of potassium nitrate give up five atoms of oxygen, as shown in the following equation:

\[ 4\text{KNO}_3 + 5\text{C} \rightarrow 2\text{K}_2\text{CO}_3 + 3\text{CO}_2 + 2\text{N}_2. \]

The potassium oxide coming from the decomposition of the nitre acts as a basic flux.
Common salt, NaCl, melting point 819° C., is a neutral substance sometimes used as a cover for crucible fusions to exclude the air. When molten it rests on top of the charge and does not enter into it.

Fig. 50a. Oil Muffle Furnace.

All of the reagents used must be pure and in a finely divided condition. Sodium carbonate shows a tendency to form lumps. These should be broken up and the entire mass put through a moderately fine screen.

Furnaces and Equipment. The major operations in fire assaying are usually conducted in muffle furnaces. The muffle is a box-like receptacle made of fire clay, so placed in the furnace that it is heated on top, bottom and all sides except the front. In it are placed the refractory vessels containing the material to be assayed. There is thus no direct contact with the fuel or products of combustion. The fuel used may be coal, oil, gasoline or gas.

Cupels. The separation of the precious metals from the lead alloys produced in fire assaying is effected in small shallow vessels of bone ash, known as cupels. The material consists mainly of calcium phosphate, with small percentages of magnesium phosphate, calcium fluoride and calcium carbonate. It is a product of the burning of animal bones, preferably those of the sheep. It should be ground fine enough to pass a 40-mesh screen, in which case about 50 per cent of it will pass a 150-mesh screen. The cupels are made by moistening the bone ash with a small amount of water and then compressing it in the cupel mould, which consists essentially of a ring and die. The bone ash
is forced into the shape desired at a considerable pressure, so as to insure sufficient rigidity in the cupel. The amount of water needed varies, but should be as low as possible. The cupels should be dried very slowly, so as to avoid cracking. By using high pressures good cupels can be made from perfectly dry bone ash.

The requirements of a good cupel are that it should be infusible at ordinary furnace temperatures, that it should not be attacked by metallic oxides, that it should be porous, and that it should be sufficiently rigid to permit of considerable handling.

Cupels can be made of Portland cement, magnesia, or of mixtures of these materials with bone ash. They are considerably cheaper but not so satisfactory as those made of bone ash alone.

The Assay-Ton System. As the precious metals are bought and sold by the Troy system of weights and measures, and ores by the Avoirdupois system, considerable time would be lost in calculating assay results, were there no way of avoiding it. To simplify the calculation Prof. C. F. Chandler, of Columbia University, invented the assay-ton system of weights. The assay-ton is equal to 29.166 milligrams. As there are 29,166 2/3 Troy ounces in an Avoirdupois ton of 2000 pounds, the number of milligrams and fractions of a
milligram of precious metals found in an assay-ton of ore corresponds to the number of Troy ounces in an Avoirdupois ton.

**Fig. 59c.** Cross Section of Two-Muffle Assay Furnace.

**Sampling.** It goes without saying that good results in assaying presuppose accurate sampling. Silver is reported in assay certificates to the nearest tenth of an ounce; gold usually to the nearest one hundredth of an ounce. One tenth of an ounce means one part in 291,667; one hundredth of an ounce, one part in 2,916,667. In the preparation of the sample, therefore, the ratio between the weight of any fractional portion and the weight of the largest particle in it must be very large, so that the accidental inclusion of a number of rich pieces in any portion shall not affect the results beyond the limits of error in assaying. The final pulp sample should be of a fineness ranging from 80-mesh, in the case of low grade silver ores, to as fine as 200-mesh in the case of non-uniform gold ores. Small particles of metallic gold in the material necessitate fine grinding and very thorough mixing. It is a good rule to mix all pulp samples on a rubber cloth before weighing the portions for assay.

**Balances and Weights.** The balances used in fire assaying are somewhat different from those found in chemical laboratories. They are known as flux, pulp and assay balances. The assay balances are for weighing the gold and silver, often exceedingly small in amount, and are the most delicate type of commercial balances made. They should be quick in action and not liable to changes in adjustment. The beam should be short, light and rigid. The
balance should be sensitive to .01 milligram at least. It need not have a capacity of more than .5 gram but should be accurate with that load.

![Diagram of apparatus for fire assay](image)

**Cupel Tongs**, **Pliers**, **Parting Flask**

*Fig. 394. Apparatus for Fire Assay.*

In large laboratories separate balances are furnished for weighing the gold. These balances should be adjusted before each weighing and should be handled with the greatest of care. In the assay of gold ores, when using a half assay-ton portion, every error of .01 milligram in weighing the gold means a variation in the value of the ore of forty cents per ton.

**The Crucible Assay.** This method of fire assaying is adapted to the great majority of gold and silver ores and to many metallurgical products. The process consists in treating a weighed portion of the sample, carefully mixed with the necessary reagents, in a fire-clay crucible. In order to do this effectively the character of the material to be assayed must be known. Thus, ores may be oxides or sulphides. They may be basic, acid or neutral. They may be strongly oxidizing or strongly reducing. Each case requires a particular method of treatment.

The amount of sample usually taken is one half assay-ton, run in duplicate. Twenty-gram fire-clay crucibles are used, that is, crucibles capable of holding twenty grams of ore and the necessary reagents. In most cases the total charge will fill the crucible to within one inch of the top.

**Lead Reduction with Oxidized Ores.** Experience has shown that the best results are obtained when the lead reduced from the charge amounts to from 25 to 30 grams. If the ore is oxidized, a reducing agent must be added to precipitate the necessary lead. Flour is the reagent ordinarily used, although charcoal or argol can be substituted for it. The lead is reduced according to the following equation:

$$2\text{PbO} + \text{C} \rightarrow 2\text{Pb} + \text{CO}_2.$$

That is, 12 parts of carbon theoretically will reduce 414 parts of lead from...
litharge. Hence, the theoretical reducing power of carbon is $\frac{414}{3}$ or 34.5. In practice, the reducing power of charcoal is found to range between 25 and 30, and that of flour from 10 to 12. Argol has a reducing power of about 8 or 9. In most oxidized ores, therefore, from 2$\frac{1}{4}$ to 3 grams of flour will be required to reduce from 25 to 30 grams of lead from the litharge.

![Figure 50e. Apparatus for Fire Assay.](image)

If the ore contains ferric oxide, manganese dioxide, or some other easily reducible oxide, more flour must be added. Some iron-manganese ores require as much as 5 grams of flour to throw down the necessary lead. With unknown ores the right amount can be determined only by trial.

**Lead Reduction with Sulphide Ores.** In the case of ores containing sulphides, arsenides or other reducing substances, there will be a reduction of lead without the addition of carbon. In fact it is usually necessary to add an oxidizing agent to prevent the precipitation of too much lead. The following reactions show the effect of a number of sulphide minerals when heated in contact with litharge and sodium carbonate.

1. $\text{PbS} + 3\text{PbO} + \text{Na}_2\text{CO}_3 = 4\text{Pb} + \text{Na}_2\text{SO}_4 + \text{CO}_2$
2. $\text{ZnS} + 4\text{PbO} + \text{Na}_2\text{CO}_3 = 4\text{Pb} + \text{ZnO} + \text{Na}_2\text{SO}_4 + \text{CO}_2$
3. $2\text{FeS}_2 + 15\text{PbO} + 4\text{Na}_2\text{CO}_3 = 15\text{Pb} + \text{Fe}_2\text{O}_3 + 4\text{Na}_2\text{SO}_4 + 4\text{CO}_2$

The sodium carbonate induces the complete oxidation of the sulphur to $\text{SO}_3$, with the formation of the very stable compound sodium sulphate. In the absence of an alkaline carbonate most of the sulphur is oxidized to $\text{SO}_2$ only, and the amount of lead precipitated is correspondingly decreased.

Reaction (3) shows that pyrite has a greater reducing power than flour itself. If, therefore, a half-assay-ton of ore consisting mainly of pyrite were to be subjected to a crucible fusion, without the addition of some oxidizing agent, anywhere from 100 to 150 grams of lead would be reduced. This would be entirely too much for the subsequent process of cupellation. In order to prevent the reduction of an excessive amount of lead, potassium nitrate is added to the charge. The following reactions show the oxidizing power of this reagent:

4. $2\text{KNO}_3 + 5\text{Pb} = 5\text{PbO} + \text{K}_2\text{O} + \text{N}_2$
5. $2\text{FeS}_2 + 6\text{KNO}_3 = \text{Fe}_2\text{O}_3 + 4\text{SO}_2 + 3\text{K}_2\text{O} + 3\text{N}_2$

Reaction (4) shows that 202 parts of nitre will oxidize 1035 parts of lead to litharge. The theoretical oxidizing power of nitre, as measured against
FIRE ASSAY FOR GOLD AND SILVER

lead, is, therefore, 5.12. Reaction (5) when compared with reaction (3), given above, shows that 606 parts of nitre will oxidize the pyrite needed to

Fig. 50f. Assay Balances for Small Weights.

reduce 3105 grams of lead from litharge. Here again the oxidizing power of nitre is shown to be 5.12. In practice, it is found to be somewhat less, more nearly 4.5.

The fire assay of sulphide ores, therefore, involves either a preliminary assay, or a calculation from the chemical analysis, in order to determine the amount of nitre to be added. With unknown ores it is better to make a preliminary fusion, using 5 grams of the ore, 75 grams of litharge, 20 grams of sodium carbonate and 10 grams of borax glass. The button of reduced lead is weighed and its weight divided by 5. This gives the reducing power of the ore. From this can be calculated the reducing power of one half assay-ton of the ore, and the amount of nitre necessary to add in order to cut down the weight of the reduced lead to about 30 grams. An excess of silica or borax glass decreases somewhat the amount of lead by causing the formation of difficultly reducible lead silicates or borates.

Amount of Litharge. The amount of litharge for a half assay-ton charge
usually ranges from 60 to 75 grams. Only about half of this is needed to produce the 25 to 30 grams of metallic lead used as the collector. The excess litharge serves to prevent the reduction of other base metals, such as antimony, bismuth, iron, copper and zinc, to help flux the silica, to act as a solvent for some of the refractory gangue materials, and to make sure that every particle of the ore in the crucible is in close proximity to one or more particles of litharge. In special cases it may be advisable to use a very large excess of litharge, as in the assay of rich gold telluride ores, zinc precipitates and saturated cupels.

**Amount of Sodium Carbonate.** The amount of sodium carbonate to be used depends somewhat upon the character of the ore, although the modern practice is to use about the same quantity in assaying a great variety of ores and metallurgical products. The principal function of the sodium carbonate is to flux the silica and alumina, which are nearly always present in greater or less degree. The reactions are as follows:

1. \( \text{Na}_2\text{CO}_3 + \text{SiO}_2 = \text{Na}_2\text{SiO}_4 + \text{CO}_2 \)
2. \( 2\text{Na}_2\text{CO}_3 + \text{SiO}_2 = \text{Na}_2\text{SiO}_4 + 2\text{CO}_2 \)
3. \( \text{Na}_2\text{CO}_3 + \text{Al}_2\text{O}_3 = \text{Na}_2\text{Al}_2\text{O}_4 + \text{CO}_2 \)

The two silicates and the aluminate are both quite fusible at ordinary furnace temperatures.

The silicates used in assaying and in metallurgy are usually classified according to the ratio between the oxygen in the acid radical and that in the base. Only four of these type silicates are of any practical importance. They are shown in the following table:

<table>
<thead>
<tr>
<th>Silicate Type</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sub-silicate</td>
<td>( 4\text{RO}, \text{SiO}_2 )</td>
</tr>
<tr>
<td>Mono- or singule-silicate</td>
<td>( 2\text{RO}, \text{SiO}_2 )</td>
</tr>
<tr>
<td>Sesqui-silicate</td>
<td>( 4\text{RO}, 3\text{SiO}_2 )</td>
</tr>
<tr>
<td>Bi-silicate</td>
<td>( \text{RO}, \text{SiO}_2 )</td>
</tr>
</tbody>
</table>

In the above silicates, the ratios are \( \frac{1}{3} \) to 1, 1 to 1, \( 1\frac{1}{2} \) to 1, and 2 to 1, respectively.

Reactions (6) and (7) show that to flux one part of silica to bi-silicate and mono-silicate requires about \( 1\frac{1}{2} \) parts and \( 3\frac{1}{2} \) parts, respectively, of sodium carbonate. If the half assay-ton of ore, therefore, consisted of almost pure quartz, it would take 25 grams of sodium carbonate to flux it to sodium bi-silicate, and 50 grams to flux it to the mono-silicate. As a matter of fact, the bi-silicate slag is satisfactory in this case. In general, the acid silicates have lower melting points but greater viscosity than the basic silicates. The excess litharge in the charge also combines with silica, and may thus produce more basic silicates. At any rate, a mixture of silicates usually has a lower melting point than that calculated from the melting points of its components.

Reaction (8) shows that 1 part of sodium carbonate is required to flux 1 part of alumina.

In practice from 30 to 35 grams of sodium carbonate are used in a half-assay-ton charge. In many cases this may seem to be a large excess. It must be remembered, however, that this reagent serves also to assist in the oxidation of the sulphides through the formation of sodium sulphate, that it has a solvent effect upon refractory oxides and other substances, and that it
increases the bulk of the charge, thus protecting the ore from the action of the air and from the escape of the more volatile metals and their compounds. Being very fusible itself, an excess also serves to increase the fusibility of very refractory charges.

**Amount of Borax Glass.** The rational formula of borax glass, $\text{Na}_2\text{O}, 2\text{B}_2\text{O}_3$, shows that it is an unsaturated compound and can take up more of the base. This base may be sodium oxide or one or more of the heavier oxides. The result of the addition is a fusible complex borate. This is shown in the following reaction:

$\text{(9)} \quad \text{Na}_2\text{O}, 2\text{B}_2\text{O}_3 + 5\text{CaO} = \text{Na}_2\text{O}, 5\text{CaO}, 2\text{B}_2\text{O}_3$.

The compound produced is a mono-borate and shows the fluxing of 1.4 parts of lime by one part of borax. The solvent power of borax glass for various substances has been referred to above. In practice it does not matter whether there is chemical combination or solution. What is desired is perfect liquidity at furnace temperatures.

The amount of borax glass ordinarily used in a half-assay-ton charge varies from 10 to 15 grams. If the ore is very basic and refractory, more borax should be used. As in the case of sodium carbonate, an excess of borax glass ordinarily can do no harm, as it is quite fusible.

Some assayers use silica in the assay of very basic ores. It is a good flux for iron and manganese oxides, producing fusible silicates. It is also very cheap. It cannot be used in excess, because of its very high melting point.

**Assay Slags.** The slags produced in crucible fusions in fire assaying are often very complex mixtures of silicates, borates, oxides and other compounds. In the molten state there can be chemical combination, solution and suspension, all at the same time. Ordinarily it is quite useless to attempt the formation of a definite silicate or borate. If a sufficient amount of the proper fluxes is used, and a high temperature at the finish, there is usually no trouble in getting a good fusion. As a general rule the greater the complexity of the slag the lower its melting point.
Weighing and Mixing the Charge

It is usually most convenient to mix the charge within the crucible. The fluxes should be put in first, the most bulky one at the bottom. They should be measured rather than weighed, in order to save time. Only the flour and nitre need to be measured accurately. The ore is carefully weighed on a pulp balance and placed on top of the fluxes. The mixing is best done by means of a steel spatula, and should be very thorough. Good mixing is shown by the uniform appearance of the charge. The fluxes should be free from lumps. The practice of using a salt or borax cover on the charge is not so common as it was. Ordinarily it is not necessary. When a salt cover is used in assaying rich ores, there is some danger of the production of volatile silver and gold chlorides. Borax glass as a cover is expensive.

Fusing the Charge. The fusion of the charge is best conducted in a muffle furnace, although it can be made in a coke furnace, or even in a blacksmith's forge. The crucibles should be placed in the muffle when the latter is at a bright red heat. The temperature is then gradually raised until at the end of 45 minutes it reaches a light yellow heat, say 1150° C. Sulphide ores should be run rather more quickly than oxide ores, so as to oxidize the sulphides before they have a chance to melt down into a matte. If the heat be raised too rapidly, there is danger of boiling over, due to the large volume of gases liberated.

The crucible fusion may be divided roughly into three stages. There is first the preliminary heating stage, accompanied by some reduction of lead from litharge, the partial fusion and decomposition of nitre if present, the partial reduction of higher oxides, and some fluxing of silica by sodium carbonate and litharge. During the second stage most of the chemical reactions take place and the entire charge seems to be in a state of violent agitation. Lead is reduced from the litharge by flour, sulphur or other reducing agent, and the multitude of small shots pick up the adjacent particles of gold and silver. Gold tellurides and silver sulphides are decomposed by litharge, setting the metals free. Sodium carbonate and borax react upon the acid and basic constituents, respectively, of the charge, and produce slags. Alumina and other oxides either combine with these reagents or dissolve in the slag mixture. There is a copious evolution of gases, such as carbon dioxide, carbon monoxide, sulphur dioxide, and nitrogen. The third stage is known as the period of quiet fusion. It is for the purpose of completing the slag-forming reactions and of rendering the slag as liquid as possible. This enables all of the small particles of lead to fall down through the slag, collecting the remaining traces of gold and silver. The latter are washed out of the slag much as a shower of rain sweeps the dust particles out of the air. The slag must be thoroughly liquid in order to insure a perfect separation from the lead.

A high temperature at the beginning of the fusion should be avoided, as it not only increases the chances of boiling over, but may cause some volatilization of compounds of the precious metals. After these metals are reduced and alloyed with lead, the temperature can be raised with less danger of loss. A row of empty crucibles or a prism of coke should be placed in front of the crucibles containing the fusions, and the muffle door should be kept closed.
The time required ranges from 40 to 55 minutes, according to conditions. A long-continued fusion at a low temperature usually means a small lead button and an imperfect collection of the gold and silver.

The period of quiet fusion should last about 10 to 15 minutes. The crucibles are then taken out of the muffle, tapped gently with a whirling motion, to collect stray shots of lead, and the contents poured into conical iron moulds. The greater part of the slag should be poured off first, so as to avoid splashing of the lead against the sides of the mould. When cold the lead buttons are taken out and hammered into rough cubes, so as to remove the adhering slag. The lead buttons are now ready for cupellation.

Crucible Charges. It is impossible to give a crucible charge that would be satisfactory in every case. Modifications in the amount and kind of reagents must be made to suit the character of the material to be assayed. However, the variations are not so great as is generally supposed, and many assayers use stock fluxes for a great variety of ores and metallurgical products. Changes are made only when the conditions seem to require them.

The following table gives the approximate amount of the different reagents used in an ordinary crucible fusion:

<table>
<thead>
<tr>
<th>Reagent</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ore</td>
<td>( \frac{1}{2} ) assay-ton</td>
</tr>
<tr>
<td>Sodium carbonate</td>
<td>25 to 35 grams</td>
</tr>
<tr>
<td>Borax glass</td>
<td>10 to 15 grams</td>
</tr>
<tr>
<td>Flour or Nitre</td>
<td>As required. (See Preliminary Assay)</td>
</tr>
<tr>
<td>Litharge</td>
<td>60 to 75 grams</td>
</tr>
</tbody>
</table>

The Scorification Assay. The scorification assay is used principally in those cases in which an undue amount of interfering base metals would be reduced along with the lead if crucible fusions were made. Thus, if a crucible fusion be made upon an ore containing copper or antimony, either of these two metals will be reduced along with the lead and produce a button which is difficult to cupel. Even with sulphide ores there is a considerable reduction of the copper or antimony, as is shown in the following reactions:

\[
(10) \quad \text{Cu}_2\text{S} + 3\text{PbO} + \text{Na}_2\text{CO}_3 = \text{Cu}_2 + 3\text{Pb} + \text{Na}_2\text{SO}_4 + \text{CO}_2, \\
(11) \quad \text{Sb}_2\text{S}_3 + 9\text{PbO} + 3\text{Na}_2\text{CO}_3 = \text{Sb}_2 + 9\text{Pb} + 3\text{Na}_2\text{SO}_4 + 3\text{CO}_2.
\]

Nickel and cobalt are reduced in the same way.

In the scorification assay the operations are carried out under oxidizing conditions so as to prevent the reduction of the interfering metals. Metallic lead is used as the collector and is added as such. The flux is mainly litharge, coming from the oxidation of the lead, and a small amount of borax.

The operation is conducted in shallow fire-clay dishes known as scorifiers, from 2 to 3 inches in diameter. The amount of ore taken is usually \( \frac{1}{10} \) assay-ton, sometimes \( \frac{1}{6} \) or \( \frac{1}{8} \) assay-ton. About 25 grams of granulated lead are spread over the bottom of the scorifier and the ore then added and thoroughly mixed with the lead. The mixture is then covered with about 25 grams more of granulated lead and one or two grams of borax glass. Usually from 5 to 20 portions of the ore are weighed up so as to lessen the chances of error. The scorifiers are placed in a muffle heated to redness and the door closed. As soon as the lead melts the door is opened, in order to admit air and increase the rapidity of the oxidation. The ore is seen to be floating on
the lead. The latter begins to oxidize and the litharge produced in turn oxidizes the sulphides in the ore, assisted by the oxygen of the air. The temperature at this point must be low in order to prevent volatilization of gold and silver. The ore is not protected by a large bulk of fluxes as it is in the crucible assay. As the oxidation proceeds, a ring of slag, mainly litharge, begins to form around the bath of lead. The ore gradually disappears, the gold and silver going into the molten lead and the gangue combining with or dissolving in the litharge. Owing to the strong oxidizing conditions, most of the copper and practically all of the antimony present go into the slag. As the ring of slag increases, the temperature is raised. Finally, the lead becomes completely covered, and the muffle door is closed in order that the slag may become thoroughly liquid. The contents of the scorifiers is then poured into conical moulds, as in the case of the crucible fusions. The lead buttons should weigh from 15 to 20 grams. Very small buttons usually mean low results. With high copper material it is sometimes necessary to scoriify two or three times and to use a large amount of lead. The buttons are cleaned and cupelled in the usual way.

The scoriification assay is not adapted to ores containing volatile constituents, such as tellurides, arsenides and metallic zinc. Carbonates and highly oxidized ores are also unsuited to this method. If the ore contains much basic gangue it should not be scoriified, as there is not enough acid flux to take care of it. Low grade gold ores are not usually assayed by scoriification because of the small amount of ore taken. In practice the method is limited to ores and metallurgical products containing considerable quantities of antimony, copper, nickel and cobalt. It is a standard method for the assay of copper matte. Scoriification is also sometimes used to reduce the size of and to purify lead buttons produced in the crucible method.

**Cupellation.** Cupellation is the process by which the gold and silver are separated from the lead and other base metals with which they are alloyed. The cupels have already been described. They must be thoroughly dry and somewhat heavier than the lead buttons that are to be cupelled. A bone ash cupel will absorb about its own weight of litharge, but the absorption becomes slower when the saturation point is approached.

In the cupellation process the lead is oxidized to litharge which is taken into the pores of the cupel by capillary attraction. This takes place because litharge is molten at the temperature of the operation. Most of the other base metal oxides are infusible at this temperature. When in moderate amounts, however, they dissolve in the liquid litharge and are carried into the cupel. If the lead contains much copper and antimony, the oxides of these latter metals accumulate on the cupel and may ruin the assay. Hence the need for scoriification in these cases.

The cupels should be heated in the muffle for at least 20 minutes before putting in the lead buttons. Cupellations are best started at a bright red heat, say about 900° C. As soon as the buttons are put into the cupels, the muffle door should be closed. If the temperature is too low, an infusible oxide will form on the lead as soon as the latter is melted and refuse to go into the cupel. The disappearance of this film of oxide on further heating is referred to as the "opening" or "uncovering" of the lead. Sometimes it is necessary to hasten the opening by means of a burning stick of wood placed
immediately over the cupel. This reduces the oxide and at the same time raises the temperature. When all of the cupellations are uncovered, the muffle door is opened and the temperature lowered rapidly to the lowest possible point at which the operation can proceed. This must be done because a temperature higher than necessary increases the loss of gold and silver. This loss occurs by absorption into the cupel and by volatilization. If the temperature falls too low, the buttons "freeze"; that is, the litharge, which melts at 883° C., solidifies on top of the liquid lead, which melts at 327° C., and the operation stops.

At first thought it would seem that a temperature slightly above 883° C. would be the proper one for cupellation. As a matter of fact the temperature of the muffle need not be above 750° C. This is due to the fact that the oxidation of the lead generates a considerable amount of heat, and the buttons are thus hotter than either the muffle or the cupels. A good indication of the right cupellation temperature is the formation of solid flakes of litharge, known as "feathers," upon the inner edge of the cupels. The volatilized litharge strikes the comparatively cool bone ash and sublimes as flake crystals.

The presence of impurities usually increases the loss of gold and silver, and adds to the difficulties of the operation. Copper or nickel in quantity may cause the buttons to freeze even at moderately high temperatures. Antimony causes the formation of a hard, insubstantial crust of lead antimonate which retains silver and which often splits the top of the cupel.

The surface of the lead in the cupel is convex, owing to the high surface tension of the metal. During cupellation the drops of molten litharge can be seen rolling off of the lead and disappearing into the cupel. The surface tension of the melted litharge is less than the attractive force of the bone ash. In scorification, where the vessel is not porous, the litharge forms a concave surface and climbs up the sides of the scorifier. This explains in part the high gold losses in the cupellation of lead containing gold and tellurium. Some of the gold telluride passes into the cupel just as in the case of litharge. Gold telluride is also more volatile than metallic gold.

As the operation proceeds, the lead and other base metals gradually oxidize and disappear. Copper and bismuth are less readily oxidized than lead, and hence tend to remain until most of the lead has gone. The temperature should be raised slightly at this point in order to prevent the buttons from solidifying before the base metals are completely oxidized. Small amounts of these metals usually remain, even in a well-conducted cupellation. The melting point of gold and silver being considerably higher than the temperature of the muffle, the buttons solidify soon after the base metals are gone. At the moment of solidification the buttons flash or "blick," owing to the release of the latent heat of fusion. If the buttons are large and consist mainly of silver, they may "sprout" or "spit" on being withdrawn quickly. This is due to dissolved oxygen which escapes when the button solidifies. The sprouting may be prevented by covering the silver button with a hot inverted cupel as soon as the cupellation is finished, and allowing the covered cupel to remain in the muffle for several minutes. This insures a slow cooling of the silver bead. After cooling the buttons are removed from the cupel by means of forceps and the adhering bone ash brushed off. The buttons are then weighed on an assay balance to the nearest one-tenth of a milligram. If a
half-assay-ton of ore was used, the results multiplied by two equal the ounces per ton of combined gold and silver.

Cupellation involves the greatest precious metal losses of all the processes in fire assaying. For that reason it must be conducted with care and skill. The loss in silver ranges from 1 to 2 per cent, even under favorable conditions. If there are large amounts of impurities, or if a very high temperature is used, the silver loss may be several times as great. The gold loss is less than that of silver and should not be more than $\frac{1}{2}$ of 1 per cent. In all cases the percentage losses of gold and silver increase as the amounts in the ore decrease.

Parting. Parting is the separation of gold from silver in an alloy containing these metals, and is effected in fire assaying by means of nitric acid. This acid converts the silver into soluble silver nitrate, but is almost without action upon the gold. In order to part readily the alloy must contain at least three times as much silver as gold. Even at this ratio it is difficult to dissolve all of the silver. In practice, it is better to have a much larger proportion of silver, except in the assay of gold and silver bullion. If the buttons produced in the assay of an ore are known to contain enough gold to render parting difficult or impossible, they are subjected to the process known as inquartation. The buttons after weighing are wrapped with about 10 times their weight of pure silver foil in 3 to 5 grams of sheet lead and then cupelled. The resulting buttons are flattened and parted in the usual manner.

An important point in parting is the strength of the acid. If a strong acid is used at first, the gold in the button is liable to break up into a fine powder which is difficult to manage without loss. By using a rather weak acid, containing from 10 to 20 per cent of HNO₃, the gold has a tendency to coalesce into a coherent mass which can be washed and weighed as one piece. The treatment with weak acid is always followed by one with a stronger acid, in order to remove the last traces of silver. The second acid should be about 1.26 sp.gr., made by diluting the concentrated acid with its own volume of water. In the case of buttons containing a small proportion of gold, the first acid should be very weak, not more than 10 per cent HNO₃. With more gold a stronger acid can be used, although the weak acid is usually effective, except when the buttons are very large.

The parting may be done in porcelain capsules or in small glass flasks, known as parting flasks. Only a few cubic centimeters of acid are necessary. This should be heated to boiling and the flattened beads then dropped into it. Solution of the silver begins immediately. At the end of about 20 minutes, or when all visible action has ceased, the weak acid solution is decanted into a white casserole, carefully avoiding the loss of any gold. About 3 cubic centimeters of the stronger acid is now added to each flask or capsule and then heated almost to the boiling point. The heating is continued for at least 10 minutes, when all of the silver should be in solution. The acid is then poured off and the gold washed three times by decantation with chlorine-free water. If capsules are used, the water is drained out as completely as possible and the capsules then placed on a hot plate or in front of the muffle for drying. If parting flasks are used, a fire-clay annealing cup is inverted over the top of each completely filled flask and the flask then quickly reversed, allowing the gold to fall quietly into the annealing cup. After removing the flask by a quick side motion, the water is poured off of the gold and the cup placed
on the hot plate. The final process is known as annealing. The capsules or annealing cups are placed in the muffle and heated to low redness for about 5 minutes. The heating causes the brownish-black spongy or fibrous gold to coalesce into a dense flake or bead having the characteristic yellow color of the metal. The annealing also serves to drive off any volatile impurities which may be present, and to render it easier to separate any specks of dust or dirt from the gold. After cooling the gold is weighed on a delicate balance to the nearest .01 milligram—with a little care to the nearest .005 milligram. The weight of the gold is deducted from the weight of the button before parting and the difference represents the silver in the portion taken for assay.
The Assay of Bullion

Bullion is an alloy of gold and silver with variable amounts of one or more of the base metals, and is the semi-final product of most non-ferrous metallurgical plants. In lead smelting this product is usually known as base bullion, in copper smelting as blister copper, and in amalgamation and cyanide processes as retort bullion or doré silver. The base metals may include antimony, arsenic, bismuth, cobalt, copper, lead, mercury, nickel and zinc. Small amounts of selenium and tellurium are usually present, as well as traces of the platinum group of metals. In all cases the assay of bullion resolves itself into a problem of the separation of metals from each other, there being practically no non-metallic elements present.

Bullion Sampling. The sampling of bullion involves some difficulties not encountered in the sampling of ores. Most alloys on solidifying segregate to some extent, so that the cooled metal is never uniform in composition. Whenever possible the samples should be taken from the thoroughly stirred molten alloy and then chilled quickly, either by pouring into water or by pouring into small moulds with thick metal sides and bottoms. When there is danger of oxidation, this method of course is not entirely satisfactory. In impure bullion there is often a very uneven distribution of the gold and silver, and it is necessary to drill or saw entirely through the bar in order to obtain accurate results. In copper anode plates and other forms of blister copper the plates or bars are drilled in series, so that the combined sample represents a proper percentage of drillings from all parts of each piece. Lead bullion is sometimes sampled in a similar manner, although in this case the bars are usually punched instead of being drilled. The modern tendency is to take melted samples of all metallic products, even in the case of blister copper.

The Assay of Lead Bullion. The assay of lead bullion ordinarily involves only cupellation and parting. The bullion is often impure, however, and it may then be advisable to scorify the weighed portions before cupelling. If the sample contains much copper or antimony, it should always be scorified. The precious metal loss in scorification is less than it is in cupellation, especially in the case of an impure bullion requiring a high temperature in order to cupel it.

Lead bullion is usually run in four portions of one half assay-ton each. The four silver buttons are weighed separately and if there is a satisfactory agreement in the weights, the average is taken and the result multiplied by two. The buttons are parted in pairs, thus saving time in washing and weighing. Great care should be exercised in the cupellation of lead bullion and in the subsequent parting, as the bullion is a high grade product, and ordinarily no correction is made for losses in the cupel or otherwise.

The Assay of Copper Bullion. Copper bullion may be assayed by the scorification method, but the results are satisfactory only in the case of the gold. The silver obtained is always much too low. Most of the loss can be recovered by assaying the slag and cupels, but this requires additional time and materials.

The best way to determine gold and silver in copper bullion is to use the so-called combination method, in which the copper is first removed by solution in acid. Formerly nitric acid was used for this purpose, but it was found that the results were usually low in gold. There was a tendency for some of the
gold to go into solution. The nitric acid method is a convenient way of
determining the silver, as the copper dissolves very rapidly in nitric acid,
and the precipitation of silver as chloride is very complete.

For the assay of both gold and silver the sulphuric acid-mercuric nitrate
method is recommended. One assay-ton of the finely ground, well-mixed
copper borings is treated in a large beaker with 30 cc. of water and 10 cc. of
a solution of mercuric nitrate containing 25 grams of mercury per liter. The
beaker is well shaken so as to amalgamate the copper, and 100 cc. of concen-
trated sulphuric acid then added. The beaker is covered, placed on a hot
plate and heated until all of the copper is dissolved. This will require from
one to two hours, according to the temperature and fineness of the sample.
The beaker is now removed and the solution is allowed to cool. 100 cc. of
cold water are added, the mixture stirred, and then 400 cc. of boiling water
added, with further stirring until all copper sulphate has dissolved. A solution
of common salt is now added, just sufficient to precipitate all of the silver
and mercury. Only a slight excess must be used, as silver chloride is soluble
in strong sodium chloride solution. The beaker is replaced on the hot plate
and the contents boiled so as to coagulate the silver chloride. The beaker is
then removed, the solution diluted to 600 cc. with cold water and allowed
to cool. The solution is then filtered through double filter papers, and the
beaker and filter washed with hot water. The beaker should be wiped out
with a filter paper and this added to the material in the filter. The filter
and its contents are now transferred to a 2½-inch glazed scorifier and the
filter paper burned off at a low temperature, so as to avoid loss of silver.
After the paper is burned off, 30 grams of test lead are added and the material
scorified until 12 to 15 grams of lead remain. The scorifier is poured and the
lead button cupelled at as low a temperature as possible. The gold and silver
are parted in the usual way. The results are very accurate.

The object of the mercuric nitrate is to hasten the solution of the copper
by forming a galvanic couple. It prevents also the formation of copper
sulphide which is insoluble in dilute sulphuric acid.

Assays should be made in duplicate or triplicate.
The Assay of Gold and Silver Bullion

In the fire assay of gold and silver bullion a correction must always be made for the metal losses, because of the great value of the bullion and because the refining losses on a commercial scale are considerably less than the losses in assaying. The assays are, therefore, always run with a check or "proof center." The check is an artificial sample made up so as to have as nearly as possible the exact composition of the bullion to be assayed. Two checks and three portions of the bullion, all five of the same weight, are cupelled and parted under exactly the same conditions. The weights of gold and silver found in the bullion samples are then corrected by adding or subtracting the loss or gain experienced by the gold and silver in the checks. In the assay of gold bullion there is sometimes a gain in the weight of the gold, due to the imperfect elimination of the copper. This, however, should be the same in both checks and bullion samples. Results are reported in "fineness" or parts per 1000.

Silver Bullion or Doré Bullion Assay. A sample of about 500 milligrams of the bullion is accurately weighed out on the assay balance. The weight need not be an even 500 milligrams but its exact amount should be recorded. The bullion is wrapped in from 6 to 8 grams of sheet lead and cupelled with the formation of feathers of litharge. The button is covered with a hot cupel to prevent sprouting. The cupel and button are drawn out of the muffle gradually, and the button is then cleaned, flattened and parted in the usual way. To the weight of the silver a loss of from 1 to 1½ per cent is added. The weight of the comparatively small amount of gold can be taken as it is. The weight of the original button, less the sum of the corrected silver weight and the weight of the gold, represents the amount of base metal. This is usually copper, but may be one or more of a number of other metals. The assayer can usually determine what metals are present by the appearance of the bullion and that of the cupel.

Two checks are now prepared by weighing in each case pure gold, pure silver and pure copper or other base metal in the amounts as found in the preliminary assay just described. Three 500-milligram portions of the bullion are also weighed up. The checks and bullion samples are each wrapped in an amount of sheet lead corresponding to that in the following table, taken from Bugbee’s "Text-book of Fire Assaying":

<table>
<thead>
<tr>
<th>Lead Ratio in Cupellation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wt. of Lead</td>
</tr>
<tr>
<td>Au. and Ag.</td>
</tr>
<tr>
<td>950</td>
</tr>
<tr>
<td>900</td>
</tr>
<tr>
<td>850</td>
</tr>
<tr>
<td>800</td>
</tr>
</tbody>
</table>

The table shows that as the base metal, usually copper, increases, the amount of lead must be increased.

Cupellation is performed in a single row of cupels, all of the same size. The checks are placed in the second and fourth cupels. The heat should be
FIRE ASSAY FOR GOLD AND SILVER

kept low enough to allow of the formation of feathers of litharge until at the finish, when the temperature must be raised.

The beads are cleaned, weighed, flattened and parted. The amount of gold and silver loss in the checks is determined and the proper correction applied to the weights of gold and silver found in the bullion samples.

If the bullion contains antimony, the process must include scorification, which is applied to checks and samples as well. When bismuth, selenium or tellurium is present in quantity, the silver must be separated by means of solution in nitric acid and subsequent precipitation as chloride.

Gold Bullion Assay. The assay of gold bullion is in principle the same as that of silver bullion. As the gold is usually in excess of the silver, however, the process involves inquartation, with the use of a stronger first acid than when parting ordinary silver buttons.

U.S. Mint Method. Sample portions of 500 milligrams are taken for assay. A preliminary cupellation is made as in the case of doré bullion. The amount of silver to be added for the final assay is determined by the touchstone method. The cupelled gold and silver button is rubbed on a piece of black jasper and the streak made compared with those made by alloys of known composition. This gives the fineness within 2 per cent, which is close enough. A ratio of silver to gold of 2 to 1 is used in making up the checks. If no copper is present, about 3 or 4 per cent is added as it facilitates the removal of the last traces of lead in cupellation. The cupelled buttons are flattened by hammering, annealed at a red heat, and then passed through a pair of jeweller's rolls, until they are converted into fillets about 2½ inches long and ½ inch wide. The fillets are again annealed and rolled up into “cornets” or spirals. Sufficient space should be left between the turns to permit of easy contact with the acid. The parting is done by boiling for 10 minutes in nitric acid of 1.28 sp.gr., and then transferring to another vessel containing acid of the same strength and boiling for 10 minutes longer. The cornets are then washed three times with distilled water, dried, annealed and weighed.

The proofs usually show a slight gain in the weight of the gold, so that the correction is made by subtracting the gain from the average weight of the gold found in the sample portions.

The gold after parting should be in one piece and have smooth edges, as otherwise there is danger of loss.
The Assay of Cyanide Solutions

A number of methods have been devised for the determination of gold and silver in cyanide solutions. Only two of these methods will be described here.

Evaporation in Lead Tray. This method is adapted to cyanide solutions containing only small amounts of base metals or other impurities. A small tray or boat is made of lead foil, capable of holding the amount of solution to be assayed. A wooden block or form is used to make the trays if many assays are required. The solution has about the same specific gravity as water, so that 29.2 cc. are assumed to be equal to an assay-ton. An amount of solution varying with its richness is put into the lead tray and slowly evaporated to dryness on the hot plate. The lead tray is then folded up and cupelled in the usual manner.

The Chiddey Method. This method, first described by Alfred Chiddey, is adapted to almost every grade and character of cyanide solutions.

From 1 to 20 assay-tons of solution are heated in a beaker or evaporating dish. To the solution is added from 10 to 20 cc. of a 10 per cent solution of lead acetate containing 40 cc. of acetic acid per liter. From 1/2 to 2 grams of zinc dust or zinc shavings is then added. The gold, silver and lead immediately begin to precipitate on the zinc. The solution is heated for about 20 to 25 minutes, but not to boiling. The lead should coalesce into a spongy mass. Boiling the solution is liable to break up the sponge. The excess zinc is now dissolved by adding slowly 20 cc. of hydrochloric acid of 1.12 sp.gr. The heating is continued until effervescence ceases. It may be necessary to stir slightly in order to make sure that all zinc is dissolved. The solution is now decanted off and the lead sponge washed two or three times with water. The excess water is squeezed out of the sponge with the fingers, the sponge further dried by pressing between filter paper and then rolled into a ball with lead foil and the necessary silver for parting. A hole should be left in the lead foil for the escape of steam. The ball is then dried and cupelled.

As the lead sponge begins to break up and go into solution as soon as all of the zinc is dissolved, no time should be lost in decanting the solution after the zinc has disappeared.

Special Methods of Assay. There are many ores and metallurgical products that require special methods for the determination of the gold and silver that they contain. It is impossible to refer to these methods here. A knowledge of the composition of the sample, however, will usually enable the skilled assayer to so modify the ordinary processes as to obtain satisfactory results.

**FIRE ASSAY FOR GOLD AND SILVER**

**Summary. General Outline.**

An assay ton (A.T.) or multiple is taken, of the 80–200-mesh ore or 20-mesh shavings of metals and is heated with a flux of lead oxide, a suitable slag forming material and a reducing or oxidizing reagent as the case requires, (see preliminary assay below), in order to obtain by reduction about 18 g. of lead from the lead oxide. The molten lead alloys with the silver and gold (and copper) and sinks to the bottom of the melt. The charge is cooled and the slag hammered off the lead and the button or cube of lead is heated on a bone ash cupel in presence of air. The bone ash absorbs the oxides of lead (and copper) leaving the precious metals in the form of a bead. As the last trace of lead is removed a play of colors is seen with a final flash of light as the alloy of silver and gold appears ("blick"). The combined gold and silver button is weighed, the silver now dissolved (parting) from the gold and the residual gold weighed. The difference between the first and second weight is due to silver.

**Preliminary Assay.** This is to ascertain the nature of the material as neutral, oxidizing or reducing products require different treatment. Usually one-sixth of the charge of ore is taken with the regular charge of flux, without a reducing or oxidizing agent. A typical example of a charge is one-sixth A.T. of ore, 100 g. litharge, 20 g. sodium bicarbonate and 5 g. borax. Using this charge the following cases will illustrate the method of interpretation.

**A. Reducing Ores.** Suppose a 2 g. Pb button is obtained. This is equivalent to $2 \times 6 = 12$ g. on a customary charge of 1 A.T. of ore. Additional reducing agent is necessary to get the 18 g. Pb desired. 1 g. charcoal reduces about 30 g. Pb, hence $(18 - 12) \div 30 = 0.2$ g. charcoal required.

On the other hand suppose a 4 g. Pb button results, equivalent to 24 g. with full charge of ore. It is necessary to add an oxidizing agent to counteract the reducing action of the ore to the extent of $24 - 16 = 8$ g. Pb excess. 1 g. NaNO$_3$ oxidizes 4 g. Pb. Therefore $6 + 4 = 1.5$ g. NaNO$_3$ is required.

**B. Neutral and Oxidizing Ores.** In this case no lead is reduced. A second run must be made with say 1 gram of charcoal (30 g. Pb equivalent). If 30 g. Pb results the ore is neutral and $18 + 30 = 0.6$ g. charcoal is required.

On the other hand suppose 28 g. Pb results, then the ore is an oxidizer and 1 A.T. of the ore will oxidize $2 \times 6 = 12$ g. Pb. To counteract this $12 + 30 = 0.4$ g. charcoal is necessary and $18 + 30 = 0.6$ g. charcoal to reduce 18 g. Pb, making a total of $0.4 + 0.6 = 1$ g. charcoal required.

**Precaution.** All reagents used should be tested by regular assay.

A 20–25 gram button of lead is generally required in the assay of ores high in silver.

**Solution Assay.** Place 10 assay tons of the solution in a 1000 cc. beaker. Add about 30 cc. of a 20% lead acetate solution (the amount being governed by the strength of the solution). Dilute to about twice the volume and heat. Add about 5 grams of zinc shavings, heat until solution clears. Add 30–40 cc. HCl. When clear, decant off solution, wash the lead and squeeze into a button. Assay the button.

The writer is indebted to Mr. W. G. Derby for several cuts appearing in this chapter.
DETERMINATION OF PLATINUM, PALLADIUM, GOLD AND SILVER

Platinum, Palladium and Gold. Scorify the lead buttons from two or more \( \frac{1}{2} \) assay ton crucible fusions together, adding at least six times as much silver as the combined weight of the Pt, Pd and Au present, and cupel hot. In rich materials such as slimes or concentrates, two \( \frac{1}{2} \) assay ton fusions suffice, but low-grade ores may require 10 or more \( \frac{1}{2} \) assay ton fusions combined for each determination.

Part the silver beads with HNO₃ (1 : 6), followed by stronger parting acid (1 : 1) and wash with water as usual. All Pd goes into solution, together with considerable Pt. The residue consists of Au plus some Pt. Dissolve residue in strong aqua regia and reserve the solution (solution A). Precipitate the silver in the nitric-acid solution—containing Ag, Pd and some Pt—with HCl. Practically all the Pt will remain in solution; but the precipitated AgCl is pink in color and contains considerable Pd. Filter off the AgCl, scorify and cupel it and part again with HNO₃ (1 : 6); all should dissolve. Re-precipitate the Ag with HCl. The liquid now contains most of the remaining Pd, but some is co-precipitated with AgCl. Filter off the AgCl and add the filtrate to the first filtrate from AgCl. Again scorify and cupel the silver chloride, dissolving the silver in nitric acid as before and re-precipitating the silver as chloride. In most cases the filtrate from this silver chloride contains all the remaining Pd. If however, the AgCl is distinctly pink, another separation must be made.

Unite all filtrates from AgCl precipitations and evaporate to small bulk, adding the aqua-regia solution of the Au and Pt (solution A). The liquid now contains all the Au, Pt and Pd present in the original ore, together with traces of Ag due to solubility of AgCl in excess of HCl, and also traces of Pb gathered from the lead retained in the silver buttons from several re-cupelations.

Evaporate the liquid to dryness on the steam bath; take up with dilute HCl (1 : 3) and evaporate again to dryness; take up with five drops of HCl and 40 cc. H₂O. Pay no attention to any insoluble residue of AgCl or PbCl₂. Precipitate the gold by adding, say, 3 gm. of oxalic acid to the solution and boiling it. Let stand over night and filter off the Au. If Pt and Pd are high, it is necessary to re-dissolve the Au in aqua regia, evaporating with HCl to dryness and repeating the oxalic-acid precipitation, uniting the filtrate with that from the first gold precipitation. Burn the filter containing the gold and scorify it with six times its weight of silver and a little test lead; cupel, part and weigh the gold as usual.

To the oxalic-acid filtrates from Au add 5 cc. of HCl and make volume up to 150 cc.; heat to boiling and precipitate Pt and Pd with a rapid current of H₂S in hot solution, passing the current of gas for some time and keeping the solution hot during precipitation. Filter and wash the Pt and Pd sulphides

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1 By A. M. Smoot, Eng. and Mining Journal, April 17, 1915.
2 In materials rich in palladium the small amount of AgCl + PbCl₂ may be distinctly pink in color and retain weighable quantities of Pd. If this is the case, the Pd may be recovered in the solution from the nitric acid parting of the gold. To do this, precipitate the silver in this liquid by adding HCl, filter off the silver chloride and evaporate the filtrate to dryness. Take up with a drop of HCl and a little water, let stand over night and filter through a very small filter. This liquid may be added to solution B before precipitating palladium with glyoxime.
with H₂S water containing a little HCl. Wash the precipitate from the filter with a fine water jet into the original beaker; spread the filter paper (which will contain a small amount of precipitate impossible to wash off) with the precipitate side down over the lower side of a watch glass-cover. Add aqua regia to the precipitate in the beaker and place the cover on the beaker; warm gently to dissolve the Pt and Pd sulphides. The fumes arising from the acid dissolve the traces of Pt and Pd adhering to the filter paper. When solution is complete and filter paper is white, remove the watch-glass cover and wash the paper with hot dilute HCl thrown against it in a fine stream.

Evaporate the aqua-regia solution to dryness, take up the residue with HCl and evaporate again to dryness to remove all HNO₃. Take up the residue with two or three drops of HCl and about 2 cc. of H₂O. The solution is usually perfectly clear, but it may be slightly cloudy owing to the presence of a little AgCl in it. No attention need be paid to this however. Add 5 to 10 cc. of a saturated solution of NH₄Cl, stir well and allow to stand over night. Platinum is precipitated as ammonium-platinum chloride—(NH₄)₂PtCl₆. Filter and wash the precipitate with 20% NH₄Cl solution. All Pd passes into the filtrate which is reserved (solution B). Dissolve the Pt precipitate in boiling hot 5% H₂SO₄; heat the liquid to actual boiling and precipitate with H₂S as before, filtering and washing with H₂S water. Burn the filter and precipitate at a low temperature in a crucible; add six times as much Ag as Pt, scorifying with lead, cupel and part the silver bead containing the platinum with H₂SO₄; decant off the silver solution and wash once with strong H₂SO₄, followed by 50% H₂SO₄ until practically all the silver is washed away; finally wash with water, anneal and weigh. A minute quantity of Ag is retained with the platinum, but it can usually be neglected. In very important work where the amount of platinum is large dissolve in aqua-regia, evaporate the solution to dryness, take up with a drop of HCl, dilute largely with water and let the AgCl settle over night; filter on a small paper, cupel it with a little sheet lead and deduct the weight from the weight of platinum. This refinement need not be considered in materials running less than 15 or 20 oz. to the ton.

It may seem an unnecessary step to precipitate the platinum as sulphide, scorify it with silver and part it as described in the foregoing. General practice has been to ignite the ammonium-platinum-chloride precipitate and weigh the metallic residue. When this is done, however, there is danger of losing considerable platinum, which is carried away mechanically during the decomposition of the compound; furthermore, it is extremely difficult (if not impossible) to collect the finely divided residue for weighing, and the precipitate invariably contains lead and silver. Precipitation as sulphide, scorification and cupellation with excess silver and parting with sulphuric acid overcome the difficulties inherent in handling the ammonium precipitate.

The palladium is all contained in the filtrate and washings from the platinum ammonium-chloride precipitates (solution B). Add to this solution at least seven times as much di-methylglyoxime as there is Pd present (in any case, at least 0.1 gm. glyoxime). The precipitant should be dissolved in a mixture of two-thirds strong HCl and one-third water. Dilute the liquid to 250-300 cc., heat on a steam bath for half an hour and let stand over night. Pd is precipitated as a voluminous yellow, easily filtered glyoxime compound C₂H₄N₂O₂Pd, containing, when dried at 110° C., 31.689% of Pd. Filter the Pd precipitate on a weighed Gooch crucible and wash it, first, with dilute HCl,
half and half, then with warm water and finally with alcohol; dry it at 110° to 115° C. and weigh. The disadvantage of weighing palladium on a Gooch crucible is overcome—at least to some extent—by the fact that the Pd compound contains a relatively small amount of Pd—less than one-third of its weight. This compound may also be weighed on carefully counterpoised papers; but it is better to use Gooch crucibles, if they are available, because of the relatively strong acid which is required for washing. The object in using half-and-half hydrochloric acid as a wash liquid is to dissolve out any excess of the glyoxime precipitant. This is easily soluble in moderately strong HCl, but is substantially insoluble in water.

**Determination of Silver in Ores and Concentrates Containing Platinum and Palladium**

Make the usual crucible fusion on one-quarter, one-half or full assay ton, according to the amount of silver present. Instead of cupelling the lead button, hammer it free from slag and dissolve it in dilute nitric acid. Most of the silver passes into solution together with palladium, and perhaps a trace of platinum; but gold and most of the platinum remain insoluble. The gold and platinum retain an appreciable proportion of silver which cannot be washed out. Filter out the insoluble residue and wash it thoroughly with hot dilute nitric acid, followed by hot water. Scourify the residue once more with a little lead and dissolve the lead button as before, filtering into the beaker containing the first filtrate. In this liquid precipitate the silver as AgCl by adding standard NaCl in sufficient quantity; stir well, and if the amount of silver is small, add about \( \frac{1}{2} \) cc. of strong \( H_2SO_4 \) to form a precipitate of lead sulphate. Let the silver chloride, or the silver chloride plus lead sulphate, settle over night or until the supernatant liquid is clear; filter through double filter papers; ignite and scourify the residue of silver chloride with test lead.

If the amount of the palladium contained in the sample is small, the silver bead obtained by cupeling the lead button obtained by scourifying the silver chloride may be considered as sufficiently pure for ordinary purposes. It contains, of course, some palladium, and in accurate silver determinations the lead button from the first silver chloride precipitation should be re-dissolved and the silver re-precipitated, filtered and scourified as before. The amount of palladium retained after the second precipitation and scourification is so small as to be negligible.
STRONTIUM

Sr⁺, at.wt. 87.62; sp.gr. 2.54; m.p. 900°C; oxides SrO and SrO₂.

DETECTION

Strontium is precipitated with barium and calcium, in the filtrate, from the ammonium sulphide group, by addition of ammonium carbonate to the ammoniacal solution. The precipitate is dissolved in acetic acid and treated with potassium dichromate, and the barium filtered off as BaCrO₄. Strontium and calcium in the filtrate are separated from the excess of potassium chromate by reprecipitation as carbonates by the addition of ammonium carbonate, the precipitate again dissolved in acetic acid and the excess of free acid neutralized with ammonia. Strontium may now be precipitated from the concentrated solution by boiling with an equal volume of a saturated solution of calcium sulphate.

Sodium Sulphate Test. A saturated solution of the salt added to a solution containing strontium chloride, made strongly acid with acetic acid, and the mixture boiled, will produce a distinct precipitate if strontium exceeds 0.0015 normal. Calcium does not precipitate until 1.3 normality is reached.¹

Flame Test. Strontium, preferably in the form of the chloride in a hydrochloric acid solution, placed on a platinum loop and held in a colorless flame, colors the flame crimson. (Lithium gives a red color, calcium a yellowish-red.) The test is best confirmed by means of the spectroscope.

The Spectra of Strontium. Eight bright bands; 6 are red, 1 orange, 1 blue. Two of these, known as strontium β and γ, are red, the orange is strontium α and the blue strontium δ. The delicacy of the test is 0.6 milligram Sr per cc. The test is very much more delicate with the arc spectra, e.g., 0.03 milligram Sr per cc. See chapter on barium, Preliminary Tests under Separations.

ESTIMATION

Strontium never occurs free in nature. It is found principally in the ores celestine, SrSO₄, and strontianite, SrCO₃. It generally accompanies calcium in the various forms of calcite and aragonite. It occurs with barium in barytocelestine, and is found in barytes. It also occurs associated with barium as a silicate in brewsterite, Al₂O₃·H₂O(BaSr)O₂·(SiO₄)₂·3H₂O. It is found in traces in certain mineral waters and in sea-water.

The compounds of strontium are used for medicinal purposes; for red fire in pyrotechnics; for the manufacture of iridescent glass; the dioxide for bleaching purposes; the sulphide for luminous paint; the hydroxide for refining of beetroot sugar, being preferable to lime, as the saccharate of strontia is more granular.

Chapter contributed by Wilfred W. Scott.
Preparation and Solution of the Sample

The following facts regarding solubility may be of value in the determination of strontium. 100 cc. of water dissolves 1.74 grams Sr(OH)\(_2\) at 20° C. The hydroxide is less soluble than that of barium. The peroxide dissolves to the extent of only 0.008 gram per 100 cc. 20° C. One hundred cc. of water dissolves 0.0011 gram SrCO\(_3\) (18°); 0.0114 gram SrSO\(_4\) at 18° and 0.0104 at 100°; the presence of sulphuric acid decreases this solubility, i.e., 0.00083 gram SrSO\(_4\); 0.0051 gram SrC\(_2\)O\(_4\) at 18° and 5 grams at 100° C.; the presence of oxalic acid decreases this solubility. The sulphate dissolves in concentrated sulphuric acid, and is appreciably soluble in HCL, HNO\(_3\), HC\(_2\)H\(_3\)O\(_2\) NH\(_4\)Cl, NH\(_4\)NO\(_3\), NaCl, MgCl\(_2\). The carbonate and oxalate are soluble in mineral acids.

The procedure for the treatment of ores and strontium products is the same as those described for barium and calcium. We refer to the chapters on these elements for the preparation of the strontium solution.

SEPARATIONS

Separation of Strontium from Magnesium and the Alkalies. The procedure is the same as the one given in detail under barium for the separation of the alkaline earths from magnesia and the alkalies. Either the oxalic acid method or precipitation of strontium as a sulphate in presence of alcohol will accomplish this separation. If a sulphate precipitation is made it will be necessary to fuse the sulphate with sodium carbonate to get it into solution or to effect further separation from members of the ammonium carbonate group, should these be present.

Separation of Strontium from Calcium. Strontium and calcium are converted into the nitrates and taken to dryness and all water expelled by heating to 140° C. for an hour or more. The nitrates are now extracted with equal parts of absolute alcohol and anhydrous ether or by boiling with amyl alcohol at 130° C. (hoof). Strontium remains insoluble and calcium goes into solution as the nitrate. Strontium nitrate may require further solution in water, evaporation to dryness, heating and extraction to remove calcium completely, should this be present in large excess. The nitrate of strontium is dissolved in water and strontium determined by one of the procedures given later. See detailed procedure for separation under Barium.

Separation of Strontium from Barium. The procedure is given in detail under chapter on Barium. In brief one of the following methods may be used: Strontium and barium in a mixture of the nitrates are separated from calcium by treatment with ether-alcohol mixture, in which Ba(NO\(_3\))\(_2\) and Sr(NO\(_3\))\(_2\) are insoluble. The nitrates dissolved in water are separated by precipitating barium as BaCrO\(_4\) from a faintly acetic acid solution, strontium remaining in solution.

1 Treadwell claims solubility = 0.00055, i.e., 1 part SrCO\(_3\) in 18,045 parts of water.

2 Advantage may be taken of the insolubility of strontium sulphate in ammonium sulphate in separating it from the soluble calcium salt.
GRAVIMETRIC METHODS

Strontium may be conveniently determined either as the sulphate, the carbonate or as the oxide. The first procedure is considered the best by authorities.

Determination as Strontium Sulphate, $\text{SrSO}_4$

Procedure. A slight excess of dilute sulphuric acid is added to the neutral solution of strontium, and then an equal volume of alcohol. The mixture is stirred well and settled for several hours, or overnight, if more convenient. The precipitate, $\text{SrSO}_4$, is filtered onto a small ashless filter and washed first with 50% alcohol containing a little sulphuric acid, then with alcohol until free of acid. The precipitate is dried and the paper and the greater part of the salt ignited separately, then combined and weighed as $\text{SrSO}_4$.

Factors. $\text{SrSO}_4 \times 0.477 = \text{Sr}$, or $\times 0.8037 = \text{SrCO}_3$, or $\times 0.5642 = \text{SrO}$.

Determination as StrontiumCarbonate

Strontium carbonate is not readily decomposed by ignition as is calcium carbonate, so that its determination in this form may be satisfactorily made.\footnote{N. B. Avoid a large excess of $(\text{NH}_4)_2\text{CO}_3$. $\text{NH}_4\text{Cl}$ has a solvent action on $\text{SrCO}_3$.}

Procedure. The carbonate is precipitated by adding ammonium carbonate in slight excess to the ammoniacal solution of strontium, heated nearly to boiling. The solution is allowed to stand for several hours and filtered cold. The washed strontium carbonate and filter are ignited gently and the cooled residue weighed as $\text{SrCO}_3$.

Factors. $\text{SrCO}_3 \times 0.5935 = \text{Sr}$, or $\times 1.2443 = \text{SrSO}_4$, or $\times 0.702 = \text{SrO}$.

Determination as Oxide, $\text{SrO}$

Strontium is precipitated as the oxalate by addition of ammonium oxalate to the slightly ammoniacal solution. The precipitate is filtered and washed with water containing ammonium oxalate. The residue is ignited and weighed as $\text{SrO}$.

Factors. $\text{SrO} \times 0.8456 = \text{Sr}$, or $\times 1.7726 = \text{SrSO}_4$, or $\times 1.4245 = \text{SrCO}_3$.

VOLUMETRIC METHODS

The volumetric methods for determining strontium presuppose its isolation from other elements.

Alkalimetric Method, Titration with Standard Acids

Either the carbonate or the oxide of strontium may be titrated with standard hydrochloric or nitric acids. The compound is treated with a known amount of standard acid added in excess, using methyl orange indicator. The solution is heated below boiling to complete the reaction and, upon cooling, the excess of acid is titrated with standard alkali.

One cc. normal acid = 0.04381 gram Sr, or 0.05181 gram SrO, or 0.07381 gram SrCO_3.
Titration of the Chloride with Silver Nitrate

Strontium chloride, free from other chlorides, may be determined indirectly by titration of its combined chlorine with silver nitrate by Mohr's method, using potassium chromate indicator. One cc. N. AgNO₃ = 0.04381 gram Sr.

The oxide or carbonate is slightly supersaturated with hydrochloric, then taken to dryness and heated at 120°C. in the air bath to expel the excess of acid. Chlorine is determined on an aliquot portion.