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METHODS
OF THE CHEMISTS OF THE
United States Steel Corporation

FOR SAMPLING AND ANALYSIS OF FERRO-ALLOYS AND BEARING METALS

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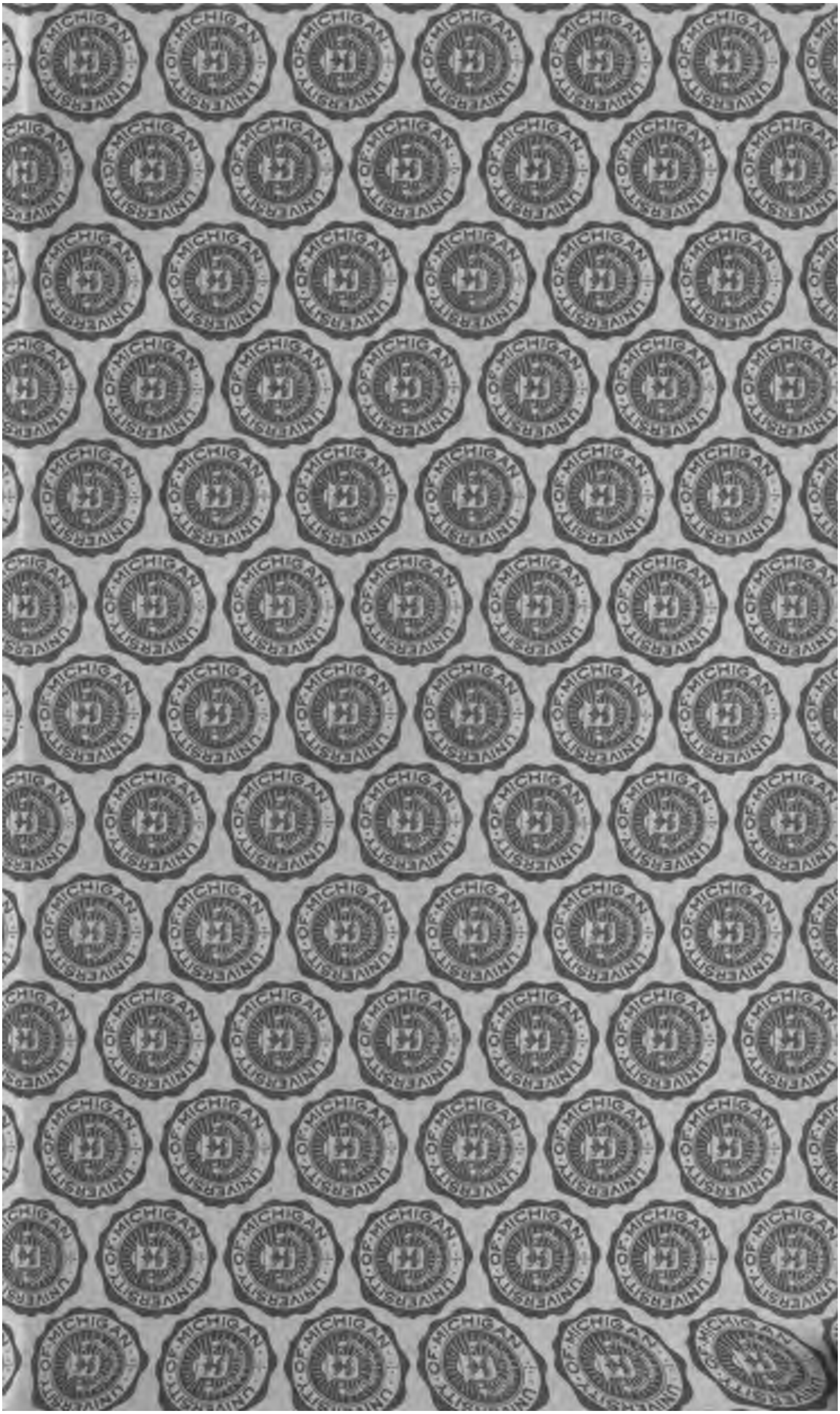
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THE METHODS

OF THE CHEMISTS OF THE

UNITED STATES STEEL CORPORATION

FOR THE

SAMPLING AND ANALYSIS

OF

FERRO-ALLOYS AND BEARING METALS

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J. M. CAMP,
CHAIRMAN CHEMISTS' COMMITTEE

PREFACE.

In pursuance of the policy of the United States Steel Corporation of standardizing the methods of sampling and analysis of the various steel works' products and materials, this pamphlet, describing the laboratory treatment of ferro-alloys and bearing metals, has been prepared and is presented by a committee of chemists. It is hoped that the adoption of the methods described herein, representing the best practice of the chemists of the Corporation, will lead to the attainment of more uniformly satisfactory results in the analysis of these alloys.

The Committee desires to express its thanks to the Electro Metallurgical Company, Niagara Falls, N. Y., Mr. J. A. Holladay, Chief Chemist, who aided in the preparation of this pamphlet by an exchange of methods, some of which are incorporated herein.

The committee, under whose direction this pamphlet is written, is composed of the following members: J. L. Harvey, Chairman, of the Homestead Works, Carnegie Steel Company; W. D. Brown, of the Duquesne Works, Carnegie Steel Company; J. L. Hyland of the Gary Works, Illinois Steel Company, and H. E. Campbell, of the Clairton Works, Carnegie Steel Company.

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INTRODUCTION.

The methods described in the following pages were compiled after a thorough examination of the methods employed by the chemists of the Corporation, consideration being given to accuracy of results and simplicity of procedure. In some cases alternate methods are given.

The ferro-alloys considered in this pamphlet are ferro-manganese, spiegel, silico-spiegel, ferro-silicon, ferro-chromium, ferro-phosphorus, ferro-vanadium, ferro-molybdenum, ferro-tungsten and ferro-titanium. The methods of analysis of aluminum, nickel, and pyrites, although not ferro-alloys, are also given, as they are, like ferro-alloys, added to steel for various purposes. In all cases, the determination of each element likely to be present is treated separately, except carbon, for which a method applicable to all ferro-alloys is given.

In the preparation of the methods for bearing metals, which include what are known as white bearing metals, bronzes and brasses, it has been the endeavor of the committee to describe a method or methods applicable to any bearing metal and to include the determination of elements likely to occur, but rarely found, in bearing metals.

FERRO-ALLOYS

SAMPLING.

BY THE MANUFACTURER.

FERRO-MANGANESE.

Samples are taken while the metal is running from the furnace. At intervals corresponding to the middle of the first, the middle and the last bed, or portion, of the cast, the molten metal is dipped from the runner with a spoon and poured into a small mould. At the end of the cast, the samples are broken, and equal portions are taken from their centers. The pieces thus selected are combined and crushed in a steel mortar to pass through an 80 mesh sieve. This powder constitutes the sample for analysis.

BLAST FURNACE FERRO-SILICON AND SPIEGEL.

The sample for each cast is taken at three different periods, corresponding to the middle of the first, second and third portions of the cast, by removing spoonfuls of the metal from the runner as it flows from the furnace. Each spoonful of the molten metal is immediately poured, in a small stream, upon a cold steel plate, where it assumes the form of small shot. Equal portions of these shot from the three spoonfuls are combined and crushed to pass through an 80 mesh sieve.

BY THE CONSUMER.

FERRO-MANGANESE, SPIEGEL, BLAST FURNACE FERRO-SILICON, AND FERRO-PHOSPHORUS.

These alloys are shipped loose, in carload lots, and an average sample is taken from each car in the following manner: The car is laid off lengthwise into four parallel lines equal distances apart, and a sample—about ½″ cube in size—taken every two feet along each line. The pieces are combined, crushed to ⅛″ and quartered until 80 to 100 grams remain. This portion is crushed in a diamond steel mortar with tightly fitting pestle to pass an 80 or 100 mesh sieve, and, after drying for one hour at 100° C., is ready for analysis.

ELECTRIC FERRO-SILICON, FERRO-CHROMIUM, FERRO-VANADIUM, FERRO-TITANIUM, FERRO-MOLYBDENUM, AND FERRO-TUNGSTEN.

These alloys are received in barrels or casks. Each container is opened and from five to ten pieces—½″ cube in size—are taken therefrom. For ferro-silicon, ferro-chromium and ferro-titanium, five samples are taken from each container, while ten should be taken for ferro-vanadium, ferro-molybdenum and ferro-tungsten. The chemist should take measures from time to time to assure himself, by proper sampling and a special analysis, that the materials in the containers are of uniform composition from top to bottom.

The samples, so obtained, are combined so that each car, or each grade in the car, is represented by a sample. The alloy is crushed to ⅛″ and quartered until 80 to 100 grams remain. This portion is crushed to pass an 80 or 100 mesh sieve, and, after drying for one hour at 100° C., the sample is ready for analysis.

In pulverizing abrasive ferro-alloys, such as electric ferro-silicon, in cast iron or steel mortars, particles of iron are worn from the mortar and contaminate the sample. A strong magnet should be used in the case of non-magnetic materials to extract this unalloyed iron as a final operation before analysis.

ALUMINUM AND NICKEL.

These metals are sampled by drilling or sawing across the end of a pig. The sample for analysis is collected after the tool has penetrated the scale on the surface of the pig.

PYRITES.

This may be received in barrels or loose in cars. In the former case, it is sampled as described under electric ferro-silicon, and in the latter case, it is sampled like ferro-manganese.

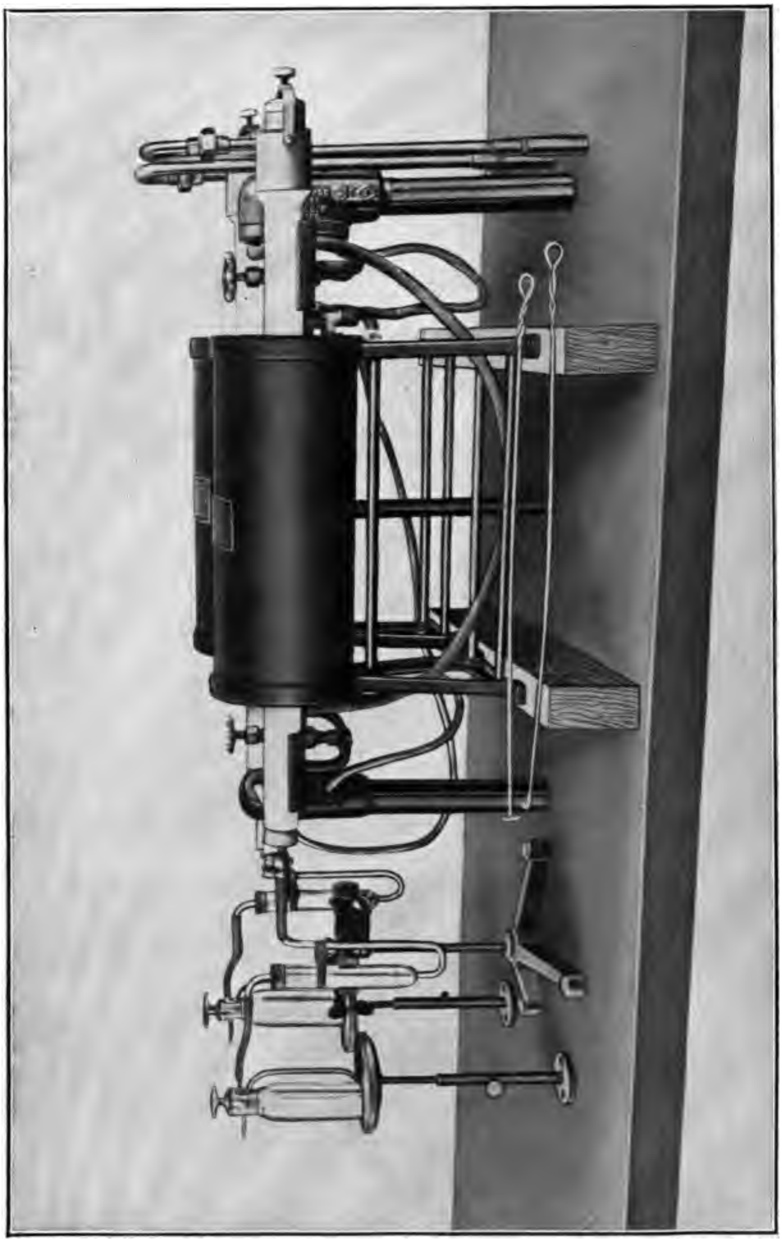
METHODS OF ANALYSIS.

GENERAL REMARKS.

For the sake of clearness and brevity the following general statements concerning reagents are made. It is to be understood that whenever the mineral acids and ammonia are mentioned, those reagents in concentrated form as received from the manufacturers are meant. When these reagents are diluted, the specific gravity will be noted or the proportions given in parenthesis, the relative amount of water, which in all cases must be distilled, being indicated by the last figure of the ratio. All acids and chemicals used should be of C. P. quality. Percentage solutions indicate the weights of solids in grams or the volume of concentrated liquids in cc. diluted to one hundred cc. Where the preparation of the solution is described in detail it is on a one liter basis, it being understood that in practice some multiple will be used, if a greater quantity is desired.

DETERMINATION OF CARBON.

In all ferro-alloys here considered, carbon is determined by the direct combustion method. The apparatus consists of an electrically heated furnace maintained at a temperature of 1000° C. excepting in the analysis of ferro-chromium, when the temperature should be 1050° C. or higher. The furnace contains a silica tube, ⅞″ or 1″ bore, and 24″ long, the ends of which are kept cool by an air blast or any other convenient arrangement. The silica tube is filled for the last. 9″ of its length with ignited asbestos (preferably with asbestos that has been impregnated with ferrous sulphate before ignition) to insure complete combustion of sulphur to sulphur trioxide, in which combination it is deposited in the delivery end of the silica tube and in the phosphoric anhydride tube that follows. The exit end of the tube is connected to a drying bulb containing phosphoric anhydride to absorb moisture in the gas. The drying bulb is connected by a piece of tubing to an absorbent bottle containing soda lime or soda asbestos to absorb the carbon dioxide, and phosphoric anhydride to absorb the water evaporated or formed from soda lime. Oxygen is obtained from a cylinder provided with a reducing valve by which the pressure can be reduced to 1 or 2 pounds at the option of the operator, and the pressure uniformly maintained during the combustion. A stopcock is inserted between the reducing valve and the



Apparatus for the Determination of Carbon by the Direct Combustion Method.

furnace. The oxygen usually requires no purification, but if it should contain an appreciable quantity of carbon dioxide, it is passed through a 500 cc. aspirator bottle containing lump soda lime before entering the combustion tube.

The cut on the opposite page shows the combustion apparatus set up in duplicate. At the entrance end is shown a coupling which takes the place of a rubber stopper. A brass end, or nozzle, which contains a nipple for the entrance of oxygen, fits over the end of the silica tube and is cemented to it with plaster of Paris. The tube is stoppered by a brass cap which is clamped tightly against a rubber gasket on the face of the nozzle by means of a yoke and screw. The stopcock, which is inserted in the oxygen line between the reducing valve and brass nozzle, is not shown in the cut. The apparatus being assembled and the absorbent bottle connected, the stopcock leading to the furnace is opened, and the pressure so regulated that the rate of flow from the absorbent is from 400 to 500 cc. per minute; oxygen is passed for five minutes, the stopcocks are closed, and the absorbent bottle is disconnected and weighed. This operation is repeated until constant weight is obtained.

For the determination, a suitable multiple of the factor weight (.2728 gram) of the extremely fine sample, is mixed with three times its weight of cupric oxide which is ground fine and previously ignited. The mixture is placed in a boat protected by alundum, chromite, emery, or other suitable refractory material. When the alloy is known or believed to contain a high percentage of sulphur, a weight of carbon free red lead, equal to the weight of the sample taken, is intimately mixed with the sample before being placed in the boat, in which case cupric oxide is omitted. The use of either cupric oxide or red lead is recommended in all determinations of carbon in ferro-alloys. Ferro-chromium is the most refractory of the ferro-alloys, and it is sometimes necessary to place upon the mixture of the sample and cupric oxide in the boat a factor weight of finely powdered iron (preferably reduced by hydrogen) or finely divided steel of low and known carbon content. In case the latter is used a proper correction must be made for the carbon in the steel used.

The absorbent bottle is connected to the train, and the boat and contents are pushed to the hottest part of the tube, which is then stoppered. The valve on the oxygen supply is immediately opened, and oxygen passed for five minutes. The valve is then closed, the stopper of the absorbent bottle is also closed, and the bottle is disconnected and weighed. The increase in weight is carbon dioxide, which, divided by the multiple of the factor weight used and multiplied by 100, gives the per cent. carbon.

ANALYSIS OF FERRO-MANGANESE.

MANGANESE.

GRAVIMETRIC METHOD.

One-half gram of the sample is transferred to a 500 cc. flask and dissolved in 20 cc. hydrochloric acid. The iron is oxidized by boiling with 5 cc. of nitric acid, the solution is diluted to 150 cc., and ammonium hydroxide added until a faint precipitate persists after thorough agitation. Twenty cc. of a 10% solution of ammonium acetate are added, when the solution is diluted to 350 cc., and boiled for one minute. The precipitate is removed by filtration, washed with hot water three times, and dissolved in hot hydrochloric acid (1:1). The iron is again precipitated as the basic acetate as just described, the precipitate removed by filtration, and washed five times. The combined filtrates from the basic acetate precipitates, after the addition of 7 cc. of acetic acid, are heated to boiling. Fifty cc. of a 10% solution of ammonium phosphate are added, followed by 50 cc. of ammonium hydroxide, added slowly, while the solution is vigorously stirred. The precipitate is allowed to settle, removed by filtration, and washed with a solution containing 25% ammonium hydroxide and 5% nitric acid. The precipitate is ignited, gently at first, and finally at a high temperature. The residue is weighed as manganese pyrophosphate, 38.69% of which is manganese.

In order to ascertain whether a complete separation of the manganese from the iron was made, the basic acetate precipitate of iron should be examined for manganese. It is dissolved in nitric acid (1.20 sp. gr.) and the solution treated and tested as described under the ammonium persulphate-arsenite method for manganese in ferro-phosphorus.

VOLUMETRIC METHODS.

CHLORATE–OXALATE METHOD.

Two-tenths gram of the sample is transferred to a 600 cc. beaker, 75 cc. of strong nitric acid are added, and heat is applied until the sample is dissolved. Enough nitric acid to bring the volume to 75 cc. is added, and, after boiling for five or ten minutes to expel nitrous fumes, the beaker is removed from the light and cooled to room temperature. Four grams of solid potassium chlorate are cautiously added, the solution is heated to boiling, and the boiling is continued for ten minutes. The addition of the chlorate to the cold solution greatly facilitates the subsequent decomposition of the manganese dioxide in the sodium oxalate-sulphuric acid solution. The beaker and contents are removed from the heat, and the precipitate of manganese dioxide is removed by filtration through an asbestos plug which is contained in a carbon filter tube and has been previously washed with nitric acid. The precipitate and plug are washed twice with strong nitric acid, which is free from nitrous fumes. Nitric acid, free from nitrous fumes, is prepared by bubbling air through the acid one-half hour. The beaker and plug are washed twice with cold water. The plug and precipitate are transferred to the original beaker, and adhering traces of manganese dioxide are washed from the carbon filter tube with boiling water. The precipitate is then broken up with a stirring rod until it is in a finely divided state. Sufficient boiling hot water is then added to make a volume of about 100 cc. Twenty-five cc. of sulphuric acid (1:1) are added, followed by .6 gram of sodium oxalate, accurately weighed. The contents of the beaker are shaken or stirred until the precipitate is completely dissolved. Should particles of the precipitate dissolve with difficulty, these should be crushed with a stirring rod until no more manganese particles may be seen on looking through the bottom of the beaker. When completely dissolved the solution is heated to 65° C. and the excess of sodium oxalate is rapidly titrated with N/20 potassium permanganate. The end point is the first pink tint which persists for thirty seconds. The manganese dioxide obtained from a ferro-manganese sample containing 75% to 80% manganese oxidizes about four-tenths gram of the sodium oxalate added, which leaves an excess of oxalate amounting to approximately two-tenths gram.

The standard permanganate equivalent in cubic centimeters of .6 gram of sodium oxalate less the number of cubic centimeters of permanganate solution used in the titration, multiplied by the manganese factor of 1 cc. of standard potassium permanganate solution and 500, equals the per cent. manganese in the sample.

Example.

50 cc. potassium permanganate equals .2 gram sodium oxalate.

Volume potassium permanganate to titrate sample equals 52 cc.

Then;

150 cc. potassium permanganate equals .6 gram sodium oxalate and (150—52) x manganese factor x 500 equals percent. of manganese in the sample.

SOLUTION REQUIRED.

N/20 Potassium Permanganate.

Potassium permanganate	1.585 grams
Water	1000 cc.

This solution, after being filtered through an asbestos filter, is standardzed by titrating two-tenths gram of sodium oxalate dissolved in hot water and sulphuric acid (1:1) as described in the regular analysis. The manganese value of one cc. of the standard permanganate solution is found by the following calculation:

$$\frac{.409925}{\text{(Volume of permanganate solution required to oxidize one gram pure sodium oxalate.)}}$$

The figure .409925 is the weight of manganese, expressed as the fraction of a gram, equivalent to one gram of sodium oxalate.

PEROXIDE REDUCTION METHOD.

One-quarter gram of the sample is transferred to an 800 cc. beaker, dissolved in 80 cc. of nitric acid, and the solution is boiled to expel the oxides of nitrogen. Five grams of sodium chlorate are carefully added, and the boiling is continued for five minutes, or until all oxidizing gases are expelled. The solution is cooled and diluted to 500 cc. One hundred cc. of hydrogen peroxide solution are then added from a pipette. The manganese dioxide will be dissolved, and the excess peroxide is titrated with standard potassium permanganate solution. A blank is determined as follows: Sixty cc. of nitric acid are boiled for about five minutes, cooled and diluted to 500 cc. One hundred cc. of the hydrogen peroxide solution are added and titrated with standard permanganate. The difference between the permanganate required for titration of the 100 cc. of peroxide, and that for titrating the excess peroxide in the test, represents the volume required for reducing the manganese.

An approximately deci-normal permanganate solution is conveniently used, and is prepared by dissolving about 3.2 grams of the salt in one liter of water and filtering through asbestos. It is standardized by titrating a standard ferro-manganese solution in the same manner as the test just described. The hydrogen peroxide standard solution is made by adding 60 cc. of 3% solution to 800 cc. of water, to which 50 cc. dilute sulphuric acid (1:1) have been added; the solution is then diluted to one liter.

ZINC OXIDE METHOD.

One gram of the sample is placed in a 100 cc. beaker which is covered with a watch glass. Twenty cc. of nitric acid are added, and heat is applied until the alloy is dissolved. The solution is transferred to a 500 cc. flask, diluted to 350 cc., and zinc oxide emulsion added in excess. The solution, when cold, is diluted to the mark and mixed thoroughly. The precipitate is allowed to settle, and a portion of the solution is filtered. One hundred cc. of the filtrate are transferred to a 750 cc. flask and diluted to 250 cc. The solution is heated to boiling and titrated with standard permanganate until a faint permanent pink color is obtained. The permanganate solution should be of such strength that the volume required by the titration is not more than 40 cc. or 1/6 of the volume of solution before titration. The potassium permanganate is standardized against a ferro-manganese standard, the manganese content of which has been accurately determined.

SILICON.

One gram of the sample is transferred to a porcelain dish and dissolved in 25 cc. of a mixture of three parts nitric acid (1.20 sp. gr.) and one part sulphuric acid (1:1). The solution is evaporated until fumes of sulphur trioxide are evolved. The dish is cooled, and the residue dissolved in 50 cc. of 10% hydrochloric acid. The silica is collected on a filter, washed with hydrochloric acid (1:1) and hot water, ignited and weighed; 46.93% of the silica is silicon.

The silica may be treated with two or three drops of 1:1 sulphuric acid followed by 5 to 10 cc. hydrofluoric acid. Then, after evaporation of these acids, the crucible is ignited, and the weight of the silica is obtained by difference.

It is usually impossible to dehydrate the silica completely by one evaporation, and the small amount remaining in solution can be recovered only by re-evaporation of the filtrate. For very accurate work, it is recommended that this precaution be taken, and the recovered silica added to that already obtained.

PHOSPHORUS.

One to two grams of the sample are transferred to a 5 inch porcelain dish with cover glass, 25 to 40 cc. of nitric acid are cautiously added, gentle heat is applied until the sample is completely decomposed, and the solution is then boiled rapidly to dryness. The temperature is raised gradually, with final heating of the uncovered dish over the full flame of an Argand or Bunsen burner to the complete expulsion of the acid. After cooling sufficiently to avoid danger of breaking the dish, 20 to 30 cc. of concentrated hydrochloric acid are added, and heat is applied until the soluble salts are dissolved. The cover is removed and with the dish placed on a suitable asbestos ring, in order to prevent the formation of a crust of metallic salts upon the sides, the solution is evaporated to the first appearance of the separation of the chlorides. The dish is removed from the heat, 10 cc. of strong nitric acid are added, and heat is again applied for about one minute. Cold water is added to a volume of about 60 cc., when the solution is stirred with a glass rod and filtered into a suitable flask. The residue, collected on a 11 cm. filter, is washed with two per cent. nitric acid until free from iron, which insures also the complete removal of the soluble phosphate.

To the clear filtrate, with a volume of about 150 cc., a slight excess of ammonia over the amount necessary to precipitate the iron is added. The flask is shaken, the precipitate is dissolved with nitric acid, and an excess of two to ten cubic centimeters is added. With the solution at a temperature of 80° C., the phosphorus is precipitated by the addition of 75 to 100 cc. of ammonium molybdate solution, and determined gravimetrically or volumetrically, as described under the molybdate method for phosphorus in ferro-phosphorus.

SULPHUR.

GRAVIMETRIC METHOD.

Five grams of the sample are transferred to a porcelain dish and treated with 50 cc. of nitric acid. Heat is applied, and when the sample is dissolved, the solution is evaporated to a small volume. Thirty cc. of hydrochloric acid are then added, and, after the addition of one gram of sodium carbonate, the solution is evaporated to dryness and baked at only a moderately high temperature. The residue is dissolved in 30 cc. of hydrochloric acid, and the solution again evaporated to dryness to insure the complete expulsion of nitric acid. The residue is dissolved in hydrochloric acid, and this solution is evaporated until the first appearance of a film of ferric chloride, which is dissolved by a few drops (three should suffice) of hydrochloric acid. The solution is then diluted with 75 cc. of cold water and filtered, the paper being washed first with 2% cold hydrochloric acid, then with hot water. To the filtrate, with a volume of 200 cc., 5 cc. of a 10% solution of barium chloride are added, and the solution is allowed to stand at least twelve hours. The barium sulphate is removed by filtration, washed with cold 2% hydrochloric acid and water, ignited gently and weighed; 13.73% of the weight of barium sulphate is sulphur. A blank determination should be made, and the necessary correction applied.

The filtrate from the barium sulphate should be reserved and allowed to stand for at least 12 hours. Any precipitate that may form should be removed by filtration and added to that already obtained.

VOLUMETRIC METHOD.

Five grams of the sample are transferred to a flask provided with an exit tube leading into the absorbent solution, and a funnel tube leading to the bottom of the flask. Ten or twenty cc. of absorbent solution are added to the absorption vessel, which is either a 10″x1″ tube or a tall 350 cc. beaker, and diluted to 60 cc. or 200 cc., depending upon the vessel employed. Sixty cc. of hydrochloric acid (1:1) are added to the flask, and a gentle heat is applied until solution of the sample is complete, then the heat is increased until the solution boils and the gases are completely driven through the absorbent by the generated steam. At this point, the flask is disconnected from the tube leading to the absorbent solution.

The contents of the absorption tube are transferred to a 500 cc. beaker, and 10 cc. of starch solution are added. Both the absorption and delivery tubes are rinsed with cold water and any adhering precipitate is dissolved by means of a fine jet of hydrochloric acid (1:1). Care is exercised that the acid solution be not unduly agitated before the introduction of the iodine solution. If the absorption is effected in the beaker, the delivery tube is removed first, cleansed with acid and water, and, with the precaution suggested above, a small excess of the dilute acid is added. The final volume of the solution should approximate 400 cc. The solution is stirred gently in order to neutralize the alkali of the absorbent. The iodate or iodine solution is then added in successive portions, while the solution is stirred, until the addition of a final drop yields a permanent blue color.

Starch Indicator. To one liter of boiling water in a suitable flask, a cold emulsion of six grams of starch suspended in 100 cc. of cold water is cautiously added, and the boiling continued five minutes. The solution is cooled to room temperature, and, with the addition of six grams of zinc chloride in 50 cc. of cold water, it is mixed thoroughly, and set aside for a day or two with occasional shaking. After the final subsidence of the heavier residue, the starch solution is siphoned into a container and the settlings rejected. The zinc chloride is added as a preservative. Preliminary boiling of water tends to lessen frothing, or the formation of large bubbles on the addition of the starch.

Standard Iodine or Iodate Solution. Ten grams of potassium iodide and 4.5 grams of resublimed iodine are transferred to a one liter flask, 25 cc. of water are added, and the flask is allowed to stand with occasional shaking until the iodine is dissolved. Water is then added to a volume of 1000 cc. In place of the iodine solution, an iodate solution may be used. If potassium iodate is preferred for a titrating agent, this solution is prepared by dissolving 10 grams of potassium iodide and 1.12 grams potassium iodate in water and diluting to 1000 cc. The solution, in either case, is standardized against a steel of known sulphur content.

Absorbent Solution. An ammoniacal solution of cadmium chloride answers admirably and is made by dissolving five grams in a mixture of 375 cc. of water and 625 cc. of ammonium hydroxide.

IRON.

PERMANGANATE OR BICHROMATE METHODS.

One gram of the alloy is placed in a beaker, and ten to twenty cc. of hydrochloric acid are added. This variation in the amount of acid is due, aside from the variation in the percentage of iron in different samples, to the fact that, while in the permanganate method the minimum amount of free acid should be present, with the bichromate method an excess of acid is essential. The beaker is covered with a watch glass, and heated gently until the metals are completely dissolved. In case the permanganate method is to be used, the volume of the solution is reduced by evaporation to a maximum of 10 cc. This evaporation, however, is unnecessary with the bichromate method. To this hot solution, stannous chloride solution is added from a burette, drop by drop, until the color due to the ferric chloride disappears. One drop is then added in excess. The solution is diluted to about 350 cc. with cold water, 5 cc. of mercuric chloride are added, the solution is thoroughly stirred, and the iron is immediately titrated by the method selected, as described below.

PERMANGANATE TITRATION.

From 10 to 30 cc. of the manganese sulphate solution are added and the solution is stirred until thoroughly mixed.

Standard permanganate solution is added with constant stirring and at the full speed of the burette until the pink tint tardily disappears; the solution is then added, drop by drop, to the final pink end point, which may be the first stable pink coloration, or a definite excess of one or more drops as desired.

BICHROMATE TITRATION.

A number of drops, of an adopted uniform size, of the ferricyanide solution are spaced on the waxed surface of the plate which has been prepared as follows:

The clean surface is rubbed over with a stick of clean white paraffin until a light coating of wax is obtained; this coating is then rubbed lightly with a clean piece of filter paper until quite smooth and of uniform thickness.

Standard bichromate solution, almost sufficient to oxidize the iron, is added to the solution in the beaker, a test drop is transferred to the test spot on the plate, and the addition of the titrating solution is continued with frequent tests until the blue tint of the ferrous iron has given way to the yellow or brown of the oxidized iron.

SOLUTIONS REQUIRED.

Stannous Chloride.

Stannous chloride, c. p.	250 grams
Hydrochloric acid	500 cc.
Water	500 cc.

Mercuric Chloride.

A cold saturated solution.

Manganese Sulphate.

Manganous sulphate, c. p.	90 grams
Water	650 cc.
Sulphuric acid (1.84 sp. gr.)	175 cc.
Phosphoric acid (1.75 sp. gr.)	175 cc.

The solution is filtered if necessary.

Potassium Permanganate Standard.

Potassium permanganate, c. p.	5.7 grams
Water	1000 cc.

The permanganate salt is dissolved in the boiling water, and, after allowing the solution to cool, it is filtered through an asbestos plug contained in a carbon filter tube.

Potassium Bichromate Standard.

Potassium bichromate, c. p.	8.9 grams
Water	1000 cc.

Potassium Ferricyanide Indicator.

Potassium ferricyanide, c. p.	1.0 grams
Water	1000 cc.

This solution should be made fresh each day and only clear crystals of the salt used.

The permanganate and bichromate solutions are standardized against the Corporation Iron Ore Standard. In all cases, however, such standardizations must be made, as nearly as possible, under the same conditions as are maintained in the actual analysis.

ANALYSIS OF SPIEGEL AND SILICO-SPIEGEL.

SILICON.

One gram of the sample is transferred to a porcelain dish, dissolved in 15 cc. of hydrochloric acid, and the solution is evaporated to dryness. The residue is dissolved in 50 cc. of hydrochloric acid (1:10) and the silica is collected on a filter. The determination is completed and the precaution taken for the complete recovery of silica, if deemed necessary, as described under determination of silica in ferro-manganese.

MANGANESE.

CHLORATE METHOD.

The filtrate from the silicon determination is evaporated to a low volume. Fifty cc. of nitric acid are added and the solution is again evaporated to a small volume, in order to insure the complete removal of hydrochloric acid. Fifty cc. of nitric acid are again added, and the solution is evaporated until the separation of ferric nitrate. Seventy-five cc. of nitric acid are added and the solution is boiled; chlorate is then added in small portions (about 5 grams in all) until the manganese is completely precipitated as dioxide. The solution is boiled five minutes, cooled and filtered through a plug of prepared asbestos which has previously been digested with strong hydrochloric acid to free it from soluble salts. The precipitate is washed with nitric acid which is free from nitrous oxides.

The manganese dioxide is dissolved from the plug by pouring thereon a 1% solution of ammonium bisulphite and allowing it to remain until solution is complete. The plug is then washed thoroughly with hot water and the solution transferred to a 600 cc. beaker. Ten cc. of hydrochloric acid are added, and the contents of the beaker boiled to expel sulphur dioxide. Two cc. of nitric acid are then added, and the contents of the beaker again boiled to oxidize the iron. The solution is cooled and ammonium hydroxide added until a faint precipitate is formed that is not dissolved by stirring. The solution is diluted, if necessary, to 250 cc. with hot water, and, after the addition of 10 cc. of 10% ammonium acetate solution, is boiled one minute. The basic acetate precipitate of iron is removed by filtration, washed, and dissolved in hot hydrochloric acid (1:1). A basic acetate separation is again made as just described, and, if desired, the second precipitate is dissolved and tested for manganese as explained in the gravimetric method for manganese in ferro-manganese. In the combined filtrates, the manganese is precipitated as phosphate and weighed as pyrophosphate, as described under manganese in ferro-manganese.

ETHER METHOD.

To the hydrochloric acid solution, after the separation of silica as described above, 2 cc. nitric acid are added to oxidize the iron, and the solution is evaporated to a volume of 10 cc., when 25 cc. of hydrochloric acid (1.13 sp. gr.) are added. The solution is cooled, and transferred to a separatory tube. The dish is washed with hydrochloric acid (1.13 sp. gr.), and the washings are transferred to the separatory tube, which should contain a final volume (solution and washings) of not more than 50 cc. Fifty cc. of ether are then added, and the greater part of the iron is separated by shaking. The acid solution is drawn off and heated gently to evaporate the ether in solution. The iron is oxidized with nitric acid, a basic acetate separation made, and the determination concluded as given under the chlorate method.

VOLUMETRIC METHODS.

The manganese is determined as described under volumetric methods for ferro-manganese by titrating a solution of one gram of the sample.

PHOSPHORUS, SULPHUR, AND IRON.

These elements are determined as in ferro-manganese.

ANALYSIS OF FERRO-PHOSPHORUS.

PHOSPHORUS.

MAGNESIUM PHOSPHATE METHOD.

To .2787 gram of the finely ground sample in a small dry beaker, 5 cc. of concentrated sulphuric acid are added, and heat is applied until the decomposition is complete. After cooling, 20 cc. of water and 10 cc. of hydrochloric acid are added, and heat is again applied until the salts are dissolved. The solution is then filtered, and the filtrate retained in a 400 cc. beaker. Five grams of citric acid, dissolved in water, are added. The acids are neutralized with ammonium hydroxide, and 50 cc. added in excess, after which addition the solution is diluted to 250 cc. and cooled. Twenty cc. of magnesia mixture are added drop by drop, with vigorous stirring. The precipitate is allowed to settle for about one hour, removed by filtration, washed with a solution containing 250 cc. ammonium hydroxide and 50 cc. nitric acid per liter, ignited and weighed. The weight, expressed as the fraction of a gram, multiplied by 100, equals the percentage of phosphorus.

SOLUTION REQUIRED.

Magnesia Mixture.

Magnesium chloride	55 grams
Ammonium chloride	140 grams
Ammonia (.90 sp. gr.)	175 cc.
Water	825 cc.

AMMONIUM MOLYBDATE METHOD.

One-half gram of the sample is transferred to a nickel or iron crucible containing about 5 grams of sodium peroxide. The sample and peroxide are well mixed and heated over a Bunsen burner until fused and then for about 30 seconds or until the fusion is tranquil. The crucible and contents are transferred to a porcelain dish, and the fusion is extracted with water. After the action is over, the crucible is removed and washed with hydrochloric acid (1:1). Hydrochloric acid is added with stirring until the residue is dissolved, and the solution is then evaporated to dryness to dehydrate the silica. The residue is dissolved in hydrochloric acid, and the solution again evaporated until the excess of the acid is expelled. Water is added to the contents of the dish, which are boiled and filtered, the filtrate being retained in a 250 cc. volumetric flask. The solution is cooled to room temperature and diluted to 250 cc. Fifty cc. are removed by a pipette and transferred to a 500 cc. flask. After the addition of ten cc. of nitric acid, the solution is boiled a few minutes and diluted to 100 cc. Twenty-five cc. of ammonium hydroxide are added, the resultant precipitate is dissolved in nitric acid, and 8 cc. of this acid are added in excess. The solution is heated to 80° C. and, after the addition of 100 cc. of ammonium molybdate, shaken for five minutes and allowed to stand one-half hour. The yellow precipitate is removed by filtration, and the phosphorus determined by either of the following volumetric or gravimetric methods.

VOLUMETRIC METHOD.

The yellow precipitate is washed with 2% nitric acid until free from iron and soluble salts, then with 1% sodium nitrate solution until the washings are free from acid. The paper and contents are transferred to a beaker or flask, and an excess of standard sodium hydroxide solution is added. The paper is macerated with a glass rod or by shaking; five drops of a one-tenth per cent. alcoholic solution of phenolphthalein and 75 cc. of cold, boiled water are added, followed by standard nitric acid solution until the pink color disappears. The titration is completed by adding standard alkali solution until the appearance of a permanent pink color. The difference between the total volumes of standard alkali and of standard acid represents the phosphorus.

The standard alkali solution is made by dissolving 6.6 grams of sodium hydroxide in 500 cc. of water; 1 cc. of a 2% solution of barium hydroxide is added to precipitate any carbonate. This precipitate is removed by filtration, and the filtrate is diluted to one liter.

The standard acid solution is made by diluting 10 cc. of nitric acid to one liter. The acid and alkali solutions are adjusted so that they exactly agree, and one cc. is equivalent to one-hundredth per cent. phosphorus when a 2 gram sample of steel of known phosphorus content is used as a standard.

GRAVIMETRIC METHOD.

The yellow precipitate is transferred to a tared paper, which has been previously dried for one hour at 110° C., and weighed between watch glasses. After washing with 2% nitric acid, the paper and contents are lightly and carefully pressed between blotting paper, dried for one hour at 110° C., and weighed between watch glasses. 1.65% of the weight of the yellow precipitate is phosphorus.

The ammonium molybdate solution is made by dissolving 65 grams of 85% molybdic acid in 142 cc. of water and 143 cc. of ammonium hydroxide. This solution is cooled and added, with constant stirring, to 715 cc. of cold nitric acid (1.20 sp. gr.). In order to insure a clear solution, 1 drop of a 10% solution of ammonium phosphate is added. The solution is allowed to stand for 12 hours and filtered, preferably through an asbestos filter.

MANGANESE.

Two-tenths of a gram of the sample contained in a 50 cc. beaker is treated with 5 cc. of concentrated sulphuric acid. Heat is applied, and, when the alloy is dissolved, the solution is diluted with 5 cc. of water and transferred to a 50 cc. flask or an 8" x 1" tube. Then 10 cc. of nitric acid (1.20 sp. gr.) are added. The flask or tube is heated, 15 cc. of silver nitrate solution containing 1.33 grams of silver nitrate per liter of water are added; and this is followed by approximately one gram ammonium persulphate to oxidize the manganese. After the color has developed, the solution is cooled, diluted with about 50 cc. water, which may contain sufficient chloride to combine with the silver present, and titrated with sodium arsenite solution to the disappearance of the pink color.

The sodium arsenite solution is made by dissolving 1.1 gram of the salt in one liter of water. It is standardized against a solution of standard potassium permanganate or standard steel, and adjusted so that 1 cc. equals one-tenth per cent. manganese on a two-tenths gram sample.

SULPHUR.

FUSION METHOD.

One gram of the sample is fused with a mixture of equal parts of sodium carbonate and peroxide in an iron or nickel crucible. After the fusion is quiet, it is allowed to cool and is then disintegrated in water. The resultant solution is boiled, filtered into a 600 cc. beaker, acidified with hydrochloric acid, transferred to a dish, and evaporated to dryness. The residue is moistened with a small amount of hydrochloric acid, water is added, and heat applied. The solution is filtered, the filtrate is heated to boiling, and barium sulphate is precipitated by the addition of 5 cc. of 10% barium chloride solution. The solution is kept warm and allowed to stand for 4 hours. The precipitate is then collected on a filter, washed with hot water, ignited and weighed; 13.73% of the weight is sulphur. The amount of sulphur occurring in the iron or nickel crucible and the fluxes should be determined by conducting a blank, and a correction applied for the amount of barium sulphate found.

The determination of sulphur by gravimetric methods is in all cases conducted with great care to prevent contamination from outside sources. Fusions, ignitions and evaporations are preferably carried out by means of electric appliances, and if gas is used, contamination, due to sulphur in the products of combustion of the same, must be adequately guarded against.

MAGNESIA METHOD.

One gram of the sample, powdered to pass a 100 mesh sieve, is mixed in a crucible with 6 grams of a mixture of two parts magnesia and one part sodium carbonate, and a covering of the mixture laid thereon. The crucible is then placed in the front of an extremely hot muffle furnace, then gradually moved toward the hot zone, where it is allowed to remain for four hours. The contents of the crucible are transferred to a beaker, water and 10 cc. of bromine solution are added, and the solution is boiled to dissolve the sulphate. The solution is then filtered, acidulated with hydrochloric acid, and heated to boiling. The determination is finished as in the preceding method.

SILICON.

One gram or the double factor weight (.9386 gram) of the sample is treated with 10 cc. of sulphuric acid. Heat is applied until the sample is dissolved, the solution is cooled, and 50 cc. of water and 5 cc. of hydrochloric acid are added. A gentle heat is applied until all salts are dissolved. The silica is removed by filtration, washed with hot hydrochloric acid (1:1) and water, weighed, and calculated to per cent. silicon.

IRON.

One-half gram of the sample is dissolved in a 250 cc. beaker with 10 cc. concentrated sulphuric acid. When solution has been effected, 40 cc. of water are cautiously added, followed by 15 cc. hydrochloric acid. The solution is boiled three minutes, when the iron is reduced with stannous chloride solution and the determination finished by potassium bichromate titration as for iron in ferro-manganese.

ANALYSIS OF ELECTRIC FERRO-SILICON.

SILICON.

One-half gram or the factor weight (.4693 gram) of the sample is mixed in an iron or nickel crucible with 8 grams of sodium peroxide and fused at a gentle heat. The fusion is disintegrated by placing the crucible and contents in a porcelain dish containing water, and the solution, after removal of the crucible, is acidified with hydrochloric acid and evaporated to dryness on a sand bath. The residue is dissolved in hydrochloric acid (1:1), and the silica is removed by filtration and washed. The filtrate is again evaporated to dryness, or evaporated with 30 cc. sulphuric acid (1:1) to fumes of sulphur trioxide, and the small portion of silica not rendered insoluble by the first evaporation is recovered by filtration and added to the main portion. The combined papers and contents are ignited and weighed. The impure silica is moistened with water and 3 drops of sulphuric acid. Sufficient hydrofluoric acid is then added to dissolve the silica, and the contents of the crucible are evaporated to dryness. The crucible is then heated in the muffle furnace or by blast lamp and weighed. The loss in weight represents silica, 46.93% of which is silicon. If the factor weight were used, the weight of the silica times 100 gives the percentage of silicon. Sodium peroxide contains silica as an impurity. A blank analysis, using the same amount of peroxide, should, therefore, be made, and the weight of this silica deducted from that obtained in the analysis.

MANGANESE.

Two-tenths of a gram of the sample is transferred to a platinum crucible of 30 cc. capacity, and 10 cc. of nitric acid (1.20 sp. gr.) are added, followed by hydrofluoric acid, drop by drop, until the alloy is dissolved. Five cc. of sulphuric acid (1:1) are then added, and heat is applied until fumes of sulphur trioxide appear. The crucible is coöled, and 5 cc. of water are added. The solution is transferred to a 1″ tube or 50 cc. flask, and the crucible washed with 10 cc. of nitric acid (1.20 sp. gr.). The manganese is then determined by the persulphate-arsenite method, as described under manganese in ferro-phosphorus.

PHOSPHORUS.

One gram of the sample is transferred to a platinum dish, and 30 cc. of nitric acid (1.20 sp. gr.) are added, followed by hydrofluoric acid, drop by drop, until the reaction ceases. Five cc. of sulphuric acid (1:1) are then added, and the solution is evaporated until fumes of sulphur trioxide appear, and all hydrofluoric acid is expelled. The residue is dissolved in water with the aid of heat. The solution is transferred to an Erlenmeyer flask, and ammonium hydroxide added in slight excess, followed by 8 cc. of nitric acid. The solution is heated to 80° C., and the phosphorus precipitated by the addition of 50 cc. of ammonium molybdate solution. The element is then determined volumetrically or gravimetrically, as described under the molybdate method for phosphorus in ferro-phosphorus.

IRON.

One gram of the sample is treated in a platinum dish with 60 cc. of the hydrofluoric-nitric-sulphuric acid mixture. A few cubic centimeters of hydrofluoric acid are added, if the alloy is not entirely decomposed by the acid mixture. When solution has been obtained, the dish is placed over a burner, and the liquid evaporated to fumes of sulphur trioxide. After cooling and digesting the residue with water, the contents of the dish are transferred to a beaker for titration. It may be necessary, after treating with water, to use a few cc. hydrochloric acid (1:1) to remove the last traces of salts from the dish.

The solution is evaporated to a volume of 30 cc., 10 cc. of hydrochloric acid are added, the iron is reduced by stannous chloride solution, employing one drop in excess. The analysis is finished by titration with a standard potassium bichromate solution as described under the determination of iron in ferro-manganese.

SOLUTION REQUIRED.

Hydrofluoric-nitric-sulphuric Acid Mixture.

Hydrofluoric acid (48%)	50 cc.
Nitric acid (1.20 sp. gr.)	50 cc.
Sulphuric acid (1:1)	10 cc.
Water	150 cc.

The constituents are measured in a platinum dish or crucible and the mixture is kept in a ceresin bottle.

SULPHUR.

Sulphur is determined as in ferro-phosphorus, care being taken in the magnesia method that the alloy does not touch platinum.

ALUMINUM AND COPPER.

One gram of the sample is dissolved as for the determination of iron. The solution is evaporated until all fumes of sulphur trioxide are expelled. Thirty cc. of hydrochloric acid (sp. gr. 1.13) are added to the dish, and gentle heat is applied until all salts are in solution. After cooling, the liquid is transferred to a separatory funnel, and the dish is rinsed with hydrochloric acid (sp. gr. 1.13), keeping the total volume under 50 cc. Sixty cc. of ether are now added, and the funnel is stoppered and shaken for a few minutes. After allowing 5 minutes to separate and drain, the lower layer is carefully drawn into a 350 cc. beaker and the ether is expelled by heating.

If determination of copper is desired, it is precipitated from the solution, after diluting to 300 cc., by saturating with hydrogen sulphide gas. When the precipitate has settled, it is removed on a paper, washed with hydrogen sulphide water, and carefully ignited to the oxide in a weighed crucible. Too great a temperature in the ignition causes the copper oxide to fuse to the crucible. Since copper oxide is somewhat hygroscopic, care should be observed that the residue in the crucible does not absorb moisture from the air. The per cent. copper is calculated by multiplying the weight of copper oxide by the factor 79.89.

To determine the copper volumetrically, the oxide is dissolved in the crucible with the least amount of nitric acid; the solution is transferred to a 250 cc. beaker, evaporated to the smallest volume possible, and finished as described for copper in ferro-molybdenum.

The filtrate, reserved after removing the copper, is boiled to expel the hydrogen sulphide, the last traces being eliminated by a few crystals of chlorate, when the solution is ready for the precipitation of the aluminum. In case copper is not determined, the solution, after the ether separation, is diluted to 300 cc. and 5 cc. of nitric acid are added. It is then heated to boiling, whereupon it is ready for the aluminum determination.

To either solution, made ready as above, ammonium hydroxide is added until slightly ammoniacal, and the solution is boiled for a minute to precipitate completely the hydroxides, which are removed by filtration. The filtrate, containing manganese, calcium and magnesium, is retained for the determination of lime and magnesia.

Cold hydrochloric acid (1:1) is employed to dissolve the hydroxides from the filter. The solution thus obtained is diluted to 400 cc., and 20 cc. of a 10 per cent. solution of ammonium phosphate are added, followed by ammonium hydroxide until a faint permanent precipitate is obtained. One and one-half cc. of hydrochloric acid are then added, followed by 20 cc. of a 20 per cent. solution of sodium hyposulphite. This solution is heated to boiling, at which point 15 cc. of a 20 per cent. ammonium acetate solution and 8 cc. of acetic acid are added. Boiling is continued for ten minutes. The precipitate is allowed to subside, collected on a filter paper, washed with hot water, ignited in a porcelain or alundum crucible and weighed; 22.19 per cent. is aluminum. If titanium is present, it should be separated and determined as described under titanium in ferro-titanium.

CALCIUM.

The filtrate remaining from the separation of the hydroxides is concentrated to 200 cc., and about one gram of ammonium persulphate and 25 cc. of ammonium hydroxide are added to the boiling solution. The manganese dioxide thus precipitated is removed by filtration. To the filtrate 10 cc. of a saturated solution of ammonium oxalate are added, and the solution is boiled ten minutes. The precipitate of calcium oxalate is collected on a filter, washed with hot water, ignited to calcium oxide and weighed; 71.46 per cent. is calcium.

Calcium and magnesium rarely occur in electric ferro-silicon in more than minute quantities. If they are not detected by these methods, the amount of either may be safely disregarded in ordinary practice. In the event, however, that determination of minute amounts of these elements is required, as large an initial weight of the sample as can be handled should be taken for the analysis.

MAGNESIUM.

To the filtrate from the calcium oxalate, obtained as above, 5 cc. of a 10% solution of ammonium phosphate and 25 cc. of ammonium hydroxide are added, and the solution is allowed to stand at least 12 hours. The precipitate is then collected on a filter paper, washed with dilute ammonia (1:4), ignited at a low temperature and finally at a high temperature and weighed as magnesium pyrophosphate, 21.84% of which is magnesium.

UNALLOYED METALLIC IRON.

Abrasive materials of the nature of electric ferro-silicon derive a large amount of metallic iron when they are ground in an iron or steel mortar. A magnet may be employed to extract this unalloyed iron, but it is difficult to make a complete separation. A quantitative determination of unalloyed iron which remains in the prepared sample after treatment with a magnet may be made as follows:

Five grams of the alloy are placed in a 250 cc. beaker, and 25 cc. of nitric acid (sp. gr. 1.13) are added. The contents are heated to boiling for a few minutes, diluted to a volume of 50 cc. with water, and the alloy is immediately removed on a paper and washed well with hot water. Any iron in the filtrate is precipitated with ammonia, separated by filtration, dissolved in the least amount of hot hydrochloric acid (1:1), and, after reduction with stannous chloride, is titrated with standard permanganate solution, as described under iron in ferro-manganese. The per cent of unalloyed metallic iron is subtracted from 100, and the figure obtained is divided into the per cent of each constituent found, thereby reducing all the analytical results to the basis of the original sample. In the case of iron, the percentage of unalloyed iron is subtracted from the total iron before the correction is applied.

ANALYSIS OF BLAST FURNACE FERRO-SILICON.

SILICON.

One gram, or the double factor weight (.9386 gram), of the sample is transferred to a porcelain dish with cover, and 20 cc. of hydrochloric acid are added, followed by 25 cc. of a mixture of 3 parts nitric acid (1.20 sp. gr.) and one part sulphuric acid (1:1). A gentle heat is applied until all the material is in solution, when the heat is increased and the solution is evaporated until fumes of sulphur trioxide appear. The cover glass is removed from the dish, the residue is dissolved in 50 cc. of 10% hydrochloric acid by heating, and the silica is removed by filtration, ignited, weighed and calculated to silicon.

IRON.

One gram of the alloy is dissolved in 25 cc. hydrochloric acid; the iron is reduced with stannous chloride solution, and the determination is finished by titration with potassium bichromate as described under iron in ferro-manganese.

MANGANESE, PHOSPHORUS AND SULPHUR.

Manganese and phosphorus are determined as in electric ferro-silicon. Sulphur is determined volumetrically as in ferro-manganese, or gravimetrically as in electric ferro-silicon.

ANALYSIS OF FERRO-TITANIUM.

SILICON.

One gram of the sample is transferred to a beaker or dish, dissolved in 50 cc. of sulphuric acid (1:4), and the solution is evaporated until fumes of sulphur trioxide appear. When cold, 100 cc. of water are carefully added, and heat is applied to dissolve the iron salts. The residue, which contains the silica and some titanic acid, is collected on a filter, ignited in a platinum crucible and weighed. The silica is volatilized with hydrofluoric acid to which several drops of sulphuric acid are added. The residue is weighed and reserved. The difference in weight multiplied by .4693 is silicon.

TITANIUM.

The filtrate from the impure silica is diluted to 400 cc., ammonia is added until a faint permanent precipitate is formed; then in succession, 1½ cc. of hydrochloric acid, 10 cc. of glacial acetic acid, and 50 cc. of a 20% thiosulphate solution are added. The contents of the beaker are boiled 10 minutes and the precipitated titanic acid is removed by filtration. The precipitate is washed with 2% acetic acid, ignited in the crucible containing the residue from the silica volatilization, and fused with sodium carbonate. The fusion is disintegrated in water, and the sodium titanate filtered from the soluble sodium phosphate and aluminate. The paper containing the sodium titanate is transferred to a beaker, hydrochloric acid (1:1) added, and heat applied until the titanate is dissolved. The contents of the beaker are then filtered, the filtrate is neutralized with ammonium hydroxide, and a second precipitation made as just described. The precipitate of titanic acid is washed with 2% acetic acid, ignited and weighed; 60.05% is titanium.

IRON.

One-half gram of the sample, in an Erlenmeyer flask, is dissolved in 50 cc. sulphuric acid (1:4) and evaporated to fumes of sulphur trioxide. The residue is carefully dissolved in 300 cc. of water, hydrogen sulphide is conducted into the solution until the odor of the gas is perceptible on stirring. A rubber stopper, equipped with a Bunsen valve, is inserted into the neck of the flask and the solution is boiled to expel the excess hydrogen sulphide. After cooling to 80° C., the iron is titrated to a permanent pink with standard potassium permanganate solution as described under iron in ferro-manganese.

The number of cubic centimeters of standard permanganate used times the iron factor of the solution, multiplied by 2, gives the percentage of iron in the sample.

PHOSPHORUS.

One gram of the alloy is fused in a platinum crucible with 10 grams of sodium carbonate and 1 gram sodium nitrate. The fusion is leached with water, and the solution boiled and filtered. The filtrate is acidified with hydrochloric acid and evaporated to dryness. The residue is dissolved in hydrochloric acid (1:1), and the silica is removed by filtration. The hydrochloric acid is eliminated by evaporation on an asbestos ring, and the determination is finished as described under phosphorus in ferro-manganese. The filtrate from the sodium titanate, obtained in the determination of titanium, contains all the phosphorus and may be used for the determination of that element.

MANGANESE.

Two-tenths of a gram of the sample is dissolved in 5 cc. of sulphuric acid (1:4). When solution is complete, 10 cc. of nitric acid (1.20 sp. gr.) are added, when the manganese is oxidized by ammonium persulphate and silver nitrate, and titrated with sodium arsenite solution as described under manganese in ferro-phosphorus.

SULPHUR.

One gram of the sample is intimately mixed in a platinum crucible with 10 grams sodium carbonate and 1 gram powdered sodium nitrate. After fusion over a sulphur-free flame, the cooled mass is leached in 150 cc. water. The insoluble portion is separated on a filter, washed well with 2% sodium carbonate water, and the filtrate which should be about 200 cc. in volume, is carefully acidified to a slight excess with hydrochloric acid. To the hot solution, 5 cc. of a 10% solution of barium chloride are added and the precipitate is allowed to settle at least 12 hours. The analysis is concluded as detailed under sulphur in ferro-manganese.

ANALYSIS OF FERRO-CHROMIUM.

CHROMIUM.

PERMANGANATE TITRATION.

Three-tenths of a gram of the sample is fused in a porcelain or nickel crucible with 5 grams of sodium peroxide. The high temperature, which is attained in fusing ferro-chromium with peroxide, sometimes causes porcelain to crack, in which case a nickel crucible is employed. The fusion is cooled and transferred to an 800 cc. beaker containing 300 cc. of water. The resultant solution and precipitate after removal of the crucible, are boiled 15 minutes, then acidulated with 50 cc. of sulphuric acid (1:1). Two cc. of hydrochloric acid (1:1) are added to decompose any permanganate formed from the manganese in the sample, and the solution is boiled until free from chlorine. To the cold solution, an excess of standard ferrous ammonium sulphate solution is added, and the volume used noted. Standard potassium permanganate is now introduced from a burette until the excess of ferrous ammonium sulphate solution is oxidized, as signified by the first appearance of a permanent pink color.

An amount of ferrous ammonium sulphate solution equal to the quantity employed to reduce the chromium is transferred to a suitable beaker and diluted with 350 cc. of water. Potassium permanganate solution is now added until the first pink color is observed, and the number of cubic centimeters used is noted. The difference in cubic centimeters between the volume of permanganate solution required in the blank titration and that required in the actual determination, representing the volume of permanganate equivalent to the chromium in the alloy, is multiplied by the chromium factor of the standard permanganate. This result divided by the weight of the sample taken for analysis, times 100, gives the percentage of chromium in the sample.

SOLUTIONS REQUIRED.

N/10 Ferrous Ammonium Sulphate Solution.

Ferrous ammonium sulphate	39.2 grams
Sulphuric acid (1:1)	100 cc.
Water	900 cc.

N/10 Sodium Oxalate Solution.

Sodium oxalate	6.7 grams
Water	1000 cc.

N/10 Potassium Permanganate Solution.

Potassium permanganate	3.17 grams
Water	1000 cc.

To standardize the potassium permanganate solution, 50 cc. of the sodium oxalate solution, accurately measured, are transferred to a beaker and diluted with 350 cc. water and 10 cc. of cold recently boiled sulphuric acid (1:1). The permanganate solution is now added slowly with stirring until the end point is reached. The solution may be adjusted, if necessary, to make it exactly one-tenth normal.

One cubic centimeter of N/10 permanganate solution equals .001733 gram chromium, but permanganate equal to .6% of the chromium is required to overcome the green color of the chromic salt in solution. Therefore, the factor of normality, multiplied by .01744, gives the strength in chromium of 1 cc. of the permanganate.

BICHROMATE TITRATION.

Five-tenths of a gram of the sample is fused with sodium peroxide, and the analysis is conducted to the addition of hydrochloric acid the same as described in the preceding method. In this case, twenty cubic centimeters of hydrochloric acid (1:1) are added, and the solution is boiled to eliminate the chlorine. After cooling, sufficient ferrous ammonium sulphate solution is added to reduce the chromium and provide an excess, which is titrated with potassium bichromate. The end point is reached when, after vigorous stirring, a test drop removed from the beaker and placed upon a drop of potassium ferricyanide solution will not produce a blue color, thus showing the ferrous salt completely oxidized. The ferrous ammonium sulphate solution is titrated in a like manner with bichromate, and a comparison obtained. The difference between the bichromate equivalent of the ferrous ammonium sulphate used, and the bichromate used in the back titration, multiplied by the chromium value of 1 cc. of bichromate solution, equals the chromium present. The product thus obtained is divided by the weight of the sample, multiplied by 100, and the result represents the percentage of chromium in the sample.

SOLUTIONS REQUIRED.

Standard Ferrous Ammonium Sulphate Solution.

Ferrous ammonium sulphate	84 grams
Sulphuric acid (1:1)	100 cc.
Water	900 cc.

Standard Potassium Bichromate Solution.

Potassium bichromate	8.9 grams
Water	1000 cc.

Potassium Ferricyanide Indicator.

Potassium ferricyanide	1 gram
Water	1000 cc.

This solution should be freshly prepared each day.

The potassium bichromate solution is standardized with one gram of the Corporation Iron Ore Standard as described in the Iron Ore Pamphlet, and its value in iron obtained. The iron value multiplied by the factor .3104 gives the value in chromium of one cubic centimeter of the standard bichromate solution.

SILICON.

One gram of the sample is dissolved in 70 cc. of sulphuric acid (1:6), and the solution heated until fumes of sulphur trioxide are evolved; 100 cc. of water are then carefully added, and the solution is boiled and filtered, the filtrate being received in a suitable beaker, and reserved. The insoluble residue so obtained is ignited and fused with sodium carbonate. The fusion is leached in water and, when disintegrated, is acidified with hydrochloric or sulphuric acid and evaporated to dryness or until fumes of sulphur trioxide are evolved. The residue is dissolved in hydrochloric acid (1:1) and water. The solution is filtered from the silica, which is washed, ignited and calculated to silicon.

IRON.

DIRECT TITRATION.

One gram of the alloy is treated in a 250 cc. beaker with 70 cc. sulphuric acid (1:6) and gently heated. A few drops of hydrofluoric acid are added from time to time until the sample is decomposed, when the solution is evaporated to sulphur trioxide fumes. Thirty cc. of water are cautiously introduced; the solution is boiled three minutes to eliminate reducing substances; and 20 cc. of hydrochloric acid are added. While the solution is still hot, stannous chloride solution to one drop in excess (a total of about 5 drops) is added, and the contents of the vessel are transferred to an 800 cc. beaker containing 600 cc. of water and 10 cc. of a cold, saturated solution of mercuric chloride. A deficiency of stannous chloride is indicated if no precipitate of mercurous chloride appears in the solution.

A standard solution of potassium bichromate is added from a burette, and the titration conducted with an outside indicator as described under iron in ferro-manganese. Small drops of ferricyanide solution are used on the test plate, and the end point is attained when the test spot, after the drop of solution has been added, shows no change in tint from the previous spot thus treated.

PRECIPITATION OF IRON BEFORE TITRATION.

One gram of the alloy is dissolved as in the preceding method for iron. When decomposition has been effected, the solution is evaporated to the evolution of sulphur trioxide fumes. Ten cc. of water are cautiously added, followed by 100 cc. of nitric acid. The solution is heated to boiling, when 5 grams of sodium chlorate are introduced to oxidize the chromium. The liquid is boiled 20 minutes, when an additional 50 cc. of nitric acid and 2 grams of sodium chlorate are introduced, followed by boiling until the volume of the solution is reduced by one-half. This will eliminate the excess of chlorate. Water is added to make the total volume about 500 cc., the solution is heated to boiling, and the iron is precipitated with ammonium hydroxide, a liberal excess being employed. After boiling for a few minutes, the precipitate is removed by filtering and washed.

The hydrates on the paper are dissolved into the original beaker with cold 20 per cent. hydrochloric acid and reprecipitated. The resulting precipitate, having been removed on a filter, is washed thoroughly and dissolved in hydrochloric acid as above. The iron is reduced with a solution of stannous chloride, one drop in excess is added, and the determination concluded by titration with potassium bichromate as under iron in ferro-manganese.

MANGANESE.

To the filtrate from the insoluble residue obtained in the silicon determination, 5 cc. of nitric acid are added, and the solution is boiled until the iron is oxidized, when it is transferred to a volumetric flask. Sodium hydroxide solution is added until the excess acid is almost neutralized. An emulsion of zinc oxide is then added and the flask filled to the mark and well shaken. It is allowed to stand until the precipitate has settled, when the solution is filtered through a dry filter. An aliquot part, representing .2 gram of the sample is withdrawn by a pipette from the filtrate and transferred to a flask or test tube. The manganese is determined by the persulphate-arsenite method as described under manganese in ferro-phosphorus.

SULPHUR.

Two grams of the sample, which should be ground to pass a 100 mesh sieve, are fused with 15 grams of sodium peroxide in a large nickel crucible which is lined with fused sodium carbonate. The lining is made as explained under phosphorus in ferro-chromium. Two grams of sodium peroxide are melted in the bottom of the lined crucible and allowed to cool. The alloy and peroxide, intimately mixed, are placed in the prepared crucible, covered with a thin layer of sodium peroxide, and the fusion conducted either in an electric furnace or over an alcohol flame. The heat is gradually applied until the reaction starts. By gently rotating the crucible, unattached particles may be stirred up and spattering prevented. A few minutes additional heating at a medium red heat will insure complete decomposition.

When cool, the fusion is dissolved in 200 cc. of water, the crucible is removed, and the solution is boiled five minutes, care being exercised to avoid bumping. After settling, the precipitate is removed by filtration and thoroughly washed with hot water. All of the sulphur, as sodium sulphate, passes into the filtrate.

Hydrochloric acid is added to the filtrate to slight excess, approximately 5 cc. of 30% hydrogen peroxide are introduced, and the solution is boiled for several minutes. The hydrogen peroxide serves to reduce the chromium, which permits a purer precipitation of the barium sulphate and also adds to rapidity in filtration and washing. To the hot solution, 10 cc. of a hot 10% barium chloride solution are added, and the precipitate is digested on a sand bath over night.

The barium sulphate is separated on a close filter, washed, ignited and weighed. If the precipitate is slightly colored due to contamination from chromium, as is frequently the case, it is fused with approximately 2 grams of sodium carbonate in a covered platinum crucible in an electric furnace or over a sulphur-free flame. The fusion is dissolved in about 50 cc. of hot water and filtered from the residue. After making the filtrate slightly acid, adding a drop of 30% hydrogen peroxide and boiling several minutes, the sulphur is precipitated with 5 cc. of a solution of 10% barium chloride. The determination is finished as in the first precipitation. The weight of barium sulphate found, less any blank on the crucible and reagents, multiplied by 13.73 and divided by 2 gives the percentage of sulphur in the sample.

A blank is determined by fusing 15 grams of sodium peroxide in a sodium carbonate lined crucible and putting it through all the operations of a regular determination.

Care must be exercised when using this method to avoid contamination from outside sources, as otherwise a serious error may result. All ignitions and evaporations should be made by means of electrical appliances, or in case gas is used, contamination due to sulphur in the products of combustion of the same must be adequately guarded against.

PHOSPHORUS.

Two grams of the finely powdered sample are intimately mixed with approximately 15 grams of sodium peroxide and fused in a nickel crucible which is lined with sodium carbonate. The lining is made by melting sodium carbonate in the crucible and allowing it to cool in an even layer on the bottom and sides. One to two grams of sodium peroxide are then melted in the crucible and permitted to cool in a cake on the bottom; the layer of sodium peroxide serves to prevent particles of the alloy sinking to the bottom and being caught in the sodium carbonate lining, thus preventing its complete decomposition. The mixture of the sample and sodium peroxide is placed in the prepared crucible and fused at a low temperature. Sodium carbonate does not melt at the comparatively low temperature required for the peroxide fusion and thus protects the crucible from attack.

After cooling, the crucible and contents are placed in a 500 cc. beaker and covered with approximately 150 cc. of hot water. As soon as the violent action is over, the crucible is rinsed and removed. The solution is boiled for five minutes to decompose all sodium peroxide; it is then acidified with 50 cc. sulphuric acid (1:1) and finally made ammoniacal. The resulting precipitate consists largely of ferric hydroxide but it also contains all of the phosphorus as ferric phosphate and small amounts of chromium and silica; it is removed on a paper, washed and dissolved into an evaporating dish with hot hydrochloric acid (1:1) and the paper is well washed with hot water. The solution is evaporated to dryness. After cooling sufficiently to avoid danger of breaking the dish, 20 cc. of concentrated hydrochloric acid are added, and heat is applied until the soluble salts are dissolved. The cover is removed, and with the dish placed upon a suitable asbestos ring, the solution is evaporated to the first appearance of the separation of the chlorides. The operations from this point are conducted in a manner similar to the estimation of phosphorus in ferro-manganese.

Sodium peroxide and sodium carbonate often contain some phosphorus, which fact requires that occasional blank tests be made on the same weights of materials as used in the regular analysis.

OTHER ELEMENTS.

Other elements which may be present in the alloy in small amounts are titanium, aluminum, magnesium and copper.

UNALLOYED METALLIC IRON.

This is determined by the same method as discribed for unalloyed iron in electric ferro-silicon.

ANALYSIS OF FERRO-VANADIUM.

VANADIUM.

HYDROCHLORIC ACID REDUCTION.

One-half gram of the alloy is treated in a platinum dish with a mixture of 30 cc. of water, 20 cc. of sulphuric acid (1:1), and 30 cc. of nitric acid (sp. gr. 1.20). A few drops of hydrofluoric acid are introduced from time to time until the sample is completely decomposed. The solution is evaporated to copious fumes of sulphur trioxide, 20 cc. of water are carefully added, and the solution is transferred to a 250 cc. flask. Fifty cc. of hydrochloric acid are added, and the solution is again evaporated to fumes. After adding 100 cc. of water, the solution is titrated at 80° C. with standard potassium permanganate. The deci-normal solution described under chromium in ferro-chromium is used; 1 cc. equals 1.02 per cent. vanadium.

As a check on the first result, the solution remaining from the titration may be utilized. It is evaporated to low volume; 50 cc. of concentrated hydrochloric acid are added and evaporation is continued until sulphur trioxide fumes are evolved. Water is carefully added and the solution is titrated as before.

FERROUS AMMONIUM SULPHATE REDUCTION.

One-half gram of the sample is dissolved in a platinum dish in a mixture of 30 cc. water, 20 cc. sulphuric acid (1:1) and 30 cc. nitric acid (sp. gr. 1.20). A few drops of hydrofluoric acid are introduced from time to time until the sample is completely decomposed. The solution is evaporated until copious fumes of sulphur trioxide are evolved. Twenty-five cc. of water and 15 cc. sulphuric acid (1:1) are carefully introduced, and heat is applied until the salts are dissolved. The solution is transferred to an 800 cc. beaker, diluted to 400 cc. and cooled. Potassium permanganate solution is added carefully to the first pink coloration in the solution. The vanadium is then reduced by the addition of an approximately deci-normal solution of ferrous ammonium sulphate until a drop of the solution withdrawn from the beaker and placed on a drop of potassium ferricyanide indicator shows ferrous iron present. Five cc. excess of ferrous ammonium sulphate solution are now added, and after stirring the solution at least one minute, the excess of ferrous sulphate is oxidized with 8 cc. of 15% ammonium persulphate. The solution is stirred one minute, when the vanadium is titrated with standard deci-normal potassium permanganate solution. The standard permanganate solution is added slowly, with vigorous stirring of the solution until the first permanent pink appears. One cubic centimeter of deci-normal permanganate is equal to 1.02 per cent. vanadium when .5 gram is taken as the initial weight of the sample.

SOLUTIONS REQUIRED.

N/10 Ferrous Ammonium Sulphate Solution.

Ferrous ammonium sulphate	39.2 grams
Sulphuric acid (1:1)	100 cc.
Water	900 cc.

N/10 Potassium Permanganate Solution.

This solution is prepared and standardized as described under chromium in ferro-chromium.

Potassium Ferricyanide Indicator.

Potassium ferricyanide	1.0 gram
Water	1000 cc.

SILICON.

One-half gram of the sample is fused in a platinum crucible with 6 grams of sodium carbonate and one-half gram of sodium nitrate. When the fusion has cooled, it is leached in water; the solution is acidified with sulphuric acid (1:1) and evaporated until fumes of sulphur trioxide are freely evolved. One hundred cubic centimeters of water are carefully added and the solution is heated to dissolve the soluble salts, then filtered from the silica, which is ignited and weighed; 46.93 per cent. is silicon.

Ferro-vanadium containing little silicon is often soluble in acids, in which case, the sample is treated directly with acids. One-half gram of the sample is dissolved in a mixture of 30 cc. of water, 20 cc. of sulphuric acid (1:1) and 30 cc. of nitric acid (sp. gr. 1.20) and the solution is evaporated until fumes of sulphur trioxide are evolved. One hundred cubic centimeters of water are carefully added, and the determination is finished as explained in the paragraph above.

MANGANESE.

One-tenth gram of the sample is placed in a platinum crucible and treated with 10 cc. of nitric acid (1.20 sp. gr.). Hydrofluoric acid is added, drop by drop, until the alloy is dissolved. Then, 5 cc. of sulphuric acid (1:1) are added, and the solution is gently heated until fumes of sulphur trioxide are evolved. The crucible is cooled, 15 cc. of water are added, and heat is applied until the salts are dissolved. The manganese is then determined by the persulphate-arsenite method which appears under ferro-phosphorus. If the manganese content is over 1%, an aliquot portion of the solution is used.

PHOSPHORUS.

One gram of the sample is dissolved in a platinum dish with a mixture of 20 cc. of nitric acid (1.20 sp. gr.) and 10 cc. of sulphuric acid (1:1) and the addition of hydrofluoric acid, drop by drop. The solution is evaporated to dryness and heated until fumes of sulphur trioxide are no longer evolved. The dish is then cooled, water is added and, if necessary, nitric acid (1.20 sp. gr.) to dissolve the salts, after which the solution is transferred to a 250 cc. flask and neutralized with ammonia. Thirty cubic centimeters of nitric acid and a small crystal of sodium chlorate are added, and the solution is boiled for a few minutes; 50 cc. of ammonium molybdate solution (see phosphorus in ferro-phosphorus) are added, and the solution again boiled 10 to 20 minutes. The precipitate is collected on a filter paper, washed with

2% nitric acid until free from iron salts, and dissolved from the paper by 40 cc. of hot ammonium hydroxide (1:3). The solution is retained in a flask and, if necessary, poured again on the filter paper. When the precipitate is completely dissolved, the paper is thoroughly washed with hot water. To another flask, 50 cc. of ammonium molybdate solution, 30 cc. of nitric acid (1.20 sp. gr.) and 10 cc. of approximately deci-normal ferrous ammonium sulphate are added. To this solution, well mixed, the ammoniacal solution of impure phosphomolybdate precipitate is added slowly, while the flask is shaken. When the phosphomolybdate precipitate has settled, it is collected on a filter paper and determined gravimetrically or volumetrically, as described under the molybdate method for phosphorus in ferro-phosphorus.

SULPHUR.

This element is determined on one gram of the sample as described under sulphur in ferro-titanium.

MOLYBDENUM AND COPPER.

The solution after the determination of vanadium is almost neutralized with ammonium hydroxide, and is saturated with hydrogen sulphide gas, the excess of which is then almost completely removed by boiling. The precipitate is removed by filtration, washed with acidulated water containing hydrogen sulphide, ignited at the lowest possible temperature and weighed. Ten cubic centimeters of 10% sodium hydroxide solution are added to the crucible, and heat is applied until the molybdic acid is dissolved. After dilution, the insoluble residue is removed by filtration, washed, ignited and weighed in the same crucible that was used for the first ignition. The difference in weight is the molybdic acid, which contains 66.67% molybdenum. The insoluble residue is digested with hydrochloric acid, the solution is diluted freely and saturated with hydrogen sulphide gas; a black precipitate indicates copper, which is removed on a paper, ignited and weighed as copper oxide, containing 79.89% copper.

NICKEL.

The filtrate from the copper and molybdenum sulphides is cooled to room temperature, diluted to 300 cc. in a volumetric flask and an aliquot portion of 100 cc. taken. After the hydrogen sulphide has been completely expelled by boiling, the solution is oxidized with 3 cc. nitric acid or a few crystals of sodium chlorate. Five grams of tartaric acid or citric acid are added, and the solution is made slightly ammoniacal, heated to the boiling point and 2 cc. of 1% alcoholic solution of dimethylglyoxime are added for each per cent. of nickel probably present. The contents of the beaker are stirred one minute, cooled, and set aside for 30 minutes. The determination is finished by gravimetric or volumetric methods as preferred.

GRAVIMETRIC METHODS.

WEIGHING THE PRECIPITATE.

The solution is filtered through a 9 cm. filter paper previously dried for one hour at a temperature of 110° to 115° C. and weighed between ground-edge watch glasses. The filter and contents are washed six times with hot water, when they are dried in the same manner as the paper and weighed. The increase in weight multiplied by the factor 20.31 gives the per cent. nickel.

WEIGHING AS NICKEL OXIDE.

The solution is filtered, and the precipitate retained on an 11 cm. filter paper. The paper and contents are washed six times with hot water, transferred to a weighed platinum crucible, and then ignited and weighed. The increase in weight represents nickel oxide, 78.57 per cent. of which is nickel.

VOLUMETRIC METHOD.

The precipitate is removed by filtration, washed well with hot water and dissolved from the paper with nitric acid (sp. gr. 1.20). The solution is boiled to decompose the glyoxime, diluted to 100 cc. and made faintly alkaline to litmus, using strong ammonia at first, then dilute ammonia. Three cc. of ammonia (1:1) are added in excess. The solution is cooled to room temperature and, after the addition of 2 cc. of a 10% solution of potassium iodide, is ready for titration.

The volume should be from 100 to 150 cc. The best results are obtained by adding approximately the right amount or an excess of standard potassium cyanide solution followed by a slight excess of silver nitrate solution, which in turn is dissolved by a slight excess of standard cyanide solution. Silver nitrate solution is again added until a faint permanent cloudiness is apparent. This is the end point. The quantity of each solution used is noted. Each cc. excess of standard cyanide solution over standard silver nitrate solution required for the titration, represents two-tenths per cent. nickel.

SOLUTIONS REQUIRED.

Silver Nitrate Solution.

Silver nitrate	5.7926 grams
Water	1000 cc.

Potassium Cyanide Solution.

Potassium cyanide	4.50 grams
Potassium hydroxide	5.0 grams
Water	1000 cc.

The silver nitrate solution is carefully prepared, and the cyanide solution adjusted to exact agreement therewith. For this purpose, 10 cc. of sulphuric acid (1:1) are added to approximately 100 cc. of water in a beaker. Ammonia is added until the solution is neutral or faintly alkaline to litmus, followed by 3 cc. of ammonia (1:1) in excess. The solution is cooled, and 2 cc. of a 10 per cent. potassium iodide solution are introduced. Then, from a burette, 20 cc. of potassium cyanide solution are added, followed by silver nitrate solution until a precipitate forms, which is dissolved by an excess of cyanide solution. Silver nitrate is again added carefully until the first discernible precipitate or cloudiness appears. The quantity of each solution used is noted, and the cyanide solution is adjusted, if necessary, to equal exactly the silver nitrate solution. With agreeing solutions, one cubic centimeter of standard cyanide solution is equivalent to two-tenths per cent. of nickel when an initial weight of .5 gram is taken.

IRON.

Another aliquot part of 100 cc. from the copper and molybdenum filtrate is transferred to a 250 cc. Erlenmeyer flask. Ten cubic centimeters of sulphuric acid (1:1) are added. With the flask loosely covered, or better, equipped with a Bunsen valve, the solution is boiled to remove all the hydrogen sulphide. After cooling to 80° C., the iron and also the vanadium present are titrated to a permanent pink with N/10 potassium permanganate solution

From three times the number of cubic centimeters of potassium permanganate solution required in the titration is deducted the number of cubic centimeters of potassium permanganate used in the vanadium titration. The remainder in cubic centimeters times the iron factor of the permanganate solution, multiplied by 2 and 100, equals the per cent. of iron in the sample

The N/10 potassium permanganate solution is prepared and standardized as described under chromium in ferro-chromium. One cc. of N/10 permanganate solution is equivalent to .005584 gram of iron.

ALUMINUM.

One gram of the sample in a platinum dish is dissolved in a mixture of 20 cc. of nitric acid (1.20 sp. gr.) and 10 cc. of sulphuric acid (1:1), with the addition of hydrofluoric acid, drop by drop. The solution is evaporated until fumes of sulphur trioxide are expelled. After the residue has cooled, it is dissolved in 30 cc. of hydrochloric acid (1:13 sp. gr.); then the solution is cooled and transferred to a separatory funnel, the dish being washed with hydrochloric acid (1:13 sp. gr.). Sixty cubic centimeters of ether are added, the funnel is well shaken, and the solution is then allowed to stand until the ethereal and acid layers have formed. The lower or acid layer is drained into another separator and the ether extraction repeated. The acid solution is then drawn into a beaker, boiled to expel the ether, a few crystals of sodium chlorate are added, and the boiling is continued for two minutes.

To this solution, 15 cc. of 10% ammonium phosphate are added, followed by ammonium hydroxide until nearly neutral. Twenty cubic centimeters of 20% ammonium acetate are added, and the solution is boiled a few minutes. The precipitate is removed by filtration, washed with hot 2% acetic acid, dissolved from the paper into the original beaker with cold hydrochloric acid (1:1) and reprecipitated as above, using 5 cc. of ammonium phosphate. The purified precipitate is removed by filtration, washed with hot 2% acetic acid, ignited and weighed as aluminum phosphate, 22.19% of which is aluminum.

ANALYSIS OF FERRO-MOLYBDENUM.

SILICON AND TUNGSTEN.

One gram of the sample is transferred to a 250 cc. beaker and dissolved in 20 cc. of nitric acid (sp. gr. 1.20). Ten cubic centimeters of sulphuric acid (1:1) are then added, and the solution is evaporated until fumes of sulphur trioxide are expelled. Fifty cc. of hydrochloric acid (1:1) are added, and the solution is boiled and filtered. The residue on the paper is silica and possibly some tungstic acid.

The filtrate is diluted to 100-125 cc., boiled for a few minutes and, after removal from the source of heat, 10 cc. of cinchonine solution (125 grams of cinchonine dissolved in one liter of 1:1 hydrochloric acid) are added to recover any soluble tungsten, and the liquid is digested at a temperature somewhat short of boiling, with occasional stirring, for thirty minutes or longer. Any tungsten which precipitates by this treatment is removed by filtration and washed with dilute cinchonine solution (30 cc. of cinchonine solution in one liter of water).

The two filter papers containing the total silica and tungsten are combined in a platinum crucible, ignited strongly to volatilize any traces of molybdic acid, weighed, and then treated with 3 cc. of hydrofluoric acid and three drops of sulphuric acid. Heat is applied until the acids are completely evaporated. The crucible is then ignited and weighed; the loss in weight represents the silica, 46.93 per cent. of which is silicon. The residue consists of tungstic acid, if present in the sample, but as it may contain some ferric oxide it is fused with sodium carbonate. The fusion is leached with water, and the ferric oxide removed by filtration, ignited, weighed and deducted; 79.31 per cent. of the difference is tungsten.

MOLYBDENUM.

One-half gram of the sample, crushed to pass a 100 mesh sieve, is dissolved in a 150 cc. beaker by warming with 10 cc. of nitric acid (sp. gr. 1.13) plus a drop or two of hydrofluoric acid, if necessary; 10 cc. of sulphuric acid (1:1) are cautiously added, and the solution is evaporated to fumes of sulphur trioxide. After being allowed to cool, the residue is heated with 40 cc. of water to dissolve salts. The solution is cooled, and the acid is nearly neutralized with ammonium hydroxide, but the use of sufficient ammonia to impart a red tint to the yellow solution should be avoided. The liquid is heated almost to boiling and poured very slowly and with vigorous stirring into 75 cc. of nearly boiling 15 per cent. ammonium hydroxide solution contained in a 250 cc. beaker; the beaker is rinsed with water and then with a small amount of hot ammonium hydroxide solution to remove any adhering molybdic or tungstic acid, and the washings are added to the main solution. The precipitate of ferric hydroxide is mixed with some paper pulp, separated on a paper and washed thoroughly with hot water, the filtrate and washings being received in a 500 cc. beaker. The precipitate of ferric hydroxide is dissolved in a slight excess of hot sulphuric acid (1:4), and the resultant solution is again nearly neutralized and poured into 75 cc. of boiling 15 per cent. ammonia water. The solution is filtered and washed as before, and the two filtrates, which contain practically all the molybdenum, are collected in a 500 cc. beaker.

To the filtrate from the iron precipitate there are added three grams of tartaric acid, and when it has dissolved, the warm liquid is thoroughly saturated with water washed hydrogen sulphide, by the passage of a brisk stream of the gas through it. Under these conditions the molybdenum is converted to ammonium thiomolbydate, which imparts an intense red color to the solution. Any precipitate, formed of small amounts of sulphides that are insoluble in ammonium sulphide, is removed on a paper and washed thoroughly with hydrogen sulphide water. The filtrate is warmed and made slightly acid with sulphuric acid (1:1), which causes the precipitation of the molybdenum as trisulphide.

The cessation of effervescence on the addition of more acid, the absence of the odor of ammonium sulphide, and the disappearance of the red color of the thiomolybdate mark the point where sufficient acid has been added to complete the precipitation. After being allowed to stand 15 minutes in a warm place, the molybdenum sulphide is permitted to settle, filtered on a quantitative paper and washed with hydrogen sulphide water, containing a small amount of sulphuric acid, until all salts are removed.

The filtrate from the molybdenum sulphide sometimes contains appreciable amounts of molybdenum; to it are added 15 cc. of nitric acid, and the solution is evaporated to fumes of sulphur trioxide, more sulphuric acid being added, if sufficient to permit fuming is not already present. After allowing it to cool, 5 cc. of nitric acid are added and the solution is again evaporated to fumes. The addition of nitric acid and the evaporation to fumes is repeated once more to insure the destruction of all organic compounds and the removal of most of the sulphuric acid.

After allowing to cool, sufficient water is introduced to dissolve all salts, two grams of tartaric acid are added, and after the addition of an excess of 10 cc. of ammonia, the warm liquid is thoroughly saturated with washed hydrogen sulphide and filtered. The filtrate is acidified with sulphuric acid (1:1) and if, after standing for 15 to 30 minutes in a warm place, any molybdenum trisulphide settles out, it is removed on a paper, washed well with hydrogen sulphide water containing a small amount of sulphuric acid, and combined with the main precipitate.

The precipitation of the molybdenum in this manner effects the separation and removal of tungsten, vanadium, chromium, and all other elements likely to be present except copper.

The analysis may be finished either by the gravimetric or volumetric method at the option of the operator.

GRAVIMETRIC METHODS.

MOLYBDIC ACID METHOD.

The combined sulphide precipitates are ignited in a platinum crucible at a temperature just sufficient to burn the paper and weighed as molybdic acid, 66.67% of which is molybdenum. If copper is present, it is separated as described under molybdenum and copper in ferro-vanadium.

LEAD MOLYBDATE METHOD.

The bulk of sulphide precipitates of molybdenum is transferred to a 400 cc. beaker. That part remaining on the papers is dissolved in 20 cc. of hot hydrochloric acid (1:1) and bromine water, the solution being received in the beaker with the precipitates. Fifty cc. of hydrochloric acid and 10 grams of sodium chlorate are added, and the contents of the beaker are boiled until the molybdenum sulphide is decomposed and the sulphur is entirely oxidized. To accomplish this, it may be necessary to add more sodium chlorate.

When the precipitate has been completely dissolved, 2N sodium hydroxide is added until the solution is nearly neutral. Sufficient acid should remain to maintain a clear solution. One hundred cubic centimeters of 2N sodium hydroxide are transferred to another 400 cc. beaker and heated to boiling. The molybdic solution is now very slowly poured into the sodium hydroxide solution, while the latter is vigorously stirred. The precipitate is permitted to settle, removed on a filter and thoroughly washed with hot water. The filtrate, which should not have a volume of more than 250 cc., is made slightly acid with hydrochloric acid, employing methyl orange as an indicator, and 50 cc. of 50 per cent. solution of ammonium acetate are introduced. The solution is heated to boiling and stirred while 50 cc. of lead acetate solution are slowly added. The beaker and contents are kept warm on a sand bath for 2 hours, when the precipitate is separated by filtration and washed with hot water. The paper and contents are ignited to a red heat in a porcelain crucible and weighed. The weight of the lead molybdate, multiplied by the factor 26.14 and divided by the initial weight taken gives, the percentage of molybdenum in the sample.

SOLUTIONS REQUIRED.

2N Sodium Hydroxide Solution.

Sodium hydroxide	80 grams
Water	1000 cc.

Lead Acetate Solution.

Lead acetate	100 grams
Water	1000 cc.

The solution is made slightly acid with acetic acid.

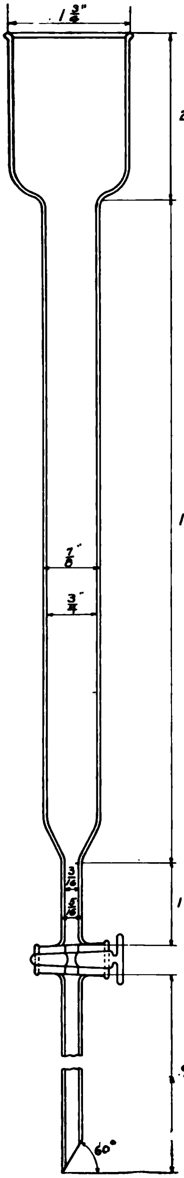
Methyl Orange Indicator.

Methyl orange	1 gram
Water	1000 cc.

VOLUMETRIC METHOD.

The molybdenum sulphide precipitates and papers are treated in a 250 cc. beaker with 6 cc. of sulphuric acid and 10 cc. of nitric acid, and the liquid is boiled until strong fumes of sulphur trioxide are emitted. After allowing it to cool, 5 cc. of nitric acid are added, and the evaporation is repeated. The evaporation with 5 cc. portions of strong nitric acid is repeated several times, until the filter paper has been completely destroyed and all traces of yellow color due to carbonaceous matter have disappeared. When this has been accomplished, the solution is heated to copious evolution of sulphur trioxide fumes for a short time and permitted to cool. Five cc. of water are added, and the solution is again evaporated to fumes. There are added 75 cc. of water, and the liquid is heated almost to boiling, which heating should give a perfectly clear solution. Five grams of pure zinc, granulated to pass a 20 mesh sieve and containing less than .002 per cent. iron, are then added, and the solution is boiled until most of the zinc has dissolved; this treatment results in the partial reduction of the molybdenum and the complete precipitation of copper, which is usually present. The liquid is filtered on asbestos to remove the undissolved zinc and copper; it is then ready for passage through a zinc reductor.

The reductor, a cut of which is shown on the next page, is prepared as follows: A coil of platinum wire, or a bed of several solid glass beads, is placed at the lower point of contraction of the tube. On the top of this bed there is placed a plug of glass wool 2 or 3 centimeters thick and then a layer of acid-washed asbestos several millimeters in thickness. The tube is then filled for a space of at least 20 centimeters with 20 mesh amalgamated zinc, which should not contain more than .002 per cent. iron. Amalgamation of the zinc is effected by treating it with a 2 per cent. solution of mercuric chloride for a few minutes and then washing it thoroughly by decantation with distilled water. When not in use, the reductor should always be kept filled to above the top of the zinc with distilled water.



AMALGAMATED ZINC REDUCTOR

The reductor, being clean and in good condition, is attached to the suction flask, and the filter pump is regulated to give gentle suction. Thirty-five cc. of the ferric sulphate-phosphoric acid solution are introduced into the suction flask. When the flask is connected to the reductor, the end of the reductor tube should dip into the ferric phosphate solution. One hundred cc. of warm 2.5 per cent. sulphuric acid are introduced into the funnel which forms the top of the reductor tube, and the stop-cock is opened. When only a little of the acid remains in the funnel, the warm molybdenum solution is transferred to it, and the beaker is rinsed with hot water. With only a small amount of the solution remaining in the funnel, 200 cc. of warm 2.5 per cent. sulphuric acid are added, followed with 50 cc. hot distilled water. In no case is the funnel permitted to become entirely empty, and the stop-cock is closed while some of the wash water still remains above the surface of the zinc. By working in this way, no air is permitted to pass through the reductor. The molybdenum salt is green as it passes through the lower part of the reductor, but on coming in contact with the ferric salt it is changed to a bright red, due to its immediate partial oxidation, which is, of course, accompanied by reduction of a corresponding amount of the ferric salt to the ferrous condition. While still warm, the solution is transferred to an 800 cc. beaker and titrated with a standard N/10 solution of potassium permanganate until a permanent faint pink color is obtained. Working under the conditions described, complete reduction from MoO_3 to Mo_2O_3 is obtained, none of the Mo_2O_3 being reoxidized by the air after passage through the reductor.

Since zinc always contains some iron, a blank determination is made on the five grams used for precipitating the copper and also on the reductor. This is done by dissolving five grams of the zinc in 75 cc. of 5 per cent. sulphuric acid, filtering on asbestos and putting the solution through the reductor in exactly the same way as the molybdenum solution. The amount of permanganate required to impart a pink tint to the liquid constitutes the blank, which must be deducted from the burette reading of every analysis.

The number of cubic centimeters of standard permanganate solution required in the titration less the number of cc. used for the blank, multiplied by the molybdenum value of each cc. and by 200, gives the percentage of molybdenum in the alloy.

SOLUTIONS REQUIRED.

Ferric Sulphate-Phosphoric Acid Solution.

Ferric sulphate	100 grams
Phosphoric acid (sp. gr. 1.75)	150 cc.
Sulphuric acid (1:1)	20 cc.
Water to make	1000 cc.

If not perfectly clear, the solution is filtered.

N/10 Potassium Permanganate Solution.

Potassium permanganate	3.18 grams
Water	1000 cc.

This solution is standardized by means of sodium oxalate. Three-tenths gram, accurately weighed, of pure sodium oxalate is dissolved in 250 cc. boiling water, 10 cc. of sulphuric acid (1:1) are added, and the hot solution is titrated with the permanganate to the first permanent pink color, care being taken not to permit the temperature to fall below 60° C. The molybdenum value of one cubic centimeter of the standard permanganate solution is found by the following calculation:

$$\frac{.4776}{\text{(Volume of permanganate solution required to oxidize one gram of pure sodium oxalate.)}}$$

The figure .4776 is the weight in grams of the quantity of trivalent molybdenum that has a reducing power equivalent to one gram of sodium oxalate.

IRON.

One-half gram of the sample powdered to pass a 100 mesh sieve is dissolved in 10 cc. nitric acid (sp. gr. 1.13) in a covered beaker. If solution is not readily obtained, a few drops of hydrofluoric acid may be used to hasten the action. When the alloy is completely decomposed, the liquid is poured slowly and with constant stirring into an excess of hot 10 per cent. sodium hydroxide solution. The resulting precipitate of ferric hydroxide is removed by filtering, washed thoroughly with hot water to remove sodium molybdate and sodium vanadate, dissolved in hot hydrochloric acid (1:1) and a second sodium hydroxide separation, followed by filtration and washing, is made to insure the complete removal of all molybdenum and vanadium.

The ferric hydroxide precipitate is redissolved with hot hydrochloric acid (1:1) and the paper is well washed. The volume of the solution is reduced to 30 cc. by evaporation and, in case the potassium permanganate titration method is to be used, the solution is evaporated until most of the excess of hydrochloric acid is removed. While the liquid is still hot, sufficient stannous chloride solution is added, drop-wise, to reduce the iron completely and to supply one drop in excess. The solution is diluted to about 350 cc. with cold water, 5 cc. of mercuric chloride are added, and the solution is thoroughly stirred. From this point, either the permanganate or bichromate method, as described under iron in ferro-manganese, may be used to finish the determination.

PHOSPHORUS.

One gram of the sample is transferred to a platinum dish containing 20 cc. of nitric acid (1.20 sp. gr.). Heat is applied until all reaction ceases when 20 cc. of sulphuric acid (1:1) are added, followed by a few drops of hydrofluoric acid. The solution is evaporated until fumes of sulphur trioxide are evolved. Thirty cc. of water are cautiously added, the solution is heated, any precipitated tungsten is removed by filtration, and the filtrate is made slightly ammoniacal. The contents of the dish are added slowly to a flask containing 50 cc. of ammonium molybdate solution and 30 cc. of nitric acid (1.20 sp. gr.) while the flask is shaken. Shaking is continued for five minutes, the solution is filtered from the precipitate, and the phosphorus in the yellow precipitate is determined by one of the optional methods as described under the molybdate method for phosphorus in ferro-phosphorus.

SULPHUR.

This element is determined on one gram of the sample as described under sulphur in ferro-titanium.

MANGANESE.

Two-tenths gram of the sample is dissolved in 5 cc. nitric acid (1.20 sp. gr.) and 5 cc. sulphuric acid (1:1) as in the preceding method for phosphorus, and the manganese is determined by the persulphate-arsenite method as described under manganese in ferro-phosphorus.

COPPER.

Two or four grams of the alloy are dissolved in a slight excess of nitric acid (sp. gr. 1.13) in a 150 cc. beaker. When solution is complete, addition is made of several drops of hydrofluoric acid (48%) to volatilize any silica. The two grams sample is used for ferro-molybdenum which contains more than two-tenths per cent. copper, while for material containing less than this amount, a four grams sample is used. After cooling the solution, addition is cautiously made of 30 cc. of sulphuric acid (1:1), and the liquid is evaporated until dense fumes of sulphur trioxide are freely evolved.

The residue of sulphates is dissolved by addition of 75 to 100 cc. of water, and boiling; in case a small amount of molybdenum salt remains undissolved, it is temporarily neglected, as the subsequent treatment will cause it to dissolve. From this solution the copper is completely precipitated in the metallic condition by placing a piece of pure sheet aluminum in the liquid and boiling briskly for about 45 minutes. The sheet of aluminum is 1″ x 3″ in size and bent into the form of a triangle, 1″ in height, which is placed on its edge in the beaker. The copper does not precipitate until all the iron and molybdenum have been reduced. After boiling for the specified time, the solution is filtered on a 7 cm. paper; the aluminum is left in the beaker, and it and the precipitate and paper are washed with hot water. A small amount of molybdenum always precipitates in the form of a black substance along with the copper. The filtrate from the copper may be further tested by boiling a second time with aluminum; usually a small amount of molybdenum will be precipitated, but no copper will be found. The paper containing the impure copper is burned in a small porcelain crucible and the residue is brushed into a 150 cc. beaker. Five cc. of nitric acid (sp. gr. 1.42) are dropped onto the aluminum to remove any adhering copper, and the acid is then poured into the beaker containing the bulk of the copper; the aluminum and the beaker holding it are also rinsed with a small amount of water. Ten cc. of hydrochloric acid and 20 cc. of sulphuric acid (1:1) are then added to the 150 cc. beaker containing the copper, and the liquid is evaporated to fumes of sulphuric anhydride to expel all nitric acid. After cooling, addition is made of 40 cc. of water, and the solution is boiled to dissolve all copper, and filtered into a second 150 cc. beaker. After diluting, if necessary, to 75 cc., the copper is precipitated with aluminum as previously described, except that in this case 10 minutes' boiling is sufficient to obtain all the copper. This second precipitation with aluminum separates practically all the molybdenum.

The solution is filtered, as much of the copper as possible being transferred to the paper, and the beaker, aluminum, and the filter paper and its contents are all washed well with hot water. The aluminum is cleaned by dropping 5 cc. of nitric acid (sp. gr. 1.42) from a pipette over it and then rinsing it with a fine jet of water and removing it. A 250 cc. beaker is placed under the funnel, and the nitric acid solution contained in the beaker which formerly held the aluminum is heated to boiling and poured slowly over the filter to dissolve the copper. A few drops of bromine water are also dropped on the paper, which is then washed with the least necessary amount of hot water. The solution containing all of the copper is rapidly evaporated to the smallest volume possible in order to remove the bromine and the bulk of the free nitric acid, and the solution is diluted with cold water to a volume of 150 cc. Strong ammonia is then added from a burette until the addition of a final drop causes the permanent bluing of the solution, after which there is added by means of a pipette six drops of acetic acid. Ten cc. of a 40 per cent. solution of potassium iodide are added, followed by the standard sodium hyposulphite solution from a burette until the color of the liberated iodine has almost disappeared. Ten cc. of the starch solution are now added, and the addition of the standard sodium hyposulphite solution is continued to the final disappearance of the blue. The number of cubic centimeters of the hyposulphite solution required, multiplied by its value in terms of copper and divided by the weight of the sample used, equals the per cent. copper in the sample.

The apparently large excess of potassium iodide is employed because of its relation to the final end point in the titration, the sharpness of which decreases in proportion as the excess of the iodide is decreased. The presence of ammonium salts in the solution also tends to lessen the permanency of the end point, hence, the necessity of the preliminary evaporation of the acid solution.

SOLUTIONS REQUIRED.

Starch Solution.

An emulsion of 6 grams of starch in 100 cc. of cold water is cautiously added to 1000 cc. of boiling water in a suitable flask. After continued boiling for five minutes, the flask and contents are cooled. When the heavier particles have settled, the supernatant liquid is carefully decanted, and is ready for use.

It is recommended that the starch be added to boiling water, as this tends to lessen the often unavoidable frothing; should frothing occur, however, its subsidence may be effected by playing a jet of air over the surface of the boiling solution. The starch indicator should be prepared fresh each day.

Standard Sodium Hyposulphite Solution.

Sodium hyposulphite........................	8 grams
Water....................................	1000 cc.

One cubic centimeter of the standard solution is equal to approximately .002 gram of copper. The solution may be standardized by titrating, as above described, a nitric acid solution of approximately .05 gram of pure copper, accurately weighed.

CHROMIUM.

Two grams of the sample are transferred to a 600 cc. beaker, 60 cc. of sulphuric acid-silver nitrate mixture are added and heat is applied until all action ceases. Ten cc. of nitric acid (sp. gr. 1.20) are introduced and the solution is boiled until fumes of the oxides of nitrogen are expelled. The contents of the beaker are then dilutedwith boiling water to a volume of approximately 300 cc. The solution is heated to boiling, and 10 cc. of a 15 per cent. ammonium persulphate solution are added. After the permanganate color has developed, two cc. of hydrochloric acid (1:1) are added, and boiling continued until the pink color disappears and the excess persulphate is decomposed. This requires about ten minutes. The solution is cooled, diluted with water to approximately 400 cc. and is now ready for titration.

Standard ferrous ammonium sulphate solution is added from a burette or pipette until the complete disappearance of the yellow, and the volume of the ferrous ammonium sulphate is noted. Standard potassium permanganate solution is then added from a burette until the solution assumes a pink color which does not fade upon continued stirring. If vanadium is present, the pink color will slowly fade owing to slow reoxidation of the vanadium. When the vanadium is completely oxidized, however, a pink color lasting one minute is obtained, which is the end point. The volume of standard permanganate solution required is then noted. The per cent. of chromium is obtained by conducting a blank titration on the ferrous ammonium sulphate solution under the same conditions as outlined for the actual determination. For this purpose the same volume of ferrous ammonium sulphate solution as used in the determination is transferred to a suitable beaker, and diluted with water to a volume of approximately 400 cc.; standard potassium permanganate solution is then added until a permanent pink color is obtained, and the volume of permanganate solution required is noted. The difference in cubic centimeters between the volume of permanganate solution required in the blank titration and that required in the actual determination, representing the volume of permanganate equivalent to the chromium in the alloy, is multiplied by the value of one cubic centimeter of standard permanganate in terms of chromium. The product thus obtained is divided by the weight of the sample used, and the result is the percentage of chromium in the sample.

Solutions Required.

Sulphuric Acid-Silver Nitrate Mixture.

Silver nitrate	5.0 grams
Water	600 cc.
Phosphoric acid (sp. gr. 1.75)	80 cc.
Sulphuric acid (1:1)	320 cc.

N/20 Ferrous Ammonium Sulphate Solution.

Ferrous ammonium sulphate	19.6 grams
Sulphuric acid (1:1)	100 cc.
Water	900 cc.

N/20 Potassium Permanganate Solution.

Potassium permanganate	1.58 grams
Water	1000 cc.

N/20 Sodium Oxalate Solution.

Sodium oxalate	3.35 grams
Water, to make	1000 cc.

Fifty cc. of the standard sodium oxalate solution are transferred to a 500 cc. beaker, diluted to 400 cc., heated to 80° C. and 10 cc. sulphuric acid (1:1) are added. The standard permanganate solution is then added from a burette until a permanent pink color is obtained, and the number of cubic centimeters required is noted. The value in percentage of one cc. of the permanganate solution in terms of chromium is found by multiplying the factor .0872 by 50 and dividing the product so obtained by the number of cc. standard permanganate solution required.

One cc. of N/20 potassium permanganate equals .0008667 gram chromium, but potassium permanganate equal to .6 per cent. of the chromium is required to overcome the green color of chromic sulphate in solution. Therefore, .0872 is taken as the factor of one cc. of N/20 permanganate in this determination.

VANADIUM.

To the solution from the chromium determination, 5 to 10 cc. of approximately N/20 ferrous ammonium sulphate are added. The contents of the beaker are then stirred thoroughly, after which 7 cc. of a 15 per cent. ammonium persulphate solution are added, and stirring is continued for not less than one minute. Standard potassium permanganate solution is then slowly added until a pink end point that remains after stirring one minute is obtained. The volume of standard permanganate used in the titration is noted. The percentage of vanadium is found by multiplying the number of cubic centimeters of permanganate solution required for the titration by the value of one cc. of permanganate solution in terms of vanadium and dividing the product by the weight of the sample used.

The standard potassium permanganate solution used in the chromium determination by the preceding method may be conveniently employed in the estimation of vanadium. It is standardized, as described, by titration on 50 cc. N/20 standard sodium oxalate solution. The value in percentage of one cc. of the permanganate solution in terms of vanadium is found by multiplying the factor .255 by 50 and dividing the product thus obtained by the number of cc. of standard permanganate required in the sodium oxalate titration.

When potassium permanganate solution is used in the titration of chromium, it is necessary to apply a correction of six-tenths per cent. of the chromium present to provide for the excess quantity of permanganate solution which is required to overcome the green of the chromic salt in solution. Likewise, a provision must be made in the titration of vanadium by permanganate solution when chromic salt is present. Since one cubic centimeter of a standard permanganate solution is equivalent to three times as much vanadium as chromium, the correction factor in this case is 3 x .6%, or 1.8%. Then, the vanadium percentage, calculated as described in the preceding paragraphs, is corrected by deducting therefrom a figure which is 1.8% of the chromium content of the sample.

ANALYSIS OF FERRO-TUNGSTEN.

TUNGSTEN.

One-half gram of the sample, ground to pass a 100 mesh sieve, is treated with 5 cc. of hydrofluoric acid (48 per cent.) in a 100 cc. flat-bottomed platinum dish provided with a platinum cover. Nitric acid is then added a few drops at a time, the dish being kept well covered to prevent mechanical loss, until decomposition is complete. The reaction is usually quite energetic. High carbon alloys do not dissolve so easily, and in some cases may have to be fused. The platinum lid is removed from the dish and the solution is evaporated to the point just short of where the tungsten begins to separate out. Five cc. of sulphuric acid are then cautiously added, and the solution is evaporated until dense fumes of sulphuric anhydride are evolved.

The contents of the dish are digested for a few minutes with 75 cc. of water and transferred to a 250 cc. beaker, the dish being cleaned with a policeman. To remove small amounts of tightly adhering tungsten and iron, the dish is rinsed with 2 to 3 cc. of concentrated hydrochloric acid, a jet of water, two or three drops of ammonia, some more water, and 2 or 3 cc. additional hydrochloric acid in the order named; a total of 5 cc. of hydrochloric acid is used. The solution is diluted to 100-125 cc. and boiled for a few minutes. After removal from the source of heat, 10 cc. of cinchonine solution are added and the liquid is digested for 30 minutes at a temperature somewhat short of boiling, with occasional stirring.

By the evaporation with sulphuric acid and the subsequent boiling, the greater part of the tungsten is precipitated as the trioxide. However, a small proportion of the tungsten usually remains in solution; the amount of this soluble tungsten increases with increasing percentages of phosphorus in the alloy. The use of cinchonine makes possible the recovery of this soluble tungsten, which under these conditions is completely precipitated as an organic compound.

The tungsten precipitate is allowed to settle, and is washed four times by decantation on a paper, 30 to 40 cc. of hot dilute cinchonine solution (30 cc. of cinchonine solution to one liter of water) being used each time and the bulk of the precipitate being retained in the beaker. After first placing the beaker containing the precipitate under the funnel, the small amount of tungsten trioxide on the filter paper is dissolved from the paper in the least necessary amount of ammonia-ammonium chloride solution. The paper is then washed several times with hot water, once with hot hydrochloric acid (1:1) to dissolve any iron, several times more with water and finally once or twice with ammonia-ammonium chloride solution, all of the washings being received in the beaker containing the main part of the tungsten. After warming the filtrate, addition is made to it of just sufficient ammonia to dissolve the tungsten completely; when this has been accomplished, the solution is evaporated until the excess of free ammonia has been entirely expelled. Free ammonia is converted into ammonium chloride when the solution is subsequently acidified, and since alkali salts have the effect of preventing the precipitation of tungsten acids, they should be kept to a minimum.

To the solution of ammonium tungstate, there are added 100 cc. of hot water and 10 cc. of hydrochloric acid, and the mixture is boiled for about 5 minutes, when the greater part of the tungsten is precipitated as tungstic acid. Ten cc. of cinchonine solution are added, and the beaker and contents are allowed to stand in a warm place for 15 to 30 minutes, with occasional stirring. The tungstic acid is removed on a 9 cm. paper and washed well with hot dilute cinchonine solution (30 cc. of cinchonine solution to one liter of water). Paper pulp may be used as an aid in filtration. The filtrate is permitted to stand in a warm place for several hours, and any tungsten precipitate which settles is recovered by filtration and added to the main precipitate.

The tungstic precipitate, including that part recovered, if any, from the filtrate on standing, is ignited in a weighed platinum crucible at a low red heat; when all of the carbon of the filter paper is destroyed, the temperature is increased to 800° C. to 900° C. The crucible is then allowed to cool, and the precipitate is moistened with hydrofluoric acid to expel any silica obtained by action of the ammoniacal solution on the glass beaker, evaporated to dryness, reignited, and weighed. The weight of tungsten trioxide multiplied by 79.31 and by 2 gives the percentage of tungsten in the alloy.

SOLUTIONS REQUIRED.

Cinchonine Solution.

Cinchonine	125 grams
Hydrochloric acid (1:1)	1000 cc.

Ammonia-Ammonium Chloride Solution.

Ammonia (sp. gr. .90)	200 cc.
Hydrochloric acid (sp. gr. 1.19)	10 cc.
Water	790 cc.

PHOSPHORUS.

One gram of the alloy is treated with 10 cc. nitric acid (sp. gr. 1.42) in a platinum dish equipped with a platinum cover. Hydrofluoric acid is added, a few drops at a time, until the sample is in solution. The cover is removed from the dish, 10 cc. of sulphuric acid (1:1) are introduced, and the solution is evaporated to a point where the free sulphuric acid has almost all been expelled. The residue should not be baked.

After cooling the dish and adding 50 cc. of hydrochloric acid (1:1), the residue is digested for a considerable time to render soluble all of the phosphorus. The solution is filtered from the tungstic acid, the filtrate is received in a porcelain dish, and evaporated on an asbestos ring to the first appearance of the separation of the chlorides. From this point, the analysis is the same as described under phosphorus in ferro-manganese.

SILICON.

A portion of the sample, weighing 1.4079 grams, that is, three times the factor weight, is finely ground in an agate mortar, and fused with approximately 12 grams of sodium peroxide in a 30 cc. nickel crucible. It is rather difficult to secure complete decomposition of high grade ferro-tungsten by means of sodium peroxide, and for this reason it is necessary that the sample be finely ground and that the fusion be kept molten (at a low red heat) for at least five minutes.

When the crucible has partly cooled, the fusion is loosened in a single solid cake by tapping the tightly covered crucible on the bench several times. The contents are transferred to a large porcelain dish and dissolved in the least necessary amount of warm water; the crucible is rinsed with water, and the rinsings are added to the dish. Fifty cc. of sulphuric acid (1:1) are cautiously added, and the solution is stirred well. Addition is made of 10 cc. of phosphoric acid (sp. gr. 1.72), and the liquid is thoroughly stirred and evaporated until fumes of sulphur trioxide are freely evolved.

The function of the phosphoric acid is to hold most of the tungsten in solution and thus to effect its separation from the silica. This separation is rendered necessary because of the fact that when the ratio of tungsten to silicon is very high, it is not possible to secure reliable results by the commonly used method of weighing the oxides of tungsten and silicon together and determining the latter by volatilization with sulphuric and hydrofluoric acids.

To the residue are added 150 to 200 cc. of water and 5 cc. of hydrochloric acid. The contents of the dish are boiled as soon as all ferric sulphate is dissolved, some ashless paper pulp is introduced, the solution is filtered through an 11 cm. paper, gentle suction being employed, and the residue and paper are washed thoroughly with hot water.

The paper and impure silica are ignited in a platinum crucible and weighed. After volatilization with sulphuric and hydrofluoric acids, the crucible is again ignited and weighed. The difference between the first and second weights gives the weight of silica, which is multiplied by 100 and divided by three to obtain the percentage of silicon in the alloy.

IRON.

One-half gram of the sample, ground to pass a 100 mesh sieve, is treated with 3 cc. of hydrofluoric acid (48%) in a large platinum dish provided with a platinum cover. It is important that no more than the specified amount of hydrofluoric acid be employed. Nitric acid (sp. gr. 1.42) is added a few drops at a time, the dish being kept well covered to prevent mechanical loss, until decomposition is complete. The cover and sides of the dish are rinsed with water. Three to four grams of sodium hydroxide (low in iron content) are dissolved in 250 to 300 cc. of boiling water in a 500 cc. beaker, and the nitro-hydrofluoric solution of the alloy is poured very slowly and with vigorous stirring into the prepared hydroxide solution, the platinum dish being carefully rinsed with a jet of water. The iron precipitate is separated by filtration and washed thoroughly with hot water to remove practically all of the tungsten.

The ferric hydroxide precipitate is dissolved with hot hydrochloric acid (1:1) and the paper well washed. The volume of the solution is reduced by evaporation, and the analysis concluded as described under iron in ferro-molybdenum.

SULPHUR.

Two grams of the sample are weighed into a flat-bottomed platinum dish provided with a platinum lid and treated with 15 cc. of nitric acid (sp. gr. 1.42). Hydrofluoric acid is then added, a few drops at a time, with heating, until the alloy has completely dissolved. The solution is evaporated almost to dryness. Baking is avoided, as this would result in the formation of material which would resist solution in the subsequent treatment. Ten cc. of hydrofluoric acid are added, and the solution is again evaporated nearly to dryness. Ten cc. additional hydrofluoric acid are introduced, and the contents of the dish are evaporated to pastiness to expel practically all the nitric acid. The hydrofluoric acid is now expelled by a double evaporation with hydrochloric acid; 10 cc. of the acid are added previous to each of the evaporations, which are continued nearly to dryness each time. Some tungstic acid may separate at this point, but it is disregarded.

The contents of the dish are transferred to a 250 cc. beaker, and the dish is given successive washings with hot hydrochloric acid, 20 cc. in all being used. Ten cc. of nitric acid are added and the solution is boiled until the volume is reduced to approximately 15 cc. Fifty cc. of water and 5 cc. of sulphate-free cinchonine solution are introduced, and the liquid is heated for 30 minutes at a temperature short of boiling, with occasional stirring. The precipitate is removed on a paper containing some paper pulp and washed well with hot dilute sulphate-free cinchonine solution. Any tungsten escaping separation at this point will subsequently be precipitated by barium chloride and vitiate the sulphur result.

The filtrate from the tungstic acid is evaporated to dryness in a 400 cc Erlenmeyer flask. Thirty cc. of hydrochloric acid are added and the solution is evaporated to a syrupy consistency. Two to four cc. of water are introduced, the solution is filtered and any residue is washed with hot water. The sulphur is precipitated in the cold filtrate in a volume of about 100 cc. with 10 cc. of a 10 per cent. solution of barium chloride. After settling for 48 hours, the precipitate is collected on a filter paper, washed with cold two per cent. hydrochloric acid and water, ignited gently, and weighed; 13.73 per cent. of the weight of the barium sulphate is sulphur. The filtrate and washings are evaporated to small volume, allowed to stand in a cool place and any precipitate of barium sulphate is recovered and its weight added to that of the main precipitate.

A blank determination should be made and the necessary correction applied.

SOLUTIONS REQUIRED.

Sulphate-free Cinchonine Solution.

One hundred and twenty-five grams of cinchonine are washed with water in a large funnel until the washings show no precipitate with barium chloride solution. The cinchonine is then dissolved in one liter hydrochloric acid (1:1).

Dilute Sulphate-free Cinchonine Solution.

Cinchonine solution, prepared as above........	30 cc.
Water....................................	1000 cc.

MANGANESE.

ZINC OXIDE SEPARATION.

One gram of the sample, crushed to pass a 100 mesh sieve, is treated with 10 cc. of nitric acid (sp. gr. 1.42) in a platinum dish provided with a platinum cover. Hydrofluoric acid is then added a few drops at a time, with heating, until the alloy is completely dissolved. The solution is evaporated, with cover removed from the dish, to a volume of about 10 cc. or to just short of the concentration where tungstic acid starts to separate. Fifteen cc. of sulphuric acid (1:1) are then cautiously added, and the solution is further evaporated until fumes of sulphur trioxide are freely evolved.

The residue is dissolved in 75 cc. of water; the solution is cooled to room temperature, almost neutralized with ammonia, and then transferred to a 250 cc. volumetric flask. Zinc oxide emulsion is added in excess, which is shown when the supernatant liquid appears milky. The solution is then diluted to the mark and thoroughly mixed. The contents of the flask are decanted through a dry filter paper, and 50 cc. portions of the filtrate, corresponding to .2 gram of the sample, are used for the determination.

A 50 cc. portion of the filtrate, obtained as above, is transferred to a suitable beaker, 10 cc. of nitric acid are added, and the solution is boiled for several minutes. Silver nitrate solution and ammonium persulphate are added and the estimation is concluded by titration with standard sodium arsenite solution as detailed under manganese in ferro-phosphorus.

DIRECT TITRATION.

One-tenth gram of the alloy is dissolved in a platinum dish with 10 cc. nitric acid (sp. gr. 1.20) and a few drops of hydrofluoric acid. The solution of the sample is transferred to a small flask or beaker, and 5 cc. of a saturated solution of boric acid are introduced to overcome the effect of the hydrofluoric acid. After heating the solution to the boiling point, silver nitrate and ammonium persulphate solutions are added, and the determination is completed by titration with standard sodium arsenite as described under manganese in ferro-phosphorus.

ANALYSIS OF COMMERCIAL ALUMINUM.

CARBON.

One gram of the coarse drillings or pieces is treated with 80 cc. of copper ammonium chloride solution. The carbon is removed by filtration on an asbestos mat in a platinum boat or an alundum thimble and burned in a current of oxygen as described under carbon in alloys. The resultant carbon dioxide is absorbed in an absorption bottle containing soda lime or soda asbestos, weighed, and calculated to per cent. carbon.

SOLUTION REQUIRED.

Copper Ammonium Chloride Solution.

Three hundred grams of the salt are dissolved in 940 cc. of boiling water. After cooling, 60 cc. of hydrochloric acid are added and the solution is filtered through a purified asbestos plug.

SILICON.

One gram of the drillings is dissolved in 20 cc. of aqua regia by heating in an evaporating dish. Seven cc. of sulphuric acid (1:1) are added, and the solution is evaporated until fumes of sulphur trioxide are evolved. The dish is cooled, 10 cc. of hydrochloric acid and 50 cc. of water are added, and the solution is heated until all soluble salts are dissolved. The solution is filtered from the residue which is washed with hot hydrochloric acid (1:1) and water, ignited in a platinum crucible, and fused with sodium carbonate. The fusion is disintegrated in water and acidified with sulphuric acid. The solution is evaporated until fumes of sulphur trioxide are evolved. After cooling, 50 cc. of water are added, heat is applied, and, when the soluble salts are dissolved, the silica is removed by filtration, ignited, weighed, and calculated to silicon.

COPPER.

One to three grams of the drillings are transferred to an 800 cc. beaker containing 7 grams of stick sodium hydroxide for each gram of sample taken. One hundred cc. of cold water are added in small successive quantities until violent action is over, after which the beaker is heated while the metal dissolves. When action ceases, 300 cc. of water are added, and the solution is filtered from copper and iron precipitates, which are washed well and dissolved with nitric acid (sp. gr. 1.20). To the solution thus obtained in a 350 cc. beaker, 10 cc. of sulphuric acid (1:1) are added, and evaporation is conducted until copious fumes of sulphur trioxide are evolved. Water is cautiously added to a volume of 300 cc., when the copper is precipitated by hydrogen sulphide gas. After the copper sulphide has settled, it is removed on a paper and well washed with hydrogen sulphide water containing a little sulphuric acid.

The precipitate and paper are ignited in a tared platinum crucible, cooled and weighed immediately to prevent absorption of moisture by the copper oxide, which is hygroscopic. The weight of the oxide multiplied by the factor 79.89 and divided by the weight of the sample taken gives the percentage of copper.

If desired, the ignited copper oxide may be dissolved in nitric acid (sp. gr. 1.20) and the copper determined volumetrically as described under copper in ferro-molybdenum.

IRON.

The filtrate from the copper sulphide in the determination of copper is received in an Erlenmeyer flask of suitable size. A stopper equipped with a Bunsen valve is inserted in the neck of the flask, and the solution is boiled to expel the hydrogen sulphide. After cooling to 80° C., the iron is titrated with N/10 potassium permanganate solution until the appearance of a permanent pink color.

The deci-normal solution of potassium permanganate described under chromium in ferro-chromium may be used. One cc. equals .005584 gram of iron. The number cc. of standard potassium permanganate used, multiplied by the factor and 100 and divided by the weight of sample taken, gives the percentage of iron.

ZINC.

The solution obtained by the first filtration in the determination of silicon is used for the analysis of zinc. It is neutralized with stick sodium hydroxide; then, 5 grams in excess are added. After heating the solution to boiling, the precipitate of copper, iron and manganese is removed on a filter and washed thoroughly. Five grams of citric acid are added to the filtrate; the liquid is stirred until the crystals have dissolved, when the solution is made just acid with acetic acid. The zinc is then precipitated by hydrogen sulphide gas, removed on a double paper, and washed with hydrogen sulphide water. Air should be excluded from contact with the zinc sulphide as much as possible by keeping the funnel well filled with wash water.

The precipitate is dissolved from the paper with hydrochloric acid (1:1), and the solution is boiled to expel the hydrogen sulphide, when it is diluted to 250 cc. with water. Ten cc. of a 10 per cent. solution of ammonium phosphate are introduced, followed by ammonia to a slight excess. The liquid is boiled until the ammonia is entirely expelled, whereupon the zinc is completely precipitated as zinc ammonium phosphate. This is collected on a filter, washed with hot water, ignited in a porcelain crucible at a low temperature until the paper is consumed and then at the full heat of a muffle furnace for a considerable time, and weighed as zinc pyrophosphate, of which 42.89 per cent. is zinc.

ANALYSIS OF PIG NICKEL

SILICON.

One gram of the sample is dissolved in nitric acid (1.20 sp. gr.), 15 cc. of sulphuric acid are added, and the solution is evaporated until fumes of sulphur trioxide are expelled. Water is added and heat applied until the soluble salts are dissolved. The silica is removed by filtration, ignited, weighed, and calculated to per cent. of silicon.

COPPER.

Hydrogen sulphide gas is passed through the diluted filtrate from the silica determination. The precipitate of copper sulphide is removed by filtration, washed, ignited, and weighed as oxide, 79.89% of which is copper.

IRON.

The filtrate from the copper sulphide separation is boiled until the hydrogen sulphide is expelled. Ten cc. of ammonium persulphate solution (50 grams per liter) are added, and the boiling is continued a few minutes. An excess of ammonium hydroxide and 10 cc. of ammonium persulphate are added, and the contents of the beaker are again boiled a few minutes. The precipitates are filtered off, washed, and dissolved with sulphuric acid (1:4) and sulphurous acid. The resulting solution is oxidized and a second precipitation is made as before, the combined filtrates being reserved for the determination of nickel. The precipitate is dissolved with hot hydrochloric acid (1:1), and the iron is determined by the usual basic acetate hydroxide separations and weighed as ferric oxide, 69.94% of which is iron.

NICKEL.

The combined filtrates from the ferric hydroxide separations are acidulated with sulphuric acid (1:1) and transferred to a volumetric flask. An aliquot part representing .5 gram of the sample is withdrawn, evaporated to about 80 cc., and transferred to a 150 cc. beaker. The free acid is just neutralized with ammonium hydroxide, and 40 cc. are then added in excess, making the total volume about 125 cc. Electrodes are inserted and a direct current of .5 to .6 amperes is passed through the solution. This is conveniently arranged by connecting in series one 60 watt, 110 volt lamp for 110 volt line, or two of the above lamps for 220 volt line. When the nickel is completely deposited, the electrodes which have been previously weighed, are removed, while the current is on, and dipped into a beaker containing distilled water. They are then removed from the water, disconnected, dipped into alcohol, dried and weighed; the increase in weight of the cathode is metallic nickel. Cobalt, if present, is weighed with the nickel.

MANGANESE.

Two-tenths gram of the sample, in an 8″ x 1″ test tube, is dissolved in 10 cc. nitric acid (sp. gr. 1.20). Silver nitrate solution is added, and the determination is finished, after the addition of ammonium persulphate, by sodium arsenite titration as explained under manganese in ferro-phosphorus.

If manganese is present in amount over 1 per cent., the initial weight taken should be less than two-tenths gram.

ANALYSIS OF PYRITES.

SULPHUR.

Five-tenths gram of the sample is transferred to a nickel crucible and intimately mixed with three grams of sodium peroxide. The crucible is covered and cautiously heated until the contents are fused. The crucible and lid are transferred to a 400 cc. beaker containing approximately 100 cc. of water. When the fusion is decomposed, the lid and crucible are removed and cleaned. Hydrochloric acid is added to the contents of the beaker until the precipitate is just dissolved. The sulphur is precipitated by adding to the boiling solution, drop by drop, 50 cc. 10 per cent. barium chloride solution. After standing on a steam-heated sand bath for 4 hours or longer, the precipitate is separated by filtration, washed 3 times with hot 1% hydrochloric acid, and then 8 times with hot water.

The barium sulphate is carefully ignited at a low heat until the paper is consumed and then for 15 minutes at a high temperature.

The barium sulphate is contaminated with small amounts of iron, nickel and alkali salts, which are, however, negligible for ordinary work. For accurate analysis the barium sulphate is transposed to the carbonate by fusing with sodium carbonate. The fusion is transferred to a beaker containing hot water, and gently heated until disintegrated. The insoluble barium carbonate is removed by filtration, washed with hot water, and dissolved with a slight excess of hydrochloric acid (1:1). The barium is precipitated as sulphate by sulphuric acid (1:1) in the usual manner. The weight of barium sulphate multiplied by the factor 13.73 and by 2 gives the percentage of sulphur.

BEARING METALS.

SAMPLING.

The material for analysis is either in the form of a pig, or irregular portions of a bearing. In both cases, the outer surface is removed, and a sample taken by sawing across the face, for which purpose either one hack saw or five or ten hack saw blades, clamped or bolted together, is admirably suited. Drillings, if more convenient, are taken in various places according to the size and shape of the sample, the drillings being prepared as fine as possible.

METHODS OF ANALYSIS.

TIN.

VOLUMETRIC METHOD.

One-half gram of the alloy contained in a 300 cc. Erlenmeyer flask is treated with 30 cc. of hydrochloric acid. A gentle heat is applied, and small amounts of sodium chlorate are added, from time to time, until the sample is dissolved. Should the metal dissolve with difficulty in hydrochloric acid, a new portion of the sample is treated with 10 cc. of sulphuric acid and, when in solution, 10 cc. of water and 30 cc. of hydrochloric acid are added. Five grams of steel drillings are then added, and the solution is boiled for ten minutes, the antimony and copper compounds being reduced to the metallic forms. The solution is filtered through cotton or paper into another 300 cc. flask, the residue washed with cold water, and the solution diluted to 100 cc. Steel drillings are again added and boiling is continued for 15 minutes; the solution is cooled in an atmosphere of natural gas or carbon dioxide. When cool, the stopper is removed and the tin titrated with the iodate or iodine solution, as used in the sulphur titration, starch (see sulphur in ferro-manganese) being the indicator. If the iodine solution is theoretically standardized, 1 cc. equals .371% on .5 gram sample. A stronger solution of iodine is made by dissolving 10.5 grams of iodine and 20 grams of potassium iodide in 50 cc. of water and diluting to one liter. One cc. should equal .005 gram tin, or 1 per cent. on .5 gram sample.

The iodine or iodate solution is preferably standardized as follows: Fifty cc. of the weak iodate or iodine solution, or 25 cc. of the strong solution are added to a beaker containing 400 cc. of water and 10 cc. of hydrochloric acid (1:1). Standard sodium thiosulphate solution (about 25 grams per liter) is added until the yellow color becomes faint, when 10cc. of starch solution are added, and the titration is continued until the blue color is bleached. In the same manner, 25 cc. of a deci-normal potassium permanganate solution are added to a beaker containing 400 cc. of water, 10 cc. of 10% potassium iodide solution, and 10 cc. of hydrochloric acid (1:1); the resultant iodine is titrated with sodium thiosulphate solution. The permanganate solution is standardized against sodium oxalate, as described under chromium, in ferrochromium, and its normality obtained. The normality of the iodine solution is found by dividing the normality of the permanganate by the number of cc. of thiosulphate required for its titration, and multiplying by the number of cc. of thiosulphate required for the iodine titration. The normality of the iodine solution, multiplied by .05935, gives the value in grams of tin of 1 cc. of the solution. Example: 20 cc. of thiosulphate are required for 25 cc. of iodine solution; 24 cc. of thiosulphate are required for 25 cc. of permanganate solution. The normality of permanganate is .102. Therefore, the normality of the [redacted] Iodine is $\frac{.102 \times 20}{24} = .085$. One cc. of [redacted] Iodine $= .085 \times .05935 = .005045$ gram of tin. The standardization may be checked by taking .25 gram of pure tin through the operations of solution, reduction and titration in the same manner as the sample.

GRAVIMETRIC METHOD.

This method is applicable only when the percentage of antimony is much lower than the percentage of tin.

One-half gram of the sample is transferred to a 250 cc. beaker, and 20 cc. of nitric acid (1.20 sp. gr.) are added. The solution is evaporated nearly to dryness, 5 cc. of nitric acid and 50 cc. of water are added, and the soluble salts are dissolved. The insoluble residue is collected on a filter, ignited, and weighed as the combined oxides of tin, antimony and phosphorus.

The percentage of antimony present, determined as described later, is multiplied by 1.266 to obtain antimonic oxide (Sb_2O_4). The percentage of tin is found by multiplying, by 78.77 and 2, the difference obtained by subtracting the sum of the phosphoric anhydride (P_2O_5), if present, and the antimonic oxide from the total oxides.

ANTIMONY.

One gram of the alloy is transferred to a 125 cc. Erlenmeyer flask and dissolved in 20 cc. of sulphuric acid. In the case of high lead alloys, boiling for a short time is necessary; any stannic or lead salt which may separate is neglected. The flask is allowed to cool, 10 cc. of water and 10 cc. of hydrochloric acid are added, and the solution is boiled until sulphur dioxide is expelled. When cold, the contents are washed into a 600 cc. beaker and diluted to 300 cc. Fifty cc. of manganese sulphate solution (see solutions under iron in ferro-manganese) are added, and antimony is titrated with standard potassium permanganate solution until a permanent pink color is obtained. One cc. of deci-normal solution is equal to .601% antimony on a one gram sample. It is standardized with sodium oxalate in the regular manner or by means of C. P. antimony, about one-tenth gram of the finely powdered antimony being treated in the same manner as described for the alloy.

LEAD.

DIRECT METHOD.

For alloys containing less than 30% lead, one gram may be used, but when the lead content is over this amount, only one-half gram should be taken. To the alloy in a 250 cc. flask, 15 cc. of water and 10 grams of tartaric acid are added, and heat is applied until the latter is in solution. Three to four cc. of nitric acid are now introduced and, when the alloy is dissolved, 10 cc. of sulphuric acid are carefully added. The solution is boiled gently until all nitric acid fumes are expelled, which can easily be observed by the sudden clearing of the atmosphere in the flask. The flask is immediately withdrawn from the heat, allowed to cool, and 100 cc. of cold water and 75 cc. of ethyl alcohol are added. The precipitated lead sulphate is allowed to settle, collected in a Gooch crucible or on a filter paper, and washed with cold 2% sulphuric acid. In the absence of silicon, and when the tin content is under 20%, the lead sulphate may be dried and weighed, 68.32% of which is lead. Or, the filter and precipitate are returned to the original flask, about 30 cc. of water and 10 grams of solid ammonium acetate, are added and heat is applied until the lead sulphate is completely dissolved. The solution is filtered into another flask or small beaker and the paper washed thoroughly with ammonium acetate solution and hot water. If the lead is in small quantity, it may be dissolved from the paper by washing with hot 10% ammonium acetate solution. To the filtrate, 5 cc. of acetic acid are added, the solution is heated to boiling and the lead reprecipitated with potassium chromate or bichromate solution added in excess. The solution is boiled for a few minutes, the precipitate allowed to settle, collected on a previously dried and weighed filter paper, washed with hot water, dried for one hour at 105° C. and weighed; 64.11% of the weight of the precipitate is lead.

OXIDE SEPARATION.

For this determination, the filtrate from the oxides of tin and antimony is used. To the solution, 10 cc. of sulphuric acid (1:1) are added and the solution is evaporated to fumes; water and alcohol are then added and the determination finished as described above.

SULPHIDE SEPARATION.

One-half gram of the alloy is dissolved in 20 cc. of hydrochloric acid, aided by a few drops of nitric acid from time to time. The solution is diluted to 80 cc. and stick potassium hydrate is added until the precipitated hydrates of tin and antimony have dissolved. Five cc. of fresh ammonium sulphide (made by passing hydrogen sulphide at a moderate rate of flow into 100 cc. of 1:1 ammonium hydroxide for twenty minutes) are added, and the solution is boiled ten minutes, filtered from the precipitate of lead, copper and other elements, which is washed with a fairly strong solution of ammonium sulphide in water. The paper and contents are transferred to the original beaker, and the precipitate is dissolved by digestion at near the boiling point with 20 cc. of nitric acid (1.20 sp. gr.). The solution is filtered and, after the addition of 20 cc. of sulphuric acid (1:1), is evaporated to fumes of sulphur trioxide. Upon dilution to a volume of 200 cc. with water and alcohol, the lead is determined as sulphate as described above.

COPPER.

CUPROUS OXIDE SEPARATION.

Two-tenths gram of brass or bronze, or one gram of babbitt, is transferred to a 250 cc. Erlenmeyer flask and dissolved in 20 cc. of hydrochloric acid with small additions of sodium chlorate from time to time. About 10 grams of tartaric acid are now added, and, when dissolved, a 40% solution of caustic potash or soda is added until a deep blue color is obtained, then 15 cc. in excess. After the solution has cooled, three to four grams of glucose or invert sugar are added; the solution is boiled about five minutes and filtered from the precipitate. This is washed with hot water and dissolved on the filter by means of hot dilute nitric acid, the solution being received in the flask in which precipitation was made. Ten cc. of bromine water are added, and the solution is boiled until nitrous and bromine fumes are completely expelled. The solution is then diluted to 50 cc., made neutral with ammonia, and 2 cc. of sulphuric acid are added. Eight to ten cc. of 50% potassium iodide solution are then added, and the liberated iodine is titrated with a standard approximately .03 normal sodium thiosulphate solution, employing starch as the indicator. The thiosulphate solution is standardized by titrating the iodine liberated on adding an excess of potassium iodide and hydrochloric acid to standard permanganate solution. A normal thiosulphate solution equals .06357 gram copper per cc. of solution.

OXIDE OR SULPHIDE SEPARATION.

To the filtrate from the lead sulphate obtained in the oxide or sulphide separation of lead, 25 cc. of 20% sodium thiosulphate solution are added, and the solution is boiled until the precipitate coagulates. The precipitate is removed by filtration, dried, ignited, and weighed as copper oxide, 79.89% of which is copper; or, the precipitate is dissolved in nitric acid and the copper determined by titration of the liberated iodine on addition of potassium iodide, as described in the method for copper in ferro-molybdenum.

COPPER AND LEAD.

ELECTROLYTIC METHOD.

This method is applicable to a bronze of high copper and low lead content.

One-half gram of the sample is treated with nitric acid as described under the gravimetric method for tin. The filtrate from the stannic oxide is received in a 150 cc. beaker, evaporated if necessary and neutralized with ammonium hydroxide, followed by 10 cc. of nitric acid (1.20 sp. gr.) and 1 cc. of sulphuric acid (1:1). The electrodes, which have been previously weighed, are placed in the beaker, and a direct current of .5 to .6 amperes is then passed through the solution. This current is conveniently obtained by connecting the electrolyte in series with a 60 watt, 110 volt lamp for 110 volt line, or two lamps for a 220 volt line. When the blue solution is colorless, all copper having been separated, the electrodes are removed while the current is on and dipped into distilled water. They are then removed from the water, disconnected, dipped into alcohol, dried, and weighed. The copper deposits as metal on the cathode, and the lead as PbO_2 on the anode. The electrolyzed solution may be utilized for the determination of aluminum, iron, manganese, zinc, nickel and other constituents.

PHOSPHORUS.

One gram of the sample is dissolved in 30 cc. of nitric acid (1.20 sp. gr.) and 5 cc. of hydrochloric acid (1:1); then, after removal from heat, 50 cc. of ammonium molybdate solution are added to precipitate the phosphorus, which is determined either volumetrically or gravimetrically, as described under the molybdate method for phosphorus in ferro-phosphorus.

IRON AND ALUMINUM.

One gram of the sample is dissolved in 10 to 15 cc. of hydrochloric acid, aided by the addition of a few crystals of sodium chlorate. The solution is diluted with hot water to a volume of 300 cc., made nearly neutral with ammonium hydroxide, and saturated with hydrogen sulphide gas. The precipitation is aided by heating and allowing the solution to stand. The precipitate is removed on a paper, the filtrate is boiled to expel hydrogen sulphide, and, after oxidation with nitric acid, is evaporated to half its volume, or to dryness if silica is present. Ammonium hydroxide is added until a faint precipitate persists, the solution being still acid to litmus, 15 cc. of ammonium acetate (20%) are added, and the solution is boiled one minute. After the precipitate has subsided, the solution is filtered, and the precipitate washed with hot water, and dissolved in the smallest possible excess of hydrochloric acid, the solution being received in a volumetric flask. One-half the solution is transferred to a beaker and evaporated to 10 cc., and the iron is reduced and titrated with permanganate as described under iron in ferro-manganese.

The other half of the solution of the basic acetate precipitate is used for the determination of aluminum. Ten to twenty cc. of a 10% solution of ammonium phosphate are added, followed by ammonium hydroxide until a faint precipitate is obtained, the solution being still acid or neutral to litmus. Then 1½ cc. of hydrochloric acid and 25 cc. of 20 per cent. sodium thiosulphate solution are added, and the solution is heated to the boiling point, when 8 cc. of acetic acid and 15 cc. of 20 per cent. ammonium acetate are added. The boiling is continued for ten minutes, and the precipitate is allowed to settle, removed by filtration, washed with hot water, ignited in a porcelain or alundum crucible, and weighed as aluminum phosphate, 22.19% of which is aluminum.

MANGANESE.

In the filtrate from iron and aluminum, the manganese is precipitated as dioxide by the addition of one gram of ammonium persulphate to the hot, strongly ammoniacal solution, removed by filtration and dissolved in nitric acid and ammonium bisulphite. The solution is boiled to expel the excess sulphur dioxide, and the manganese is determined by the persulphate-arsenite method as described under manganese in ferro-phosphorus.

NICKEL.

The filtrate from the manganese dioxide obtained above is made slightly ammoniacal, and 10 cc. of 1% alcohol solution of dimethylglyoxime for each per cent. of nickel present are added. The solution is allowed to stand until the precipitate collects, when it is removed by filtration on a dried and weighed paper. The precipitate is dried for one hour at 105° to 110° C., and weighed between watch glasses; 20.31% is nickel. It may be ignited and weighed as NiO, 78.58% of which is nickel.

MAGNESIUM.

The filtrate from the nickel glyoxime, or the filtrate from the manganese dioxide, in the absence of nickel, is acidulated with hydrochloric acid,and 25 cc. of 10% solution of ammonium phosphate are added. The solution is made strongly ammoniacal, and allowed to stand at least 12 hours, or stirred one hour. Ammonium magnesium phosphate is precipitated. It is separated on a paper, washed, ignited and weighed as the pyrophosphate, 21.84% of which is magnesium.

ZINC.

The filtrate from the ammonium magnesium phosphate, or the filtrate from the iron and aluminum hydroxide, in the absence of nickel, manganese and magnesium (in which case ammonium phosphate is added), is boiled to expel the excess of ammonia, then made exactly neutral. On warming and standing, the zinc is precipitated as ammonium zinc phosphate, which is collected on a filter paper, washed with hot water, ignited at a low temperature, and weighed as zinc pyrophosphate, $Zn_2P_2O_7$, 42.89% of which is zinc.

ARSENIC.

One gram of the sample is transferred to a porcelain evaporating dish. Ten cc. of nitric acid (1.20 sp. gr.) and 4 cc. of sulphuric acid are added. Heat is applied, and, when the sample is dissolved, the solution is evaporated until the residue is sufficiently dry to be scraped and brushed out of the dish. It is transferred to a 500 cc. distillation flask and 15 grams of ferrous sulphate, or 5 grams of cuprous chloride, are added. The flask is provided with a separatory funnel and exit tube leading through a condenser to two receiving flasks. The first flask contains 50 cc. of water and is closed by a two-hole rubber stopper, containing an entrance and an exit tube. The former extends just through the stopper, while the latter reaches to the surface of the water. The second flask contains 100 cc. of water and the entrance tube reaches to the bottom of the flask.

With the apparatus thus connected, 100 cc. of hydrochloric acid are added through the separatory funnel, and the solution is distilled until but 40 cc. remain; then another 50 cc. portion of hydrochloric acid is added and distillation continued until the volume is again reduced to 40 cc. During the distillation the receiving flasks are kept cool. In the two flasks will be found all the arsenic. The solutions are combined, heated to 70° C. and hydrogen sulphide gas passed through the solution. After having stood two to three hours, the precipitate is collected on a weighed paper, washed with hydrogen sulphide water, and dried. The precipitate of arsenious sulphide is washed on the paper with carbon bisulphide, dried, and weighed as As_2S_3, 60.92% of which is arsenic.