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METHODS

OF THE CHEMISTS OF THE

United States Steel Corporation

FOR THE SAMPLING AND ANALYSIS

OF ALLOY STEELS

64-

THE METHODS

OF THE CHEMISTS OF THE

UNITED STATES STEEL CORPORATION

FOR THE

SAMPLING AND ANALYSIS

OF

ALLOY STEELS

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PREFACE TO FIRST EDITION.

The demand for special or alloy steels has, during the last few years, increased to such a degree that, in place of being made by a few manufacturers in a very limited quantity and for very limited purposes, practically every steel works has been called upon to furnish this material in large quantities and in an ever increasing number of varieties.

The methods used for the determination of the ordinary elements in plain steels cannot, in many instances, be applied to alloy steels because of the interference of the alloying elements. The metals which are generally present in these steels are chromium, tungsten, vanadium, cobalt, nickel, molybdenum and copper.

The Chemists' Committee of the United States Steel Corporation present for their chemists' guidance, this compilation of what it believes to be the most satisfactory methods of analysis for alloy steels to be found at the present time. The compilers make no claim for originality regarding both the methods and the apparatus described, although, in a number of instances, it is believed that new points have been brought out, which should be of interest and value. Since this pamphlet is intended as a guide to the novice, as well as an aid to the more experienced chemist, all methods have been described in detail.

To facilitate the examination of steels of unknown composition, a scheme for making complete qualitative tests has been included.

The Committee of Chemists responsible for this compilation, in addition to the Chairman, consisted of Mr. A. B. Clemence, Chief Chemist of the Worcester, Mass. plant of the American Steel and Wire Co., Mr. John L. Harvey, Chief Chemist of the Homestead Works of the Carnegie Steel Co., and Mr. I. A. Nicholas, Chief Chemist of the Clairton Works of the Carnegie Steel Co., for which service the Chairman of the Committee is pleased to express his thanks.

PREFACE TO THE SECOND EDITION.

With the exhaustion of the supply of the first edition of the Commercial Sampling and Analysis of Alloy Steels, the demand for the pamphlet made a reprint of the first edition or the issuance of a new edition imperative. As considerable advancement has been made in the methods of analyses since the appearance of the first edition, it was deemed advisable to issue a new edition in which these improvements could be incorporated.

Accordingly, a committee of chemists to investigate the matter and carry out the work required was appointed. After a canvass of the various laboratories of the Corporation for suggestions as to ways of bettering the pamphlet, the work of revision was forthwith begun, and the result of this committee's labor was to produce this thoroughly revised and rewritten edition.

Many changes have been made in the methods of the previous pamphlet, and some new methods have been added. The new material deals both with elements treated in the first pamphlet and methods for the determination of uranium and zirconium, which elements were not included in the first edition.

The pamphlet describes some methods and apparatus that originated among the Corporation's chemists. Nevertheless, as the true identity of prior authors, discoverers, or inventors of many methods and apparatus is difficult to establish, this committee desires to waive all claims as to originality in the contents of the pamphlet. Consequently, they feel they are not doing any injustice by omitting all references as to authorship or discovery.

The committee appointed for the revision of the pamphlet consists of Mr. William Brady, Chief Chemist of the South Works of the Illinois Steel Co.; Mr. John L. Harvey, Chief Chemist of the Homestead Works of the Carnegie Steel Co.; and Mr. W. D. Brown, Chief Chemist of the Duquesne Works of the Carnegie Steel Co., Secretary.

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SAMPLING.

One or two tests for analysis are taken from each heat. If one test is desired, it is taken when one-half the heat has been poured; if two tests are desired, they are taken when one-third and two-thirds, respectively, of the heat has been poured.

While the stream of molten metal is momentarily slackened, a spoon is held under the nozzle of the ladle until a sufficient amount of the metal is collected. The metal is then poured from the spoon into the test mould. The use of aluminum to solidify the test is optional, but if used, it must always be added to the spoon, never to the mould.

Either one of two types of moulds may be used. Mould No. 1, Figure 1, usually designated as the split mould, consists of two similar parts made of cast iron or steel. The upper part of the inside of the mould is flared to facilitate the pouring of the liquid metal from the spoon, while a section near its middle is similarily flared externally to form a seat for its support in a holder. This holder, or stool, is a hollow one piece casting of iron, the upper inside section of which fits the externally flared portion of the mould and holds the assembled parts together. After the test is taken it is allowed to solidify, when the mould and contents are withdrawn from the holder. The mould pieces then fall apart and expose the test. Mould No. 2, Figure 2, is a one piece casting of iron or steel. It is provided with a threaded hole into which a steel handle is screwed. The test piece is removed by inverting the mould.

After the test has been removed from the mould, it is stamped with the furnace and heat number and delivered to a drill press to obtain the drillings for the analytical sample. With the exception of the steels noted below, the test is allowed to cool in the air and the sample for analysis is obtained by drilling with a ¾ inch drill. The test from mould No. 1 is drilled at a point between 1 inch and 2½ inches from the bottom end of the test piece and to such a depth as will give a sufficient quantity of drillings. The test piece may be drilled through, if necessary. The test from mould No. 2 is drilled on the bottom end to a depth not greater than one inch. In either case, to prevent contamination from scale, the drillings are discarded until the outer edge of the drill is buried.

Certain steels such as those containing tungsten, or chromium over two per cent, may require annealing before drilling. This is accomplished by heating in a furnace for one-half to three-quarters of an hour at a temperature of 700 to 800° C. and cooling slowly. The test is cooled, preferably in the furnace, or it may be placed in lime and allowed to cool. In some cases the annealing may be accomplished by immediately removing the test piece from its mould and plunging it into lime, where it is allowed to cool.

Steels containing much nickel (five to seven per cent) or manganese (approximately thirteen per cent) may be drilled with a high speed drill while the test is heated to a dull red. The drillings are slightly oxidized, but not to such an extent as to materially affect the analysis.

The drillings obtained as above may be used for the determination of all elements except carbon, though the removal of the fines is always desirable. Therefore, they are shaken on a 20 mesh sieve which nests in a 40 or 80 mesh sieve. Those drillings that pass through the 20 mesh sieve and are retained on the 40 or 80 mesh sieve are reserved for the determination of carbon, while those that are retained on the 20 mesh sieve are reserved for the determination of other elements. If the drillings are curly, so that they cannot be sieved, those that have a cross section smaller than the opening in a 20 mesh sieve are selected for the determination of carbon.

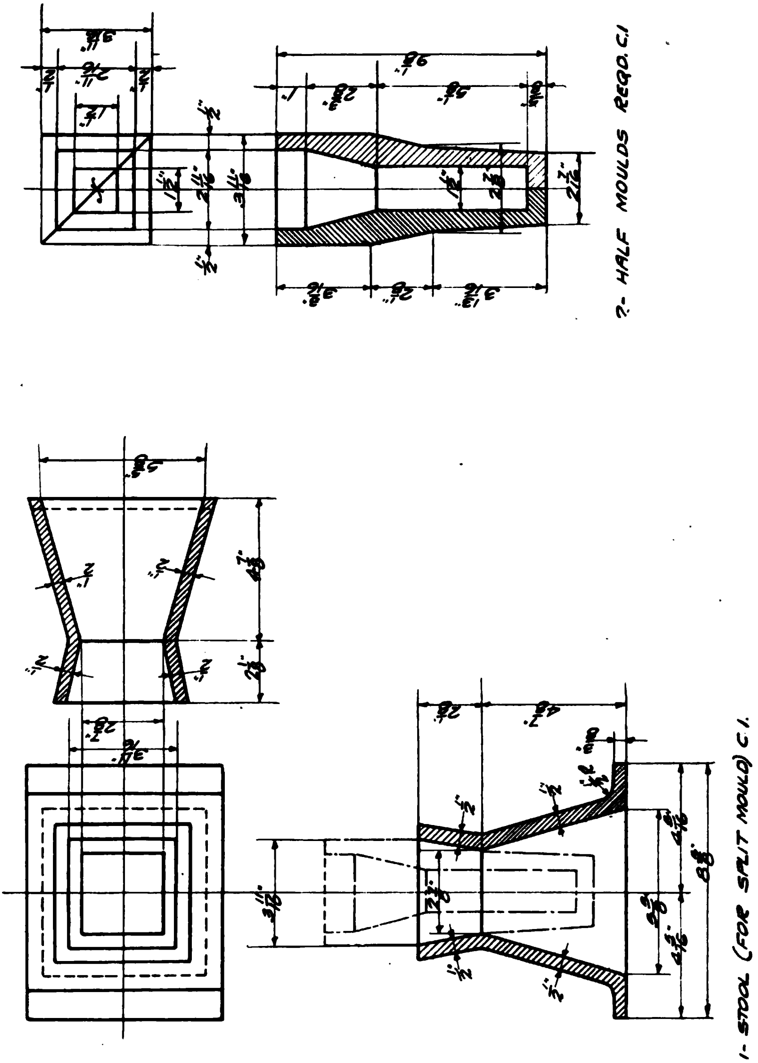


FIGURE 1.
LADLE TEST MOULD No. 1

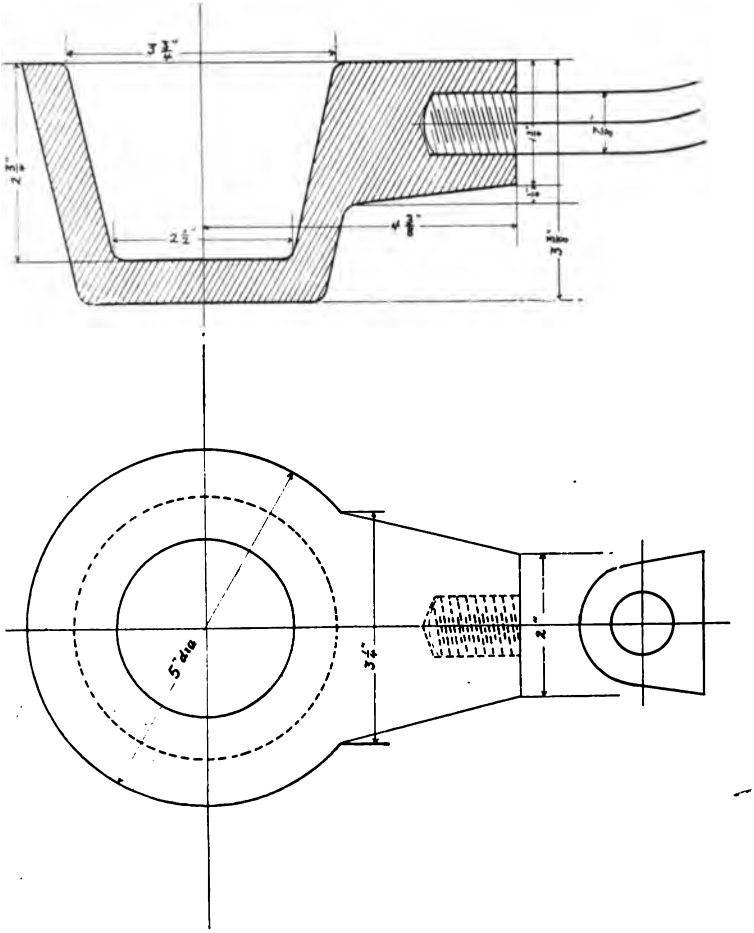


FIGURE 2.

LADLE TEST MOULD No. 2

QUALITATIVE TESTS.

As it frequently happens that the determination of an element by a given method may be interfered with by the presence of certain other elements, it is advantageous, in many cases, essential, in analyzing unknown steels to make a preliminary qualitive analysis before proceeding with the regular quantitive analysis. A number of these elements encountered in alloy steels may be detected by making the following simple direct tests upon the sample:

One gram of the sample is treated with 50 cc. of hydrochloric acid (1.13 sp. gr.). An immediate blue color on addition of hydrochloric acid indicates cobalt. After all action ceases, chromium, nickel, copper, cobalt, titanium, zirconium and uranium are dissolved; while tungsten, molybdenum and vanadium remain insoluble as a black residue. After this residue has settled, a green colored solution indicates nickel or chromium. If a black insoluble residue remains, one-half gram of sodium chlorate is added and the solution is boiled for five minutes. If the black residue changes to a lemon color, tungsten is indicated. If the residue completely dissolves, the absence of tungsten and the presence of molybdenum and vanadium are indicated. After filtering off the tungstic acid, if the residue did not dissolve, the solution is treated with 20 cc. of sulphuric acid (1:1) and evaporated until fumes of sulphuric anhydride are evolved. The residue is treated with 50 cc. of water and gently heated until the salts are dissolved, when the resulting solution may be used to confirm the presence or absence of copper, molybdenum, vanadium and titanium.

To detect copper and molybdenum, this solution is diluted to 200 cc. and almost neutralized with ammonia. It is then saturated with hydrogen sulphide gas and boiled until the precipitate coagulates. This precipitate is removed by filtration, washed and ignited at a very low heat. The oxides of molybdenum and copper are treated while in the crucible with dilute sodium hydroxide solution. The molybdenum oxide is thus dissolved while the copper oxide remains insoluble. The contents of the crucible are filtered and the filtrate may be tested for molybdenum by one of two methods. Either the filtrate is just acidified with hydrochloric acid (1:1), and one cubic centimeter of a solution of stannous chloride (five per cent) is added, followed by a few crystals of potassium thiocyanate, when the solution will assume a red color, which will not fade if molybdenum is present; or the filtrate is acidified with sulphuric acid (1:1) and is then saturated with hydrogen sulphide, when a dark brown precipitate will indicate molybdenum. To test further in the latter case, the precipitate is removed by filtration, ignited and treated with sulphuric acid (1:1) and metallic zinc. If molybdenum is present, the solution will be colored first blue, then green, and finally brown. The insoluble black residue of copper oxide is dissolved in nitric acid, the solution is diluted with water, and ammonia is added in excess. A blue color indicates copper.

To detect vanadium and titanium, the filtrate from the sulphides of molybdenum and copper is concentrated to a volume slightly less than 100 cc., when a solution of potassium permanganate is added in slight excess. The solution is boiled for a few minutes and cooled to room temperature. Ten cubic centimeters of hydrogen peroxide are then added, the solution is diluted to 100 cc. and is then divided into two equal portions which are transferred to 250 cc. beakers. If titanium alone is present, the solutions are colored yellow; if vanadium alone is present, the solutions are colored a deep brown; if both elements are present, the brown color due to the presence of vanadium is readily distinguished; while to detect titanium, one drop of hydrofluoric acid is added to one solution, whereby the yellow color due to titanium will be destroyed. This solution is then compared with the solution to which no hydrofluoric acid has been added and, if a change of color is observed, titanium is indicated.

For the detection of chromium, nickel and cobalt in the presence of tungsten, another solution of the sample is prepared as follows: One gram of steel is transferred to a 250 cc. beaker, 100 cc. of hydrochloric acid (1:1) are added and the contents of the beaker are boiled until all action ceases. The volume of the solution should now be about 50 cc. An equal volume of water containing one-half gram of sodium chlorate is then added and the solution is boiled for five minutes. The tungsten is thus converted to tungstic acid, is separated by filtration and then discarded. In order to remove the excess of iron from the filtrate, an ether separation is made as follows: Three cubic centimeters of nitric acid (1.20 sp. gr.) are added and the solution is rapidly evaporated to about 40 cc., cooled to room temperature and transferred with hydrochloric acid (1.11 sp. gr.) to a separatory funnel. The volume should not exceed 50 cc. Thirty cubic centimeters of ether are added, the funnel is well shaken, and the lower liquid containing but a trace of iron and molybdenum and all the other elements is run into a beaker. The solution is gently heated to expel traces of ether, 20 cc. of sulphuric acid (1:1) are added and the contents of the beaker are evaporated until fumes of sulphuric anhydride are evolved. After cooling, 50 cc. of water are added to the beaker and, when the separated salts have dissolved, any copper or molybdenum which may be present is precipitated by hydrogen sulphide gas as previously described. The precipitated sulphides are removed by filtration and the filtrate is boiled to expel the excess of hydrogen sulphide. To one-half the solution is then added one-fourth its volume of nitric acid followed by an excess of a concentrated solution of potassium permanganate. The solution is boiled for ten minutes, and if it is colored yellow, chromium is indicated. This solution may be tested further for chromium by transferring 20 cc. to a test tube containing 5 cc. of hydrogen peroxide. The yellow chromate solution will change to blue and upon shaking the solution with ether, the latter will withdraw the chromium compound and will be colored blue. The remaining half portion of the solution is treated with 5 grams of citric acid and, after making strongly alkaline with ammonia, the solution is saturated with hydrogen sulphide, whereby the cobalt and nickel together with iron and manganese will be precipitated as sulphides. The precipitate is removed by filtration, carefully ignited in a platinum crucible, transferred to a beaker and dissolved in hydrochloric acid. The solution is then made slightly ammoniacal, about one half gram of ammonium persulphate is added and the solution is boiled and filtered to remove oxides of iron and manganese. The filtrate containing the nickel and cobalt is divided into two portions; to one portion 5 cc. of a one per cent alcoholic solution of dimethylglyoxime are added and, if a bright red precipitate is formed, nickel is indicated. The remaining portion of the filtrate is slightly acidified with hydrochloric acid (1:1), heated to boiling, and a freshly prepared solution of nitroso-β-naphthol is added. The nitroso-β-naphthol is made by dissolving about one-half gram of the reagent in 10 cc. of hot acetic acid (seventy-five per cent). After the addition of this solution, the contents of the beaker are boiled for a few minutes, when cobalt, if present, is precipitated as a red colored compound together with some excess of the reagent. The solution is filtered while hot and the paper ignited in a porcelain crucible, whereby cobalt will be converted to the oxide. The residue in the crucible is treated with hydrochloric acid whereby the cobalt will be dissolved, coloring the solution blue. This solution may be tested further by adding ammonia, when the solution will be colored pink, if cobalt is present.

METHODS OF ANALYSIS.

GENERAL REMARKS.

In the following methods for the analysis of alloy steels, it has been the desire to give the directions in considerable detail. In order to avoid constant repetition, however, the following statements are made.

Whenever an acid or ammonia is mentioned without specifying the concentration, the pure grade of concentrated chemical as prepared by the manufacturer is understood. When these chemicals are diluted, the concentration is indicated by stating either the specific gravity or the ratio by volume of the concentrated chemical to water, the last figure in the ratio indicating the relative volume of water. It is understood that, not only the acids, but all the chemicals mentioned are of C. P. grade unless otherwise specified. Distilled water is used in all analyses.

DETERMINATION OF CARBON.

Carbon is determined by direct combustion, that is, a portion of the sample of steel in the form of fine drillings is burned in a current of oxygen, and the resulting carbon dioxide is absorbed with the proper reagent contained in a suitable vessel and either weighed or titrated. The apparatus employed for this determination varies in the number of its parts and in the construction and arrangement of these parts according to the facilities at hand and the method adopted. The essential equipment consists of a combustion tube, in which the sample of steel is burned; an electric furnace for heating this tube; a rheostat for regulating the temperature of the furnace, and possibly a transformer; a tank of compressed oxygen for burning the drillings, provided with the proper tubing and valves for regulating the flow of the gas; a tube containing reagents for purifying the oxygen, if necessary; a boat for containing the drillings during the combustion; a phosphorus pentoxide tube, which may be omitted if the volumetric method is employed, for drying the gases delivered from the combustion tube; an absorption bulb or bulbs, the construction of which depends on whether the gravimetric or the volumetric method is employed; and proper connections for all these parts. As the details connected with the assembly of the apparatus are of considerable importance, each part and its connections with the rest of the apparatus are herewith described in detail. Figure 3 illustrates this apparatus assembled in an approved manner for the determination of carbon gravimetrically.

The combustion tube is made of fused silica and is glazed inside so as to prevent the effusion of enclosed gases under a pressure of two or three pounds greater than atmospheric. The tube has an inside diameter of ⅞ inch to 1 inch, and a minimum length of 24 inches. It is prepared for use as follows: After it has been thoroughly cleaned inside, one end is closed with a one-hole rubber stopper, a plug of glass wool is inserted, and the tube is lightly packed for a distance of six or eight inches with asbestos, which has been ignited for several hours at 1000° C. or more. It is preferable to use asbestos impregnated with iron oxide for this purpose. To accomplish this impregnation 500 grams of raw asbestos are thoroughly digested in a solution of ferrous sulphate, then dried and ignited at 1000° C. The ferrous sulphate solution is made by dissolving 100 grams of the salt in a liter of a one per cent

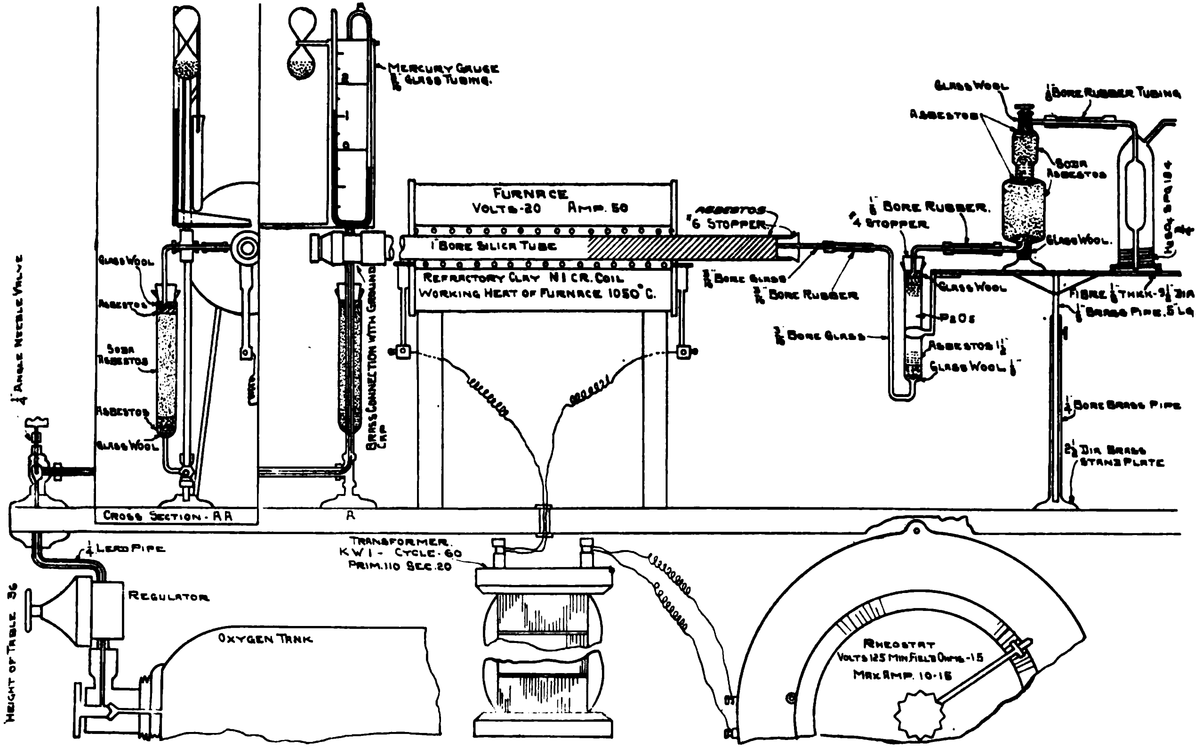


FIGURE 3. GENERAL ARRANGEMENT OF CARBON COMBUSTION APPARATUS.

solution of sulphuric acid. Upon this packing of asbestos there is next inserted a neatly fitting plug, recently ignited, of nichrome wire or gauze to hold the asbestos in place. If desired, a sleeve made of sheet nickel to fit the inside of the tube and then ignited for several hours at 1000° C. may be inserted in the central part to protect the walls of the tube from the splattering of iron oxide, which occurs if the combustion is rapid. The free end of the tube is now provided with a special stopper and oxygen inlet, preferably made of brass.

The details for the construction of such a stopper are shown by the drawings of figures 4 and 5. In the design shown in figure 4, a nozzle, A, is provided with a yoke, C, and set screw, E, which presses the cover, or cap, B, firmly against the external rubber gasket, D, thus forming a perfectly gas-tight joint. In the design illustrated by figure 5, a ground joint is provided between the nozzle, A, and the sleeve, B, and the cover, C, supports a glass plate through which the progress of the combustions may be watched. The dimensions given are those of a stopper made to fit a tube of one inch bore.

To apply this stopper the end of the tube is heavily coated with a thick mortar of plaster of Paris, and the open end of the nozzle, A, is immediately pushed over the coating of plaster as far as possible. After applying more of the plaster around the edges of the connection and allowing it to set, a perfectly gas-tight joint is secured and all danger of vitiating the results of a determination by carbon from the stopper is avoided.

The end of the tube may be closed with a one-hole rubber stopper which is provided with a glass tube inlet for the oxygen, but in this case the stopper is protected from the heat by means of brass disks arranged and held in place as shown by drawing, A, of figure 6 (page 18), and the end of the tube should be kept cool by means of a water jacket.

With the tube thus prepared, it is placed in the electric furnace so that its center is coincident with the center of the furnace, as shown in drawing of figure 3.

The electric furnace for heating the combustion tube consists of a resistance wire, made of an alloy of chromium and nickel, coiled about the tube, a casing or covering of clay or other refractory and non-conducting material, and a shell of steel to which legs may be attached for supporting

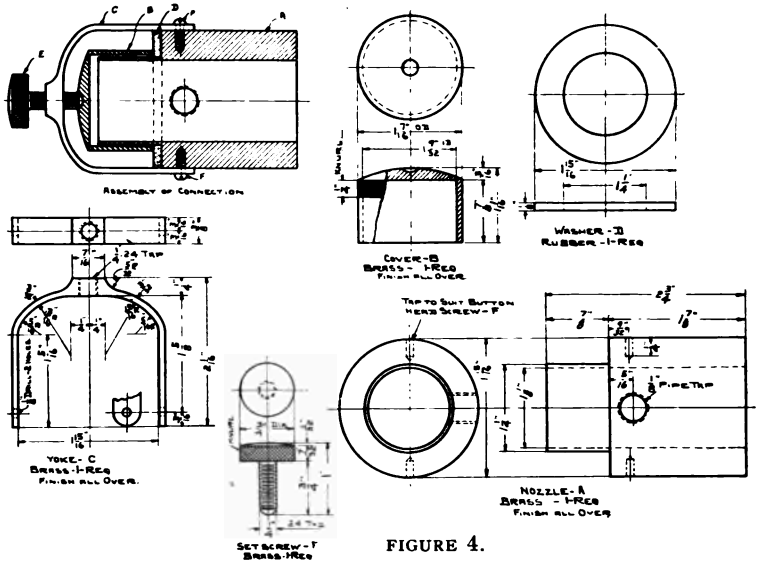


FIGURE 4.

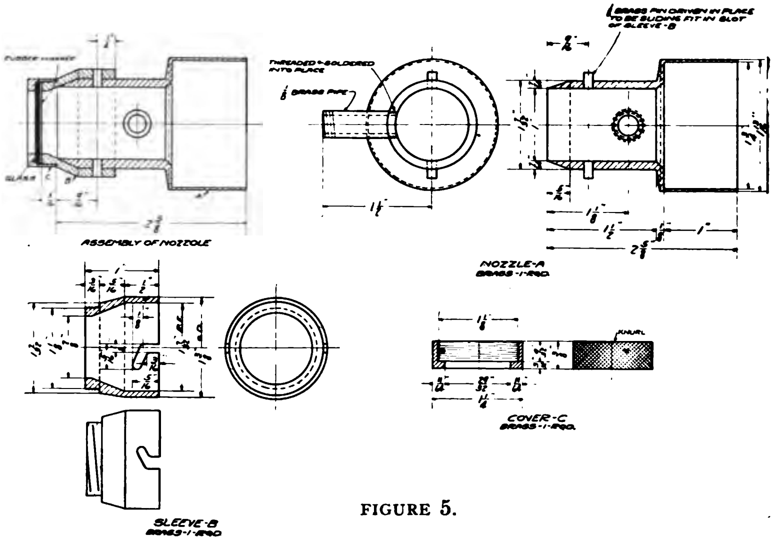


FIGURE 5.

DETAILS OF BRASS STOPPERS FOR SILICA TUBES USED IN CARBON COMBUSTION.

it at a height of six or eight inches, as shown in the figure. These furnaces may be wound to use either alternating current or direct current of any standard voltage. However, since the diameter of the wire decreases as the voltage increases, and a furnace wound with a wire of large cross section has a longer life than one wound with wire of small cross section, the low voltage furnaces are to be preferred. These furnaces must be equipped with transformers for reducing the voltage, and consequently they can use only alternating current. In any case, a rheostat for regulating the current passing through the furnace or the transformer should be provided, for it is only by this means that the temperature of the furnace can be controlled. This temperature should be maintained at approximately 1050° C. while the apparatus is in operation and should be determined at intervals by means of an accurately calibrated pyrometer.

The oxygen is contained in a high pressure cylinder which is provided with a pressure reducing and regulating valve, so as to supply the oxygen at a constant pressure of from ½ pound to 2 pounds as desired. From the regulating valve the gas is conducted to the combustion tube by means of a ¼ inch brass or lead pipe. In this line there are placed in series a needle valve for turning the gas on and off and a soda lime or soda asbestos tube for purifying the oxygen. A mercury manometer tube of glass for accurately indicating the gas pressure in the combustion tube is also connected. A sand glass or any other convenient device for timing the combustion may also be provided. The arrangement of these parts, as well as the details for packing the purifying tube are all shown in the drawings of figure 3.

The combustion boat is made of either nickel or alundum. Boats of the latter material are procured ready made from the manufacturers of alundum, and need only to be thoroughly ignited at a temperature of 1000°C. or more in a muffle furnace to be ready for use. Nickel boats are most neatly and readily made by cold stamping from sheets of about 18 gauge. For this purpose the only tools required are a set of dies made of steel, a light hand hammer and a pair of shears. The dimensions of these boats may vary somewhat, but the following will be found convenient; length 3 inches, depth ½ inch, width ½ inch at the bottom and ⅝ inch at the top. After they have been stamped, these boats are ignited for about twelve hours in a muffle furnace at a temperature of 1000°C. or more and placed in a closed container to protect them from the dust of the air until they are put into service.

When in use, these boats are filled nearly half full with either granular alundum, which is supplied by the manufacturers for the purpose, or with chrome ore that has been prepared as follows: Chrome ore that has been crushed to pass a 20 mesh sieve is sifted on a 100 mesh to free it from dust, then digested with hydrochloric acid, washed with water and dried. Like the boats, the alundum or the chrome ore, according to which is selected, is strongly ignited and thereafter protected from dust until used.

The construction and arrangement of the remainder of the apparatus, employed for the absorption of the carbon dioxide evolved during a determination of carbon, depends upon whether the gravimetric or the volumetric method is adopted.

GRAVIMETRIC METHOD.

In the gravimetric method the carbon dioxide is absorbed with soda asbestos or soda lime in a suitable container, known as the absorption bottle, and its weight ascertained from the increase in weight of the bottle. With these absorbents the gases from the combustion tube must be dried before they enter the absorption bottle. For this purpose a tube similar in form to the drying tube shown in figure 3 and about 1 inch x 6 inches in size is very convenient. In the bottom of this tube is placed a layer of glass wool, ¼ inch thick, and then a layer of asbestos 1 inch thick. The tube is then filled to within about 2 inches of the top with phosphoric anhydride, which is then covered with a layer of asbestos about ¾ inch thick, followed by another thinner layer of glass wool.

The absorption bottle is prepared in the following manner: In the bottom is placed a layer of glass wool ½ inch thick, and upon this wool a ¼ inch layer of coarse soda lime, designated as 12 mesh and having a moisture content of 15 per cent, is poured. The bottle is then filled to within a little less than one inch of the top with a mixture consisting of two parts of 60 mesh soda lime, having a moisture content of 2 per cent, and one part of 20 mesh soda lime, having a moisture content of 15 per cent. Asbestos is now spread evenly over the top of the soda lime to a depth of ¼ inch, and the bottle is filled almost to the neck with phosphoric anhydride. A small plug of asbestos is now pressed down upon the phosphoric anhydride, the neck of the bottle is cleaned of any adhering particles of the anhydride and the stopper, properly lubricated, is inserted. Instead of soda lime, soda asbestos may be employed for absorbing the carbon dioxide. This absorbent is a specially prepared mixture of sodium hydroxide and asbestos and is purchased ready for use. With it, the layer of phosphoric anhydride in the top of the absorbent bottle may be omitted, the bottle being merely filled with the soda asbestos, with a thin layer of glass wool at the top and the bottom.

The absorption bottle and the drying tube are now connected with the combustion tube as shown in figure 3. An aspirator bottle is attached to the exit of the absorbtion bottle and the needle valve on the line from the oxygen tank is opened full. By means of the regulating valve on the oxygen tank the flow of the oxygen is so regulated that approximately 400 cc. of the gas pass through the apparatus per minute, the volume per minute being measured by means of the aspirator bottle. When this rate of flow for the oxygen has been satisfactorily adjusted, the needle valve is closed and the aspirator bottle is replaced by another containing a little sulphuric acid, as shown in the drawings of figure 3, or preferably by one containing a solution of barium hydroxide. The needle valve is now opened as before, and the bubbling of the gases through the sulphuric acid or barium hydroxide solution is carefully observed, as is also the reading on the manometer tube. Thereafter, the bubbling of the gases through this bottle is used as an indicator of the correct rate of flow for the oxygen, and if barium hydroxide solution is used, it also gives warning of any failure of the absorption bottle to retain all the carbon dioxide given off by the steel in combustion. Usually, no adjustment of the regulating valve is necessary after the correct rate of flow of the oxygen has once been obtained, until the tank is nearly empty.

The combustion train is now thoroughly tested as follows: With all parts of the apparatus connected and closed as shown in the figure, the oxygen is passed through the train for ten minutes, when the needle valve on the oxygen line is closed, the absorption bottle is disconnected and its stopper is closed. The bottle is now weighed with a tare, or counter poise, which is preferably another bottle of the same design and filled in the same way as the one used for the absorption. The bottle is again placed in the train, the oxygen passed for five minutes, and the bottle weighed as before. These operations are repeated until the weight of the absorption bottle is constant. A boat about two thirds filled with the alundum or chrome ore, all prepared as previously described, is now inserted into the hottest zone of the combustion tube, which is near its center. The end of the tube is now closed, and the oxygen is passed for five minute intervals until the weight of the bottle is again constant, or until the blank, if any, becomes constant. The combustion of a standard steel of a known carbon content is now made as described below, and if the result obtained is correct, this fact is taken as final evidence that the apparatus is in a satisfactory condition for service.

After the combustion boat has been tested as outlined above, it is allowed to cool to atmospheric temperature, and the absorption bottle is replaced in the combustion train as before. A V-shaped depression, or furrow, as deep as possible and about one inch long, is made in the refractory material in the boat, and 1.364 grams, five times the factor weight, of that part of the sample which has been prepared for the carbon determination, as described under sampling, is placed therein in the form of a small pile. The brass cap or brass-shielded rubber stopper is removed from the entrance end of the combustion tube, and the boat is quickly pushed, by means of a clean metal rod, into the combustion zone. The end of the tube is immediately closed securely, and the needle valve on the oxygen line is opened full.

As soon as the temperature of the steel reaches the kindling point, which requires from one and one-half to two minutes, rapid combustion takes place, and, as the sample of steel was compactly placed in the boat, the heat of oxidation is so intense that complete fusion of the resulting oxide of iron is effected. The rapid burning of the steel consumes the oxygen rapidly, but any additional oxygen required is automatically supplied through the pressure regulating valve, which is set to deliver 400 cc. per minute through the absorption bottle.

The oxygen is passed through the combustion train for five minutes in all, after which the needle valve in the oxygen line is closed. The absorption bottle is disconnected, the stopper is closed and the bottle is weighed as described for the blank test. The difference between this weight and the previous weight of the bottle, expressed as a fraction of a gram, and multiplied by twenty, gives the per cent of carbon in the steel.

TITRATION METHOD.

In the titration, or volumetic method, the carbon dioxide is absorbed in a known excess volume of barium hydroxide solution contained in a combination Erlenmeyer flask and nine bulb absorption tube, and the excess barium hydroxide is titrated with standard hydrochloric acid, using phenolphthalein as an indicator.

A detailed drawing of the absorption flask and bulb tube is shown at B in figure 6. Since the gases from the combustion tube do not need to be dried before they enter this absorption apparatus, it is connected directly to the glass exit tube in the end of the combustion tube with rubber tubing.

Rapid combustion and fusion of the steel, as described under the gravimetric method, can be employed in this method but care must be exercised that the flow of gases through the absorbing solution is not too rapid to prevent the complete absorption of the carbon dioxide. Therefore, slow oxidation, which does not necessarily effect fusion of the steel, is recommended.

Two grams of the sample are spread loosely over the surface of the refractory material contained in the boat. By means of an overflow pipette, exactly 80 cc. of standard barium hydroxide solution are added to the Erlenmeyer flask, the rubber stopper carrying the bulb tube and inlet tube is inserted in place, and the glass inlet tube is connected to the end of the combustion tube. The Erlenmeyer flask is inclined in such a way that the bent stem of the bulb tube reaches the bottom to one side of the center, so that the gases entering the flask will force the solution into the bulb tube.

The boat is now placed in the center of the combustion tube, the stopper is inserted and the oxygen admitted, the rate of flow being about 150 cc. per minute. The first turbidity in the absorption flask will occur in about nine minutes. The current of gas is continued for a total of twenty-five minutes, after which period the stopper is removed, and the absorption flask is disconnected and stood upright, permitting the barium hydroxide solution to flow back into the flask. The interior of the tube and the exterior of the stem are washed with water, and the solution in the flask is then ready for titration.

Several drops of phenolphthalein solution are added, and the standard hydrochloric acid is added cautiously while the flask is agitated, the last five to ten cubic centimeters being added rather slowly. The end point is indicated by the disappearance of the pink color.

A blank determination with no steel in the combustion tube is carried out exactly as an actual determination, using the same volume of barium hydroxide solution. The difference between the amount of standard acid equivalent to the barium hydroxide used, as determined by this blank titration, and the amount used in the actual titration, multiplied by the carbon value of the standard acid, corresponds to the per cent carbon. The hydrochloric acid is standardized by means of a standard steel of known carbon content.

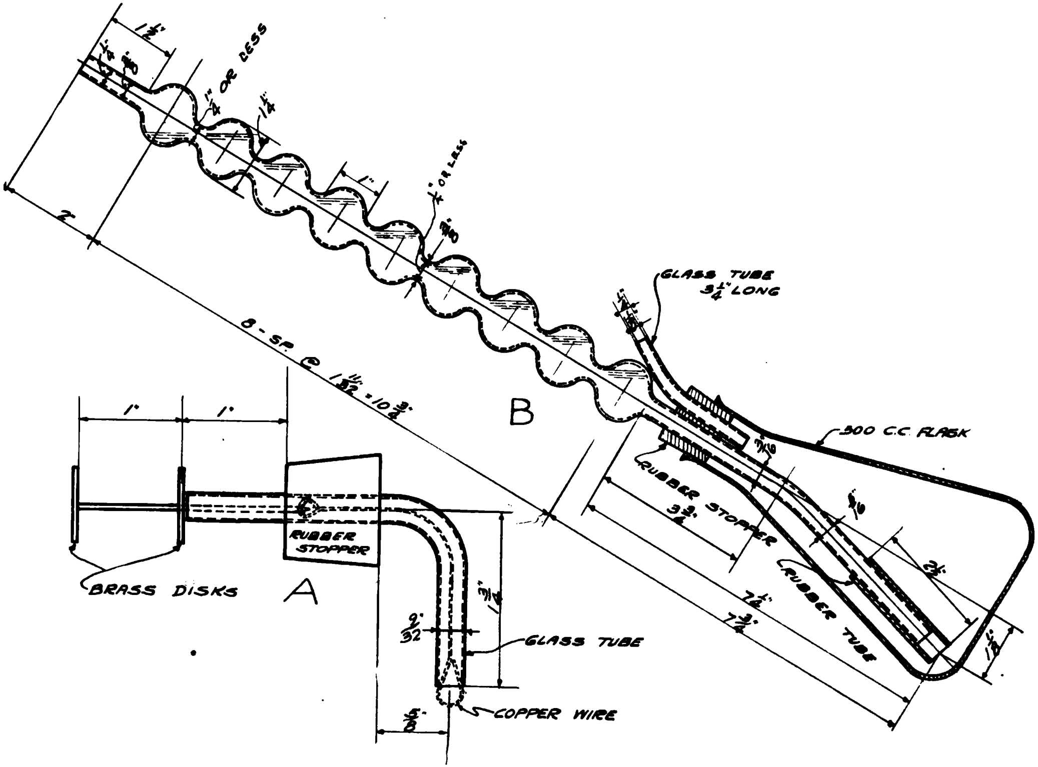


FIGURE 6.

A. RUBBER STOPPER ARRANGEMENT FOR CLOSING INLET END OF COMBUSTION APPARATUS.

B. ABSORPTION APPARATUS FOR TITRATION METHOD.

Solutions Required.

Standard Hydrochloric Acid.

Hydrochloric Acid (1.19 sp. gr.)	8 cc.
Water	1000 cc.

The water used should be free from carbon dioxide. One cubic centimeter of this solution is equivalent to approximately .03% carbon, when two grams of steel are used.

Barium Hydroxide Solution.

Barium Hydroxide	20 grams.
Water	1000 cc.

The water used should be freshly boiled. When the solution has reached room temperature, it is filtered through a 25 cm. filter paper as rapidly and carefully as possible. The solution, protected by a guard tube filled with soda lime or caustic potash solution, is conveniently withdrawn from the container by means of a suitable syphon.

Phenolphthalein Solution.

Phenolphthalein	1 gram.
Alcohol (Methyl or Ethyl)	1000 cc.

DETERMINATION OF MANGANESE.

GRAVIMETRIC METHOD.

If neither tungsten nor chromium is present, three to five grams of the sample are transferred to a 600 cc. beaker provided with a cover glass, 75 cc. of nitric acid (1.20 sp. gr.) are cautiously added and a gentle heat is applied until all action ceases. The solution is rapidly evaporated until a slight scum forms on the surface. The beaker and contents are cooled slightly and 75 cc. of nitric acid are added. The contents of the beaker are stirred and heat is applied until incipient boiling ensues. Five grams of sodium chlorate crystals are cautiously added in successive small portions and the boiling is continued for five minutes. When the beaker and contents are cool, the solution is filtered with the aid of suction through a plug of asbestos, previously washed with nitric acid. As some grades of asbestos are slightly soluble in acids, it should be repeatedly treated with hot hydrochloric acid and thoroughly washed with water before being used as a filtering medium. The beaker, to which small portions of manganese tenaciously adhere, and the asbestos plug are washed with nitric acid, which must be free from nitrous fumes, until the washings are colorless. After the final washing, another flask is substituted for the one containing the filtrate, and the filtering tube is filled with a five per cent solution of ammonium bisulphite. In order to prevent loss of solution due to effervescence which frequently occurs at this point, it is a good practice to place a cover glass over the filtering tube. The solution of the manganese dioxide is hastened by raising the cover glass and gently agitating the solution with a stirring rod. By successive treatments with ammonium bisulphite the manganese dioxide is completely dissolved and, after the plug has been washed with hot water until free from the manganese solution, the contents of the flask are transferred to the original beaker. Ten cubic centimeters of nitric acid are added, and the solution is boiled until free from the sulphur dioxide generated by the decomposition of the ammonium bisulphite.

The solution is cooled and ammonia is added until a slight permanent precipitate forms, when 15 cc. of ammonium acetate solution (twenty per cent) are added. The contents of the beaker are boiled for two minutes, filtered into an 800 cc. beaker and the filter and contents are washed twice with hot water. The precipitate is dissolved with hydrochloric acid (1:1), and the resultant solution is retained in the beaker in which the precipitation was effected. A second precipitation and filtration is then made as outlined. The filtrates are combined, 5 cc. of acetic acid are added, followed by 10 cc. of a solution of ammonium phosphate (ten per cent) and the solution is brought to the boiling point. Ammonia is added slowly while the solution is constantly stirred until a permanent opalescence ensues. The solution is vigorously stirred until the characteristic crystalline precipitate of ammonium manganese phosphate is well defined. The addition of ammonia is then continued drop by drop, with constant stirring, until a total of 25 cc. has been added. After the precipitate has settled, it is collected upon an 11 cm. filter paper and washed with a solution of ammonia and ammonium nitrate (ammonia 200 cc., water 760 cc., and nitric acid 40 cc.) until free from soluble salts. The filter paper and residue are ignited in a weighed porcelain crucible at a low temperature until the paper has disappeared, then at a high temperature for fifteen minutes. The increase in the weight of the crucible multiplied by the factor 38.69 and divided by the initial weight of the sample, is equivalent to per cent manganese.

The manganese pyrophosphate may be contaminated with a trace of silica and, in order to correct for this impurity, the residue in the crucible is treated with hydrochloric acid (1:2); heat is applied and, when the manganese pyrophosphate has dissolved, the insoluble silica, if any, is removed by filtration, ignited and weighed. This weight is deducted from the total weight of the residue, and the difference is calculated to per cent manganese.

If tungsten is present, the tungstic acid is removed as described under the methods for the determination of tungsten. The filtrate from the tungstic acid, designated for the determination of other elements, is concentrated, and the hydrochloric acid is removed by boiling with nitric acid until all chlorine is expelled. The solution is then evaporated to a volume of 10 to 15 cc., 75 cc. of nitric acid are added, the manganese is precipitated with sodium chlorate and the analysis is finished as above described.

If chromium is present, the sample is dissolved in 40 to 60 cc. of hydrochloric acid (1.13 sp. gr.) instead of nitric acid and the solution is evaporated to a volume of 10 to 15 cc. Seventy-five cubic centimeters of nitric acid are added and the solution is again evaporated to a volume of 10 to 15 cc. Then, after the addition of another 75 cc. of nitric acid, the manganese is precipitated by sodium chlorate and determined as phosphate in the manner described.

SODIUM BISMUTHATE METHOD.

ABSENCE OF CHROMIUM AND TUNGSTEN.

One gram of the steel contained in a 250 cc. Erlenmeyer flask is treated with 35 cc. of nitric acid (1.20 sp. gr.). Heat is applied until the steel is dissolved. The solution is then slightly cooled and, in order to oxidize the organic matter, small quantities of sodium bismuthate are successively added until the pink color of permanganic acid persists or the brown oxide of manganese is precipitated upon boiling. Hydrogen peroxide (three per cent) or ammonium bisulphite (five per cent) is now added, a few drops at a time, until the manganese dioxide is dissolved. The excess of the reducing reagent is expelled by continued boiling. Ammonium persulphate may be substituted for bismuthate for oxidizing the organic matter; in this case the excess persulphate is destroyed by boiling.

The solution is cooled rapidly to room temperature, diluted to a volume of 50 cc., an excess of sodium bismuthate, from .5 to 1 gram, is added and the mixture is thoroughly agitated. The solution is decanted through an asbestos filter, and the beaker and filter washed with 3 per cent nitric acid until the washings are colorless. The filtrate and washings are then transferred to a 250 cc. beaker. A solution of .03 normal ferrous sulphate is added in slight excess and the total volume noted. The excess is determined by a .03 normal potassium permanganate solution. The difference between the volume of permanganate solution required and the volume of permanganate equivalent to the total volume of ferrous sulphate solution added, is multiplied by the weight of manganese in 1 cc. of the standard permanganate solution. The result thus obtained multiplied by 100 gives the per cent of manganese.

SOLUTIONS REQUIRED.

Sodium Oxalate Solution (.03 Normal).

Sodium Oxalate	2.0100 grams
Water to make	1000 cc.

Potassium Permanganate Solution.

Potassium Permanganate	1 gram
Water	1000 cc.

The solution is set aside for twenty-four hours before standardizing. For this purpose 50 cc. of the sodium oxalate solution are transferred to a 400 cc. beaker containing 200 cc. water, and 20 cc. of sulphuric acid (1:1) are added. The contents of the beaker are heated to 80° C., and the standard permanganate solution is added slowly at first and then rapidly until a permanent pink tint is obtained. A normal solution of sodium oxalate contains 67 grams per liter and a .03 normal solution contains, therefore, 2.01 grams. The normality of the permanganate is found by dividing 50 by the number of cubic centimeters of permanganate equal to the 50 cc. of oxalate and multiplying the result by .03. The value of permanganate in terms of a fraction of a gram of manganese per cubic centimeter is found by multiplying the normality by .010986.

Example.

Fifty cubic centimeters of oxalate equals 49.5 cubic centimeters of permanganate. Therefore, the solution is .03 x 50.0÷49.5=.030303 Normal and one cubic centimeter equals .030303 x .010986=.0003329 grams of manganese or .0333 per cent on a one gram sample.

Ferrous Sulphate Solution.

Ferrous Ammonium Sulphate Crystals.........	12 grams
Sulphuric Acid (1.1)	100 cc.
Water....................................	900 cc.

Nitric Acid (1.20 sp. gr.).

Nitric Acid................................	380 cc.
Water....................................	620 cc.

SODIUM BISMUTHATE METHOD.

PRESENCE OF CHROMIUM OR TUNGSTEN.

One gram of the steel, contained in a 250 cc. Erlenmeyer flask with a watch glass cover, is dissolved in 30 cc. of sulphuric acid (1:4) and the solution is diluted to 100 cc. with boiling water. Sodium carbonate solution (eight per cent) is added until a permanent precipitate is formed and then 4 cc. additional are added. The solution is boiled one minute, allowed to stand until the precipitate settles and is rapidly filtered through an 18 cm. paper, the precipitate being washed four times with boiling water. The filtrate is heated to boiling and 30 cc. of nitric acid (1.20 sp. gr.) are added cautiously to oxidize the iron. The volume is reduced by boiling to 50 cc. and cooled to room temperature, after which the permanganate color is developed by bismuthate and the solution is titrated as described in the absence of chromium and tungsten.

PERSULPHATE-ARSENITE METHOD.

ABSENCE OF CHROMIUM AND TUNGSTEN.

Two-tenth gram of the sample is transferred to a 100 cc. flask or an 8″ x 1″ test tube and dissolved in 10 cc. of nitric acid (1.20 sp. gr.) with the aid of heat from a hot plate or hot water bath. Solution of the carbon may be hastened by the addition of one cubic centimeter of ammonium persulphate. When the clear solution is obtained, 15 cc. of silver nitrate solution are added followed by 10 cc. of a five per cent solution of ammonium persulphate. If a tube is used, it is kept in the bath until the color develops; if a flask is used, the solution is brought to a boil before the persulphate is added and the flask is set aside in a warm place until the color develops. When the color has developed, the solution is cooled by standing the tube or flask in running water.

The solution is transferred to a 250 cc. beaker and diluted to a volume of 75 cc. Ten cubic centimeters of sodium chloride solution are added to precipitate the silver chloride and the standard solution of sodium arsenite is added while the solution is stirred, to the disappearance of the pink tint of permanganic acid. The addition of sodium chloride is unnecessary, if the solution of permanganic acid is quite cold and the titration is conducted rapidly.

SOLUTIONS REQUIRED.

Silver Nitrate Solution.

Silver Nitrate	1.3 grams
Water	1000 cc.

Sodium Chloride Solution.

Sodium Chloride	2. grams
Water	1000 cc.

Standard Sodium Arsenite Solution.

Sodium Arsenite	.8 gram
Water	1000 cc.

The sodium arsenite solution is standardized by titration of the permanganic acid developed from the manganese in a standard steel.

Persulphate–Arsenite Method, Using .5 Gram of Sample.

One-half gram sample may be used for the determination, the method being essentially the same, except that the dilution on titration may be 100 to 125 cc. The silver nitrate should be fifteen times the manganese present. The method may be used with .5 gram of steel containing manganese up to 1.50%. However, it is preferable to add 20 cc. of the silver nitrate in that case.

Solutions Required.

Silver Nitrate Solution.

Silver Nitrate	5 grams
Water	750 cc.
Sulphuric Acid (1:1)	250 cc.

Sodium Chloride Solution.

Sodium Chloride	5 grams
Water	1000 cc.

Standard Sodium Arsenite Solution.

Sodium Arsenite	2 grams
Water	1000 cc.

The sodium arsenite solution is standardized by withdrawing 10 cc. of the .03 (approximately) normal permanganate used in the bismuthate method, into a 250 cc. beaker, adding 50 cc. of water and 10 cc. of sulphuric acid (1:1) and titrating with arsenite. In the example shown under the bismuthate method, 1 cc. =.0003329 gram manganese; therefore, 10 cc.=.003329 gram or .666% of .5 gram sample. Then 6.66 cc. of the arsenite should be used; if not, the solution is adjusted to agree. The manganese in a standard steel is then determined and the value obtained by this titration should equal the standard value.

PERSULPHATE ARSENITE METHOD.

PRESENCE OF CHROMIUM OR TUNGSTEN.

One-half gram of the steel is transferred to a flask, 25 cc. of water and 5 cc. of sulphuric acid (1:1) are added and the solution is heated until all effervescence ceases. If tungsten is present, 2 cc. phosphoric acid are added. Ten cubic centimeters of nitric acid (1.20 sp. gr.) are added and the solution is boiled to dissolve the tungsten. Fifty cubic centimeters of silver nitrate solution are added (this is sufficient for five per cent chromium). The solution is boiled, 15 cc. of ammonium persulphate solution (fifteen per cent) are added and the flask is removed from the heat but permitted to stand in a warm place until the color has developed, after which it is rapidly cooled. The solution is diluted and titrated as described in the absence of chromium and tungsten, with the exception that the sodium chloride added should be tripled.

SOLUTION REQUIRED.

Silver Nitrate Solution.

Silver Nitrate	5 grams
Water	1000 cc.

Other solutions are the same as those used in the absence of chromium and tungsten.

ZINC OXIDE SEPARATION.

PRESENCE OF CHROMIUM OR TUNGSTEN.

One gram of the sample contained in a 400 cc. beaker is treated with 35 cc. of sulphuric acid (1:6) and heat is applied until all action ceases. Three grams of ammonium persulphate are then added to oxidize the iron and the solution is boiled until the excess of persulphate is decomposed. The solution is diluted to about 100 cc., almost neutralized with ammonia and transferred to a 250 cc. graduated flask. Zinc oxide emulsion is added in slight excess, which is shown when the supernatant liquid appears milky. The solution is cooled to room temperature, diluted to the mark and thoroughly mixed. The contents of the flask are decanted through a dry filter paper and manganese is determined upon 50 to 125 cc. portions by the bismuthate method or by the persulphate-arsenite method.

DETERMINATION OF PHOSPHORUS.

VOLUMETRIC METHOD.

ABSENCE OF TUNGSTEN AND VANADIUM.

ACID—ALKALI TITRATION.

Two grams of the sample are transferred to a 300 cc. Erlenmeyer flask, 40 cc. of nitric acid (1.20 sp. gr.) are added and a gentle heat is applied until all action ceases and the black residue of chromium carbide, if present, is completely dissolved. A slight excess of a solution of potassium permanganate is added and the solution is boiled until the excess of permanganate is decomposed. A slight excess of a reducing solution is added to dissolve the precipitated manganese dioxide and the boiling is continued until the excess of the reducing solution is decomposed. The flask is removed from the heat, 50 cc. of ammonium molybdate solution are added and the flask is shaken for five minutes. The yellow precipitate of ammonium phosphomolybdate, after settling, is collected upon a 9 cm. filter paper, washed with two per cent nitric acid until free from iron solution, and, finally, with a one per cent sodium nitrate solution until free from acid. If it is desired to recover the molybdic acid, the washings are not allowed to mix with the filtrate, which is reserved in a suitable container.

The titration may be conducted in either a 250 cc. beaker or the flask in which the precipitation was made. If the former is used, care should be exercised to remove any precipitate adhering to the flask, while if the latter is used, the flask should be washed with sodium nitrate solution until the acid is completely removed. In either case all washings, of course, must be passed through the original filter.

The filter paper and precipitate are transferred to the beaker or flask and an excess of standard sodium hydroxide solution is added. If the titration is conducted in a beaker, the filter paper is macerated with a glass rod; if conducted in a flask, a clean rubber stopper is inserted and the contents shaken vigorously until the paper is disintegrated and the solution of the precipitate is complete. The solution is diluted to approximately 100 cc. with water free from carbon dioxide, three drops of phenolphthalein solution are added, followed by the standard nitric acid until the pink color disappears. The sides of the vessel are washed with cold water, and the titration is completed by adding standard alkali solution until the appearance of a permanent pink tint. Each cubic centimeter of standard alkali in excess over the standard acid used is equivalent to .01 per cent phosphorus.

Solutions Required.

Standard Sodium Hydroxide Solution.

Sodium Hydroxide	6.6 grams.
Water	1000 cc.

Standard Nitric Acid.

Nitric Acid	10 cc.
Water to make	1000 cc.

The sodium hydroxide is dissolved in a part of the water contained in a graduated bottle or flask. One cubic centimeter of a saturated solution of barium hydroxide is added per liter, and the solution is diluted to the mark and agitated thoroughly. After standing for twelve hours or more, some of the clear solution may be removed with a pipette for standardizing. The acid and alkali solutions are first adjusted so that they exactly agree and are then standardized by means of a steel of known phosphorus content. Finally, they are adjusted so that one cubic centimeter is equivalent to one-hundredth per cent phosphorus. The sodium hydroxide solution is then filtered through a dry filter into a syphon container and thereafter protected from the air as much as possible.

Phenolphthalein Solution.

Phenolphthalein	1 gram.
Alcohol (Ethyl or Methyl)	1000 cc.

Nitric Acid (1.20 sp. gr.)

Nitric Acid	380 cc.
Water	620 cc.

Potassium Permanganate Solution.

Potassium Permanganate	25 grams.
Water	1000 cc.

Reducing Solutions.

Ammonium Bisulphite. Five per cent solution.

Ferrous Sulphate Solution.

Ferrous Sulphate	50 grams.
Water	950 cc.
Sulphuric Acid (1:1)	50 cc.

Potassium Nitrite Solution.

Potassium Nitrite	50 grams.
Water	1000 cc.

Sugar Solution.

Sugar	500 grams.
Water	1000 cc.

This solution should be added cautiously, one drop at a time so as to avoid but little more of an excess than is necessary to reduce the manganese dioxide. Three or four drops should be sufficient.

Ammonium Molybdate Solution.

Molybdic Acid (eighty-five per cent)	65 grams.
Water	142 cc.
Ammonia	143 cc.
Nitric Acid (1.20 sp. gr.)	715 cc.

The molybdic acid is added to the water contained in a suitable flask. The ammonia is then added with rotation of the flask until the molybdic acid is dissolved. The solution is then cooled and added gradually, with constant agitation, to the nitric acid. To clarify the solution, one drop of a solution of ammonium phosphate (ten per cent) is added; and after agitation, the solution is allowed to stand for twelve hours; and it is then filtered, preferably by suction through an asbestos mat.

Recovery of Molybdic acid.

When a convenient quantity of the filtrates from the ammonium phospho-molybdate precipitate has been collected, it is boiled and a solution of commercial sodium phosphate is added. The weight of the sodium phosphate in this solution should be ten times the quantity of eighty-five per cent molybdic acid to be recovered or 33 grams of sodium phosphate for each 50 cc. of ammonium molybdate solution used. The solution is allowed to stand until the precipitate of phospho-molybdate has settled; it is then decanted, and the precipitate is transferred to a wide mouthed bottle of the capacity of about one gallon. These operations are repeated until a sufficient quantity of the yellow precipitate has collected, when it is washed with nitric acid solution (two per cent). It is then transferred to a dish and the supernatant liquid evaporated. When dry, this precipitate, or a mixture of this precipitate and molybdic acid may be employed for the preparation of ammonium molybdate solution. The recovered precipitate contains ninety-two per cent molybdic acid, hence when used alone sixty grams are sufficient for one liter of the solution, which is prepared as follows: Sixty grams of the recovered precipitate are dissolved in 230 cc. of water and 170 cc. of ammonia. A solution of 10 grams of magnesium nitrate or sulphate dissolved in 30 cc. of water is now added to precipitate the phosphorus. The flask is shaken and the precipitate is allowed to settle, when the solution is filtered and the precipitate is washed with 30 cc. of ammonia (1:4). The filtrate is cautiously added to 540 cc. of nitric acid (1:1) and the solution is reserved for use as needed.

GRAVIMETRIC METHODS.

ABSENCE OF TUNGSTEN AND VANADIUM.

WEIGHING AS AMMONIUM PHOSPHO-MOLYBDATE.

Two to five grams of the sample are transferred to a glazed porcelain dish which is provided with a cover glass, and 30 to 60 cc. of nitric acid (1.20 sp. gr.) are cautiously added. A gentle heat is applied until all action ceases, when the solution is rapidly evaporated to dryness. The cover glass is removed, and the contents of the dish are heated with the full flame of an Argand or Bunsen burner until the acid is completely expelled. After cooling, 30 cc. of hydrochloric acid are added, and a gentle heat is applied until the soluble portion is dissolved. The dish is placed upon a suitable asbestos ring in order to prevent the formation of a crust of separated salts on the sides of the dish, and the solution is evaporated until the first appearance of a film upon its surface. The dish is then removed from the heat, 10 cc. of nitric acid are added and the heating is continued for one minute. About 40 cc. of cold water are added and, after having been stirred, the solution is filtered through an 11 cm. filter paper into a 500 cc. flask. The filter paper is washed with cold nitric acid (two per cent) until the iron solution is completely removed.

To the filtrate, with a volume of not more than 150 cc., 25 cc. of ammonia are added, and the flask is shaken until the resultant precipitate coagulates. Twenty-five cubic centimeters of nitric acid, which should be sufficient to dissolve the precipitate and allow an excess of 7 to 10 cc., are added. The solution is heated to 80° C., 50 cc. of the molybdate solution are added and the flask is shaken for five minutes. After the yellow precipitate has settled, it is collected upon a 9 cm. filter paper, previously dried for one hour at a temperature of 115° C. and weighed between ground-edge watch glasses. The precipitate and filter are washed with nitric acid (two per cent), dried in the same manner as the paper and weighed. The increase in weight, multiplied by 1.65 and divided by the weight of the sample is equivalent to per cent phosphorus.

WEIGHING AS MAGNESIUM PYROPHOSPHATE.

The yellow precipitate of ammonium phospho-molybdate, while still moist, is dissolved from the filter paper in a hot ammonium citrate solution, the filter paper is thoroughly washed with hot water, and the solution is retained in a 100 cc. beaker. Five to ten cubic centimeters of magnesia mixture are added to the cold solution, which is then stirred for five minutes. After standing for not less than three hours, the precipitate is transferred to a 9 cm. filter paper and washed with ammonia (1:4) until free from soluble salts. The filter paper and precipitate are transferred to a porcelain crucible and ignited at a low temperature for ten to fifteen minutes and, finally, at a high temperature for ten minutes. The increase in weight of the crucible multiplied by 27.87 and divided by the weight of the sample is equivalent to per cent phosphorus.

SOLUTIONS REQUIRED.

Ammonium Citrate Solution.

Citric Acid	50 grams.
Ammonia	330 cc.
Water	650 cc.

Magnesia Mixture.

Magnesium Sulphate	84 grams.
Ammonium Chloride	250 grams.
Water	665 cc.
Ammonia	335 cc.

GRAVIMETRIC METHOD.

PRESENCE OF VANADIUM AND ABSENCE OF TUNGSTEN.

Two grams of the sample are transferred to a 300 cc. Erlenmeyer flask, 40 cc. of nitric acid (1.20 sp. gr.) are added and a gentle heat is applied until the sample is completely dissolved. A slight excess of a solution of potassium permanganate is then added, and the solution is boiled until the excess of permanganate is decomposed. A slight excess of a reducing solution is added to dissolve the manganese dioxide and the boiling is continued until the reducing agent is decomposed. The solution is then evaporated to a volume of 20 cc. and made ammoniacal. The precipitated hydroxides are dissolved with the exact amount of nitric acid necessary to effect complete solution, and then 5 cc. are added in excess. The solution is cooled to 30° C., and 5 cc. of a solution of ferrous sulphate (five per cent) are added, followed by 75 cc. of molybdate solution. The flask is then shaken continuously for at least ten minutes, and the precipitate is allowed thirty to forty-five minutes to settle. The determination may be completed volumetrically or gravimetrically, as desired.

GRAVIMETRIC METHOD.

PRESENCE OF TUNGSTEN.

Two grams of the sample are transferred to a porcelain dish provided with a cover glass and treated with 20 cc. of nitric acid and 60 cc. of hydrochloric acid. A gentle heat is applied until the sample is completely decomposed, when the contents of the dish are evaporated to dryness. The cover glass is removed and the residue in the dish is baked until the excess of acid is completely expelled. The dish is cooled, and 30 cc. of hydrochloric acid are added. Heat is applied until the soluble portion is dissolved, when the solution is evaporated to dryness on a sand bath. Thirty cubic centimeters of hydrochloric acid (1:1) are added, and the contents of the dish are boiled until dissolved. The solution is diluted to 60 cc. with water, boiled and filtered from the silica and tungstic acid, the filtrate being retained in an Erlenmeyer flask. The filter paper is washed with hydrochloric acid (1:10) until free from iron solution, and the filtrate is evaporated to a volume of approximately 20 cc. The solution is cooled and made ammoniacal, when the precipitated hydroxides are dissolved with the exact amount of nitric acid necessary to effect complete solution, and 5 cc. are added in excess. The further treatment of the solution depends upon whether vanadium is absent or present.

If vanadium is absent, the solution is treated with ammonium molybdate solution for the precipitation of phosphorus, the per cent of which may be determined either volumetrically or gravimetrically. If vanadium is present, the solution is cooled to about 30°C. or lower and is treated with ferrous sulphate and ammonium molybdate as in the presence of vanadium.

DETERMINATION OF SULPHUR.

VOLUMETRIC METHOD.

ABSENCE OF MOLYBDENUM AND TUNGSTEN.

The apparatus for the determination of sulphur by the evolution method consists of a 275 to 500 cc. flat bottomed flask, suitably bent glass tubing and an absorption vessel. The flask is closed by a two-hole rubber stopper, equipped with a long funnel or thistle tube and a glass exit tube bent at a right angle. The latter is connected, by means of pure rubber tubing, to a similar tube which extends to the bottom of the absorption vessel. The solution for the absorption of the evolved gases may be contained in either a tall 600 cc. beaker in which the subsequent titration is effected, or in a large test tube, preferably 10″ x 1″.

Five grams of the sample are transferred to the flask, the stopper is inserted and the flask is connected to the absorption vessel. Ten to twenty cubic centimeters of the absorbent solution are added to the absorption vessel and diluted to 60 or 200 cc., depending upon whether a test tube or beaker is used. Sixty cubic centimeters of hydrochloric acid (1:1) are added to the flask and heat is applied so that a continuous brisk evolution of gases results, until the sample is in solution. At this point the heat is increased until the solution is boiling and the gases in the flask are completely displaced by the resulting steam. The flask is then disconnected from the absorption vessel.

If the absorption is effected in a beaker, 10 cc. of starch solution are added and the delivery tube is removed and washed alternately with a jet of cold water and hydrochloric acid (1:1) until free from traces of the absorbent solution or adhering particles of the precipitate. If the absorption is effected in a test tube, the contents of the tube are transferred to a 600 cc. beaker containing 10 cc. of starch solution, and the tubes are washed with water. Cold water is added until the volume is about 400 cc., and the tubes are washed clean with a little hydrochloric acid (1:1) and water. A slight excess of hydrochloric acid (1:1) is added, the solution is gently stirred, and the iodate solution is immediately admitted from a burette in successive portions, each followed by stirring, until the blue color fades slowly. At this point the iodate solution is added cautiously, until the addition of a final drop yields a blue color that does not fade upon continued stirring and the addition of more hydrochloric acid (1:1). Each cubic centimeter of iodate solution added is equivalent to .01 per cent sulphur based upon an initial weight of five grams of the sample.

Solutions Required.

Starch Indicator.

1. An emulsion of six grams of starch in 100 cc. of cold water is added cautiously to a liter of boiling water contained in a suitable flask. After continued boiling for five minutes, the flask and contents are cooled and six grams of zinc chloride in 50 cc. of cold water are added to preserve the solution. After thoroughly mixing, the flask is set aside for twenty-four hours with occasional shaking. When the heavier particles have settled, the supernatant liquid is decanted into a suitable container, and three grams of potassium iodide are added.

2. To an emulsion of six grams of soluble starch in 25 cc. of water a solution of one gram of sodium hydroxide in about 10 cc. of water is added cautiously; and the solution is stirred until it gelatinizes. The mass is then transferred to a large bottle and diluted to one liter. After the addition and solution of three grams of potassium iodide, the solution is ready for use.

Standard Potassium Iodate Solution.

Potassium Iodate	1.12 grams.
Potassium Iodide	12 grams.
Potassium Hydroxide	1 gram.
Water to make	1000 cc.

The iodate, iodide and hydroxide are dissolved in 300 cc. of water and diluted to 1000 cc. The solution is standardized by means of thiosulphate solution which has been standardized against potassium permanganate solution, both solutions being approximately .03 Normal. The permanganate solution is standardized against sodium oxalate as described under the sodium bismuthate method for the determination of manganese.

A normal solution of iodate equals 16.03 grams of sulphur per liter. It is desired that one cubic centimeter of the solution should equal .01 per cent sulphur when five grams of the steel are used; therefore, the normality of the solution should be .03119. The normality of the iodate solution and the adjustment necessary are determined in the following manner: A solution of sodium thiosulphate, approximately .03 Normal, is made by dissolving 7.6 grams of the pure crystals in a liter of water and allowing it to stand for several weeks, after which it is filtered.

To 300 cc. of water in a 600 cc. beaker, 10 cc. of hydrochloric acid and 10 cc. of potassium iodide solution (ten per cent) are added. Then 25 cc. of standard potassium permanganate solution (about .03 Normal) are added and the liberated iodine is titrated with thiosulphate solution, while the solution is stirred; as the color fades, starch is added, followed by thiosulphate (slowly) until the blue is bleached. Also, 25 cc. of the standard potassium iodate solution are titrated in like manner and, from the results, the normality of the iodate is calculated. The iodate solution is then adjusted, if necessary, so that its normality is exactly .03119, or 1 cc. is equivalent to .01 per cent sulphur on five grams of sample.

EXAMPLE.

Normality of permanganate=.030303.

Number of cubic centimeters of thiosulphate equal to 25 cc. of permanganate solution=25.0.

Number cubic centimeters of thiosulphate equai to 25 cc. of iodate solution=25.8.

The normalities of the two solutions vary with the amount of thiosulphate necessary to reduce 25 cc. of each.

Therefore: 25.0 : 25.8 : : .030303 : X

$$X = .03127$$

The solution is too concentrated and must be diluted to 1.0026 liters for each liter of solution $\left(\frac{.03127}{.03119} = 1.0026\right)$

The iodate solution should be also standardized against a steel of known sulphur content.

ABSORBENT SOLUTIONS.

Ammoniacal Cadmium Chloride Solution.

Cadmium Chloride	5 grams.
Water	375 cc.
Ammonia	625 cc.

Sodium or Potassium Hydroxide Solution.

Sodium or potassium hydroxide	**5 grams.**
Water	**1000 cc.**

Ammoniacal Zinc Sulphate Solution.

Zinc Sulphate	**10 grams.**
Water	**375 cc.**
Ammonia	**625 cc.**

VOLUMETRIC METHOD.

PRESENCE OF TUNGSTEN OR MOLYBDENUM.

Five grams of the sample are transferred to a 500 cc. flask, provided with a stopper carrying a funnel tube reaching to the bottom of the flask and an exit tube which has two right angle bends in the same plane, the longer leg of which reaches to the bottom of a ten inch test tube. This test tube, containing 20 cc. of water, is closed with a two-hole rubber stopper. Through one hole the exit tube from the flask passes, while through the other hole a short right angled tube is inserted. This, the exit tube, is connected with rubber tubing to the glass tube extending to the bottom of the absorption vessel, which may be a tube or beaker.

When all connections have been made and the proper absorbent has been placed in the test tube or the beaker, 50 cc. of concentrated hydrochloric acid are added through the funnel tube and heat is applied. The effervescence should be very rapid, but care is exercised that the hydrochloric acid gas be not driven over unduly. When all the steel is dissolved, the heat is increased until the solution boils vigorously, the apparatus is disconnected, and the sulphide in the absorbent vessel is titrated until a blue color is obtained. The contents of the first tube are then poured into the beaker in which the titration is being made, and the titration is continued as in the absence of molybdenum and tungsten.

If the steel has been chilled, it is annealed as follows: Five grams of the sample are transferred to a porcelain crucible and covered with about one-quarter of an inch of powdered charcoal. A lid is placed upon the crucible and it is heated in a muffle for ten minutes at a temperature under 1000° C., then removed and allowed to cool. The contents are transferred to the flask and the determination is continued, the sulphur being evolved as just described.

GRAVIMETRIC METHOD.

Five grams of the sample are transferred to a 600 cc. beaker or an Erlenmeyer flask, 75 cc. of nitric acid are added and a gentle heat is applied. A too violent reaction, which occurs with certain grades of steel, is prevented by placing the beaker in cold water; a loss of incompletely oxidized sulphur is thus avoided.

If the steel does not dissolve readily, 10 cc. of hydrochloric acid are added in successive portions, and the contents of the beaker are heated until solution is complete.

When the steel is dissolved, the solution is evaporated to a small volume and, after cooling, 30 cc. of hydrochloric acid are added. The solution is again evaporated to a small volume, transferred to a porcelain dish and evaporated to dryness. The residue is treated with 40 cc. of hydrochloric acid and a gentle heat applied until the soluble portion dissolves. The contents of the dish are evaporated to dryness and heated for ten minutes at a temperature not to exceed 130° C. The residue is treated with 60 cc. of hydrochloric acid (1:1) and a gentle heat is applied until the soluble portion dissolves; 50 cc. of water are then added and the solution is boiled for five minutes. The silica and tungstic acid, if present, are removed by filtration, and the residue on the paper is washed with hydrochloric acid (two per cent) until the washings are free from iron solution. The filtrate is then evaporated on an asbestos pad with the cover glass removed, until a slight film begins to form upon the surface of the solution. At this point either of two methods may be followed.

1. The dish is removed from the heat and, after the addition of a few drops of hydrochloric acid (1:1), (usually six drops are sufficient), cold water is added to a volume of 100 cc. Any silica and possible trace of tungstic acid are collected upon a 9 cm. filter paper, and the solution is received in a 250 cc. beaker. The filter paper is washed with hydrochloric acid (two per cent) and cold water until the iron is completely removed, when the washing is conducted with hot water to a final volume of 200 cc. Ten cubic centimeters of a solution of barium chloride (ten per cent) are added to the cold solution and, after having stood for twenty-four hours with occasional stirring, the supernatant liquid is decanted through a double ashless 9 cm. filter paper. The precipitate of barium sulphate is transferred to the paper by means of a jet of hydrochloric acid (two per cent), washed with hydrochloric acid (two

per cent) until free from iron solution and, finally, with water until free from chlorides.

The filter and contents are transferred to a weighed platinum crucible, ignited uncovered at a low temperature until the paper disappears and, finally, at a slightly higher temperature for a few minutes. The increase in weight of the crucible, multiplied by 13.73 and divided by the weight of the sample used equals the per cent sulphur.

The barium sulphate obtained in the manner just described is sometimes in a very finely divided state and traces are often found in the filtrate and washings. This small amount can be recovered by filtration after the solution has been allowed to stand for twenty-four hours.

2. Five cubic centimeters of hydrochloric acid and 10 cc. of water are added, followed by 5 grams of finely granulated sulphur-free zinc (20 to 30 mesh). Heat is applied until the iron is reduced, more acid being added, if necessary. The solution is filtered from silica and undissolved zinc, and diluted to 100 cc. Ten cubic centimeters of a solution of barium chloride (ten per cent) are added and the solution is allowed to stand eighteen to twenty-four hours. The barium sulphate is removed by filtration, ignited and weighed. The weight of the barium sulphate is multiplied by 13.73 and the product is divided by the weight of the sample used. This result gives the per cent sulphur in the sample.

DETERMINATION OF SILICON.

SULPHURIC ACID METHOD.

ABSENCE OF TUNGSTEN.

To a porcelain dish provided with a cover, 2.3466 grams of the sample are transferred. The steel is dissolved in 30 cc. of hydrochloric acid. The solution is evaporated to low bulk and 15 cc. of sulphuric acid are cautiously added. Or the steel may be dissolved in 100 cc. of sulphuric acid (1:6). In either case the solution is evaporated until fumes of sulphur trioxide are freely evolved. The dish is then cooled, 60 cc. of water are added and the contents of the dish are heated gently until the soluble salts have dissolved. If molybdenum or vanadium is present, there will remain in the dish an insoluble black residue, which is dissolved by adding several crystals of sodium chlorate and boiling. The solution is then filtered through an 11 cm. filter paper, and the residue is washed with hydrochloric acid (1:10) and water until free from iron salts. The paper and contents are transferred to a platinum crucible, ignited and weighed. About 2 drops of sulphuric acid (1:1) and 3 cc. of hydrofluoric acid are added to the crucible, the contents are carefully evaporated to dryness and then to the expulsion of all fumes. The crucible is heated to full redness, cooled and again weighed. The difference between the two weights, or the loss by volatilization, is silica. Each milligram loss in weight represents .02 per cent silicon.

NITRIC—SULPHURIC ACID METHOD.

ABSENCE OF CHROMIUM AND TUNGSTEN.

In a porcelain dish, 2.3466 grams of the sample are dissolved in 30 cc. of nitric-sulphuric acid. The solution is evaporated until fumes of sulphuric anhydride are evolved and the dish is allowed to cool. Solution of the soluble salts is then effected by adding 50 cc. of hydrochloric acid (1:10) and heating the contents of the dish to boiling. The solution is filtered from the residue of silica, which is washed with hydrochloric acid (two per cent). The weight of the silica is then determined by volatilization and calculated to per cent silicon as in the previous method.

If the silicon content of the steel is over one per cent, it is preferable to use a smaller weight:—therefore, .9386 gram of the sample is dissolved in a mixture of 15 cc. of the nitric-sulphuric acid and 15 cc. of nitric acid (1.20 sp. gr.), when the solution is evaporated, and the silicon content determined as above.

NITRIC—SULPHURIC ACID METHOD.

PRESENCE OF CHROMIUM.

To the dish, containing 2.3466 grams of the sample of steel, are added 10 cc. of water, 15 cc. of nitric acid (1.20 sp. gr.) and 15 cc. of nitric-sulphuric acid. The solution is evaporated to dryness and the dish is cooled. Twenty cubic centimeters of hydrochloric acid (1:1) and 30 cc. of water are added and the solution is boiled until all salts are dissolved. The solution is filtered from the silica, which is determined by volatilization and calculated to per cent silicon as previously described. When the steel does not dissolve in the above mixture, due to a high chromium content, the sulphuric acid method as previously described is recommended.

SOLUTION REQUIRED.

Nitric-Sulphuric Acid.

Nitric Acid (1.20 sp. gr.)	667 cc.
Sulphuric Acid (1:1)	333 cc.

DETERMINATION OF SILICON AND TUNGSTEN.

Three grams of the sample contained in a porcelain dish are treated with 100 cc. of hydrochloric acid (2:1) and the contents of the dish are heated until all action ceases. Ten cubic centimeters of nitric acid (1.20 sp. gr.) are then cautiously added, and the solution is evaporated to dryness on a sand bath.

The residue is treated with 60 to 100 cc. of hydrochloric acid (1:1), and heat is applied until the soluble portion dissolves. An equal volume of water is added, the solution is boiled for five minutes and then filtered through an 11 cm. filter paper. The residue is washed thoroughly with hydrochloric acid (ten per cent) until free from iron. The filtrate may be reserved for the determination of other elements as designated in the descriptions to follow. The filter and contents are dried, ignited in a platinum crucible and weighed. The residue consisting of silica, tungstic acid and ferric oxide is treated with hydrofluoric acid. The contents of the crucible are evaporated to dryness and the crucible is ignited as before. The residue is weighed as impure tungstic acid. The loss in weight is silica, which, multiplied by the factor 46.93 and divided by the weight of the sample used, equals the per cent of silicon.

The impure tungstic acid in the crucible is fused with sodium carbonate. The fusion is removed from the crucible and transferred to a 250 cc. beaker containing 100 cc. of hot water, and the crucible is rinsed with hot water into the beaker. The contents of the beaker are boiled until the fusion is disintegrated and the sodium tungstate is completely dissolved. The solution is filtered through a 9 cm. paper and the residue of ferric oxide is washed with hot water until the washings are free from tungsten. The paper and residue are ignited and weighed. The difference between this weight and the weight of the impure tungstic acid represents tungstic acid. The per cent of tungsten is calculated by multiplying the weight of tungstic acid by the factor 79.31 and dividing the product by the weight of the sample used.

DETERMINATION OF TUNGSTEN.

One gram of the sample in a 400 cc. beaker is treated with 50 cc. of hydrochloric acid (1:1) and digested until all action ceases, when 100 cc. of water, containing one-half gram of sodium chlorate, or 100 cc. of bromine water containing 5 cc. nitric acid (1.20 sp. gr.), are added. The solution is boiled until the tungsten is converted to tungstic acid, which is then removed by filtration and washed with hydrochloric acid (ten per cent) until the washings are free from iron solution. The filtrate may be retained for the determination of other elements, as directed in the description of methods that follow. The paper and residue are transferred to a platinum crucible, ignited and weighed. If the sample contained a large amount of silicon, the residue of tungstic acid may contain traces of silica. In this case, the ignited residue is treated with hydrofluoric acid, the excess of which is removed by evaporation, and the residue in the crucible is again ignited and weighed. Since tungstic acid is usually contaminated with traces of iron, five grams of sodium carbonate are then added and heat is applied until the contents of the crucible are fused. The fusion is then leached with water and the insoluble ferric oxide is removed by filtration, ignited and weighed. The difference between the weight of the ferric oxide and the combined weight of the tungstic acid and ferric oxide is the tungstic acid. The percentage of tungsten is found by multiplying this weight by the factor 79.31.

DETERMINATION OF CHROMIUM.

PERSULPHATE OXIDATION METHOD.

Two grams of the sample are transferred to a 600 cc. beaker and 60 cc. of sulphuric-phosphoric acid mixture are added. Heat is applied until all action ceases. Then 10 cc. of nitric acid (1.20 sp. gr.) are added, and the solution is boiled until solution is complete and fumes of oxides of nitrogen are expelled.

A solution of silver nitrate, containing three-tenths gram of the salt for each one and one-half per cent chromium present, is added. The contents of the beaker are diluted to a volume of approximately 300 cc. with boiling water and heated to boiling, when 8 cc. of ammonium persulphate solution (fifteen per cent) are added. After the permanganate color has developed 2 cc. of hydrochloric acid (1:1) or 5 cc. of sodium chloride solution (five per cent) are added, and boiling is continued until the pink color disappears and the persulphate is decomposed, which requires about ten minutes. The solution is cooled, diluted with water to approximately 400 cc. and the chromium is determined by titration as follows: The chromium is first reduced by adding from a pipette an excess of ferrous ammonium sulphate solution. For this purpose 50 cc. are added, if the chromium content is below 1.50 per cent; 100 cc. if it is more than 1.50 per cent and less than 3.00 per cent, etc. Standard potassium permanganate solution is then added from a burette until the solution assumes a pink color, which does not fade upon continued stirring, for one minute. If vanadium is present, the pink color will fade slowly, owing to the slow reoxidation of the vanadium. When the vanadium is completely oxidized, however, the pink color will persist for at least one minute.

A blank titration is conducted on the ferrous ammonium sulphate solution under the same conditions as outlined in the actual determination. For this purpose the same volume of ferrous ammonium sulphate used in the determination is transferred to a suitable beaker and diluted with water to a volume of 400 cc. Potassium permanganate solution is 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 steel, is multiplied by the value of one cubic centimeter of permanganate solution in terms of chromium. The product thus obtained is divided by the weight of the sample used, and the quotient represents the percentage of chromium in the sample.

Blank due to green chromic salt.—When ferrous ammonium sulphate or vanadium is titrated in the presence of chromic sulphate a certain amount of permanganate is required before a pink can be seen through the green solution. Neglecting the small blank due to dilution, this amount is dependent directly upon the amount of chromium present, but varies slightly in actual practice according to the light in which the titration is conducted, being less for diffused light or by electric light than for direct sunlight. The mean of this blank for sunlight and for electric light is about .6 per cent; that is, the permanganate used in overcoming the green color is equivalent to .6 per cent of the chromium present. In the determination of chromium as described in the method above, more permanganate is used than is theoretically necessary. Therefore, a deduction equal to .6 per cent of the chromium must be made from the volume of permanganate used. As this is a back titration, the correction must be added to the difference between the blank and the permanganate. Rather than make this correction of .6 per cent to each determination, it is added to the factor. Consequently, while a normal solution of permanganate, theoretically, equals .01733 gram chromium per cubic centimeter, this correction makes this value .01744 gram per cubic centimeter.

SOLUTIONS REQUIRED.

Ferrous Ammonium Sulphate.

Ferrous Ammonium Sulphate................	16.0 grams.
Sulphuric Acid (1:1)........................	100 cc.
Water....................................	900 cc.

Sodium Oxalate. (.05 Normal.)

Sodium Oxalate............................	3.3500 grams.
Water to make............................	1000 cc.

Sulphuric-Phosphoric Acid Solution.

Sulphuric Acid (1:1)........................	320 cc.
Water....................................	600 cc.
Phosphoric Acid..........................	80 cc.

Potassium Permanganate.

A tenth normal solution may be used for chromium, but where many determinations are being made, it is most convenient to use a solution of such strength that, when two grams of the sample are analyzed, each cubic centimeter is equivalent to one-tenth per cent chromium or .002 gram. If a cubic centimeter of a normal solution is equivalent to .01744 gram chromium, the solution to be equivalent to .002 gram should be .11467 Normal. Permanganate solutions should be made several days previous to and filtered before standardization. If, in adjusting the permanganate solution, it is necessary to dilute it, the dilution is preferably made with a weak permanganate solution rather than with water, as water may start a decomposition of the permanganate with the resultant precipitation of manganese dioxide. Therefore, two solutions of permanganate should be made as follows:

Strong Solution.

Potassium Permanganate....................	5.8 grams.
Water..	1000 cc.

Weak Solution.

Potassium Permanganate....................	1.0 grams.
Water..	1000 cc.

These solutions are allowed to stand for at least two weeks, then filtered through asbestos and standardized. One hundred cubic centimeters of the .05 Normal sodium oxalate are withdrawn by pipette from the graduated flask in which it is made up and transferred to a beaker containing 300 cc. of hot water and 10 cc. of sulphuric acid (1:1). The solution is then titrated with the permanganate. The normalities of the permanganate solutions are calculated, and the solutions are mixed in the proper proportions to give the normality desired, which is .11467 Normal.

EXAMPLE.

Strong Permanganate required to oxidize 100c c. of oxalate	=27.05 cc.
Strong Permanganate for water blank	= .05 cc.
	27.00 cc.

Normality of strong permanganate equals .05 x 100 ÷ 27.0 or .18519 Normal.

Weak Permanganate required to oxidize 50 cc. of oxalate = 80.2 cc.
Weak Permanganate for water blank = .2 cc.

80.0 cc.

Normality of weak permanganate equals .05 x 50 ÷ 80 or .03125 Normal.

The amount to be added to a liter of the weak solution may now be found by dividing the difference in normality between the new solution and the weak solution by the difference in normality between the new solution and the strong solution, thus: $\frac{.11467-.03125}{.18519-.11467}=1.183$ liter of strong solution to be added to one liter of weak solution to make a .11467 Normal solution. This new solution is then titrated against .05 Normal solution of oxalate and its normality calculated as a check on these calculations. If its normality agrees with the normality of .11467, it is considered a standard solution.

PERMANGANATE OXIDATION METHOD.

One gram of the sample is transferred to a 600 cc. beaker, treated with 70 cc. of sulphuric acid (1:6), and heat is applied until all action ceases. If tungsten is present, an addition of 10 cc. of phosphoric acid is made. Ten cubic centimeters of nitric acid (1.20 sp. gr.) are added, and the solution is boiled until no residue remains. While boiling, successive small portions of potassium permanganate solution (four per cent) are added, until a precipitate of manganese dioxide is formed and remains undissolved after continued boiling. When such a permanent precipitate is obtained, the solution is further boiled for five minutes. Ten cubic centimeters of hydrochloric acid (1:1) are added. The solution is boiled until the precipitate is dissolved and the generated chlorine is expelled. The solution is then diluted to a volume of 300 cc. and cooled. The chromium is determined by titration, as described under the persulphate method.

DETERMINATION OF VANADIUM.

FERROUS SULPHATE REDUCTION METHOD.

ABSENCE OF TUNGSTEN.

The solution that was used for the determination of chromium by either of the methods given for that element may be used for this determination Unless the solution already contains phosphoric acid, 5 cc. of this acid are now added. Ten cubic centimeters of approximately .04 Normal ferrous ammonium sulphate are added to reduce the vanadium. This amount of the ferrous salt is sufficient for .80 per cent vanadium; 20 cc. are added if the vanadium content is higher. The contents of the beaker are stirred thoroughly, after which 8 cc. of ammonium persulphate solution (fifteen per cent) are added, stirring being continued for one minute. Potassium permanganate (.03922 Normal) is slowly added until a pink color that remains after one minute's stirring is obtained. Each cubic centimeter used is equivalent to .1 per cent vanadium when two grams of the sample are taken for analysis.

BLANK DUE TO GREEN CHROMIC SALT.

A blank determination should be made either on steel containing about the same chromium content as the sample being analyzed; or the blank may be determined as described below. A blank of .2 cc. is due to dilution. The chromium, which is generally present with the vanadium, obscures the pink color. The permanganate added thus in excess is equal to .6 per cent of the chromium present, as discussed under the determination of chromium and, because of the difference in the volumes of a normal solution equivalent to the same weights or per cents of chromium and vanadium, the vanadium value of the permanganate used in excess is equivalent to 1.8 per cent of the chromium present. Therefore, in all vanadium titrations, a blank must be deducted equal to .02 per cent plus 1.8 per cent of the chromium present.

Example.

Chromium=1.50%
Vanadium titration=2.8 cc.
Blank due to chromium=1.8% of 1.50=.03%
Blank due to dilution= .02

Total Blank= .05%
Vanadium=2.8 cc.=.28%—.05%=.23%

If desired, a new sample of the steel may be used. In this case, two grams of the steel are dissolved in 20 cc. of sulphuric acid (1:1), 40 cc. of water and 5 cc. of phosphoric acid. When action ceases, 10 cc. of nitric acid (1.20 sp. gr.) are added and the solution is boiled to the expulsion of the fumes of oxides of nitrogen. The solution is cooled and potassium permanganate is added until a pink color is obtained. The solution is then ready for reduction and titration as above.

Solution Required.

With the exception of potassium permanganate, the same solutions are used as in the determination of chromium by the persulphate method. A normal solution of potassium permanganate will oxidize 51 grams of vanadium per liter; therefore, one cubic centimeter of .03922 Normal solution is equivalent to one-tenth per cent vanadium on a two gram sample. This permanganate is made by adding the strong solution to the weak solution as described under the methods for the determination of chromium. Using, for an example, the same solutions that were cited as examples in the making up of the permanganate solutions for the chromium determination, the volume of the strong solution of permanganate to be added to a liter of the weak one equals $\frac{.03922-.03125}{.18519-.03922}=.0546$ liter=54.6 cc. After these solutions are mixed in the proportions indicated, the new solution is titrated against .05 Normal sodium oxalate, and its normality, which should be .03922, is calculated.

FERROUS SULPHATE REDUCTION METHOD.

PRESENCE OF TUNGSTEN.

Two grams of the steel are dissolved in 20 cc. of sulphuric acid (1:1) and 60 cc. of water. When action ceases, 10 cc. of nitric acid (1.20 sp. gr.)

and 2 cc. of hydrochloric acid (1:1) are added at the same time, and the solution boiled for ten minutes, diluted and filtered. To the filtrate 5 cc. of phosphoric acid are added followed by potassium permanganate to the appearance of a pink color. The solution is then ready for reduction by ferrous sulphate and titration with permanganate as in the absence of tungsten.

HYDROCHLORIC ACID REDUCTION METHOD.

ABSENCE OF TUNGSTEN.

Three grams of the sample are transferred to a 250 cc. beaker and treated with 60 cc. of hydrochloric acid (2:1). Heat is applied and, when the sample is dissolved, the iron is oxidized with 3 cc. of nitric acid and the solution is evaporated to a volume of approximately 25 cc. After cooling, the contents of the beaker are transferred to a separatory funnel, the beaker is washed with hydrochloric acid (1.11 sp. gr.) and the washings are also transferred to the funnel. The volume of the solution, including the washings, should not exceed 50 cc. An equal volume of ether (.72 sp. gr.) is added and the solution is shaken vigorously. The lower portion of the solution containing the vanadium is drawn off, warmed to evaporate the ether, cooled and 10 cc. of sulphuric acid (1.84 sp. gr.) are added. The solution is then evaporated until fumes of sulphuric anhydride are given off. After it has cooled, 5 cc. of potassium permanganate solution (four per cent) are added to destroy the carbonaceous matter and to oxidize any reduced iron. The solution is boiled for one minute, when 30 cc. of hydrochloric acid are added. The solution is again evaporated until dense fumes of sulphuric anhydride are evolved. The beaker and contents are cooled, diluted with water to 100 cc., and titrated at a temperature of 40° C. with standard decinormal permanganate solution to the appearance of a pink color, which persists for one half minute. After subtracting from this reading whatever blank may be necessary, each cubic centimeter of decinormal permanganate used equals .17 per cent vanadium, based on the three gram sample used.

In the presence of tungsten, the tungstic acid is separated as described under the rapid method for the determination of tungsten, the filtrate is concentrated, an ether separation is made and the determination completed as in the absence of tungsten.

SOLUTIONS REQUIRED.

Hydrochloric Acid (1.11 sp. gr.).

Hydrochloric Acid (1.19 sp. gr.)	543 cc.
Water	457 cc.

N/10 Potassium Permanganate Solution.

Potassium Permanganate	3.17 grams.
Water	1000 cc.

The permanganate solution should be allowed to stand several days, then filtered through an asbestos plug before it is standardized.

N/10 Sodium Oxalate Solution.

Sodium Oxalate	6.7000 grams.
Water to make	1000 cc.

Fifty cubic centimeters of the oxalate solution are transferred to a 600 cc. beaker, diluted with water to 350 cc., heated to 80° C., and then acidified with 10 cc. of sulphuric acid (1:1). The permanganate solution is added until a permanent pink tint is obtained and the number of cubic centimeters required is noted. The value of one cubic centimeter of permanganate solution, expressed as a fraction of a gram of vanadium, is found by multiplying .0051 by 50 and dividing the product by the number of cubic centimeters of permanganate solution required.

A blank is determined by treating a steel of same chromium content as the test, or it may be found and deducted as described under the ferrous sulphate reduction method. If desired, a more dilute permanganate solution may be used for the titration. In that case, fractional parts of the weights of sodium oxalate and potassium permanganate given are dissolved, each in 1000 cc. of water, and standardized as directed.

COLOR METHOD.

ABSENCE OF TITANIUM.

One gram of the sample contained in a 150 cc. flask is treated with 40 cc. of sulphuric acid (1:4). Heat is applied until the sample is dissolved, when 5 cc. of nitric acid (1.20 sp. gr.) are added, and the solution is boiled until brown fumes cease to be evolved. Ten cubic centimeters of ammonium persulphate solution (five per cent) are added to oxidize any organic matter and the vanadium. The solution is boiled for about three minutes, or until the excess of the persulphate is decomposed, then cooled to room temperature and treated with 5 cc. of hydrogen peroxide, when a deep brown color due to vanadium will be developed. Concurrent with this treatment of the sample one gram of a standard vanadium steel of the same approximate composition is treated in a manner identical to that of the sample and, when the brown color of the vanadium is completely developed, the solution is transferred to a comparison tube, diluted with water to a volume equal to some multiple of its vanadium value and mixed. The solution of the sample is transferred to a similar comparison tube and its color matched against that of the standard by viewing the solution in a camera, or before a white surface. The total number of cubic centimeters of the solution of the sample divided by the multiple used for the dilution of the standard is equal to the per cent vanadium.

Instead of using a standard steel, a standard solution of ammonium vanadate, one cubic centimeter of which equals .001 gram vanadium, may be used. One gram each of the test and a plain steel, to which has been added approximately the same amount of chromium as in the test, are dissolved and treated as described above, and the colors are developed. Standard solution of ammonium vanadate is then added to the blank until the colors match, comparison being made in 100 cc. Nessler tubes. The vanadium in the steel is found from the number of cubic centimeters of the ammonium vanadate used.

If tungsten is present, this method may be used after the tungstic acid is separated as described under the methods for the determination of tungsten. To the filtrate obtained in the separation of the tungsten 20 cc. of sulphuric acid (1:1) are added, and the solution is evaporated until dense fumes of sulphuric anhydride are evolved. The residue is dissolved in water, 5 cc. of nitric acid (1.20 sp. gr.) are added, the solution is boiled for a few minutes and the determination is completed.

SOLUTIONS REQUIRED.

Hydrogen Peroxide Solution.

Sodium Peroxide	7 grams.
Sulphuric Acid (1:1)	250 cc.
Water	750 cc.

The water and acid are mixed and the sodium peroxide is added to the mixture in successive small portions. After each addition, the solution is cooled to room temperature.

Ammonium Vanadate Solution.

Ammonium Vanadate	2.3 grams.
Water	1000 cc.

The solution is standardized in the following manner: Fifty cubic centimeters of the solution are diluted to about 300 cc. with water and 10 cc. of sulphuric acid are added. An excess of sulphurous acid or sodium sulphite is added and the solution is boiled until all the sulphur dioxide is expelled. The vanadium is determined by titrating the hot solution with standard potassium permanganate solution.

DETERMINATION OF NICKEL.

VOLUMETRIC METHOD.

ABSENCE OF COPPER AND COBALT.

One gram of the sample is transferred to a 400 cc. beaker and treated with 20 cc. of nitric acid (1.20 sp. gr.). Heat is then applied until the sample is dissolved, 8 to 10 cc. of a solution of ammonium persulphate (fifteen per cent) are added and boiling is continued for five minutes. The contents of the beaker are cooled, and 50 cc. of a solution of citric acid and sulphuric acid are added, followed by ammonia (1:1) until the solution is just alkaline to litmus, when an excess of 3 cc. is added. The neutralization of the solution should be made as soon as possible after the addition of the citric acid, as this acid may reduce traces of iron, which condition would interfere with the titration of the nickel. The solution is cooled to room temperature and, after the addition of 2 cc. of potassium iodide solution (ten per cent), the solution is diluted, if necessary, to a volume of about 125 cc. when it is ready for the nickel titration. From a burette 3 cc. of standard silver nitrate solution are added to the beaker, when a precipitate of silver iodide will be formed. Standard potassium cyanide solution is then slowly added with constant stirring until the precipitate is just dissolved and the solution is perfectly clear. Standard silver nitrate solution is again added until a precipitate of silver iodide forms, followed by standard potassium cyanide solution, until the solution is again clear. Alternate additions of the standard solutions are made until the cloudiness of the solution due to the addition of two drops of the standard silver nitrate is just dispelled by the final addition of two drops of the standard cyanide. Each cubic centimeter excess of standard cyanide solution over standard silver nitrate solution required for the titration, represents .1 per cent nickel.

When chromium is present in amount over one per cent, the method is varied somewhat; the steel is dissolved in 20 cc. of sulphuric acid (1:4), and the solution oxidized with 5 cc. of nitric acid, after which it is boiled five minutes and cooled. The nickel is then determined as usual except that it may be necessary to add more sulphuric-citric acid solution than 50 cc. to hold the chromium in solution.

Some trouble may be encountered by an analyst using this method for the first time due to the presence of the large amount of iron which slightly retards the end point. A little practice, however, soon enables a careful operator to ascertain when a sufficient quantity of the titrating solution has been added. A more distinct end point will be obtained if the sample is dissolved and the ether separation of the iron made as described in the hydrochloric acid reduction method for the determination of vanadium. The acid portion, after being boiled to expel the ether, is treated with 5 cc. of the sulphuric-citric acid solution, and the determination completed as described above.

If tungsten is present, in excess of one per cent, the tungstic acid should be separated as described under the methods for the determination of tungsten. The filtrate is concentrated and the determination completed as usual. Small amounts of tungsten do not interfere.

SOLUTIONS REQUIRED.

Standard Silver Nitrate Solution.

Silver Nitrate...............................	5.7903 grams.
Water to make............................	1000 cc.

Standard Potassium Cyanide Solution.

Potassium Cyanide.........................	4.5 grams.
Potassium Hydroxide.......................	1.0 gram.
Water....................................	1000 cc.

The silver nitrate solution is carefully prepared and the cyanide solution adjusted to exact agreement therewith. For this purpose, there is added to a 400 cc. beaker, containing 100 cc. of water, 3 cc. of ammonia and 2 cc. of potassium iodide solution (ten per cent), 30 cc. of silver nitrate solution from a burette, which is followed with standard potassium cyanide solution until the solution is perfectly clear. Silver nitrate solution is then added to a faint cloudiness, which can be dispelled by two drops of potassium cyanide solution. The volume of the cyanide solution required is noted, and the cyanide solution is adjusted so that the standard solutions are in exact agreement. With exactly agreeing solutions, each cubic centimeter excess of standard cyanide solution over the silver nitrate solution should correspond to .1 per cent of nickel. The value of the solutions should then be confirmed by titrating a standard nickel steel, the nickel content of which has been determined gravimetrically by the dimethylglyoxime method, which is subsequently described.

Sulphuric-Citric Acid Solution.

Citric Acid	200 grams.
Sulphuric Acid (1:1)	200 cc.
Water	800 cc.

LOW NICKEL.

ABSENCE OF COPPER.

When the nickel content is under .20 per cent the titration as outlined above is varied as follows: After the addition of potassium iodide, 10 cc. of weak potassium cyanide solution are added from an automatic pipette, and this addition is followed by weak silver nitrate solution to the appearance of a faint permanent cloudiness. If the silver nitrate required should be less than 4 cc., 10 cc. of cyanide are again added and the titration is then continued.

The silver nitrate is one-fifth the strength used in the high nickel determination. The potassium cyanide solution is made by dissolving 1.25 grams of the salt in a liter of water with one gram of potassium hydroxide. A blank is determined by titrating 10 cc. of the solution with silver nitrate. The nickel is found by subtracting the number of cubic centimeters of silver nitrate used in the analysis from the blank and multiplying the difference in cubic centimeters by .02.

LOW NICKEL.

PRESENCE OF COPPER.

One gram of the sample is dissolved in 10 cc. of nitric acid (1.20 sp. gr.) and 10 cc. of nitric-sulphuric acid mixture prepared as directed in the nitric-sulphuric acid method for the determination of silicon. The solution is evaporated until fumes of sulphur trioxide are evolved. The dish is cooled and the residue is dissolved in 5 cc. of sulphuric acid (1:1) and 30 cc. of water, when the solution is transferred to a beaker and heated while a stream of hydrogen sulphide is passed into it for ten minutes. The solution is boiled and filtered; 10 cc. of nitric acid are added and the solution is again boiled for ten minutes, when it is cooled and the nickel is determined as in the absence of copper.

DIMETHYLGLYOXIME METHOD.

ABSENCE OF COBALT AND TUNGSTEN.

One gram of the sample is transferred to a 400 cc. beaker and treated with 20 cc. of nitric acid (1.20 sp. gr.). Heat is then applied until the sample is completely dissolved. The contents of the beaker are cooled and 40 cc. of a solution of tartaric or citric acid (twenty per cent) are added.

The solution is filtered, if necessary, to remove insoluble matter and diluted to a volume of 350 cc. Ammonia is added until the solution is just alkaline, when it is heated to the boiling point, and 10 cc. of dimethylglyoxime solution are added for each hundredth of a gram of nickel present. Dimethylglyoxime is not very soluble in water and a large excess should therefore be avoided. The contents of the beaker are stirred for one minute, cooled and then set aside for thirty minutes. The bright red precipitate of nickel dimethylglyoxime quickly subsides, and the nickel can be determined by any of the optional methods subsequently described. If the nickel is low (under .20 per cent), the precipitate forms slowly, and the solution is allowed to stand over night before filtration.

DIMETHYLGLYOXIME METHOD.

PRESENCE OF COBALT AND ABSENCE OF TUNGSTEN.

In the presence of cobalt, to the solution of the steel there is added the same amount of citric acid as directed above, but an excess of 10 to 15 cc. of ammonium hydroxide, followed by 10 cc. of a solution of sodium chlorate (ten per cent) are added. The solution is boiled for five minutes, and nitric acid (1:4) is carefully added until there is only a faint odor of ammonia. Ten to twenty cubic centimeters of dimethylglyoxime solution for each hundredth of a gram of nickel and cobalt present are now added, and the solution is heated below boiling for fifteen minutes, then cooled in running water. The nickel may not be completely precipitated unless the solution is cooled. If no precipitate forms, ammonium hydroxide is added until in slight excess. The determination is then finished by any of the methods hereinafter to be described.

DIMETHYLGLYOXIME METHOD.

PRESENCE OF TUNGSTEN.

If tungsten is present in small amounts, it does not interfere; if present in large amounts, it should be removed as described under the methods for the determination of tungsten. The nickel can then be determined in the filtrate by this method.

WEIGHING THE PRECIPITATE.

The red precipitate of nickel glyoxime is collected upon a 9 cm. filter paper which has been dried for one hour at a temperature of 110° to 115° C. and weighed between ground-edge watch glasses. The filter and its contents are washed six times with hot water, then 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 is 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, 78.58 per cent of which is nickel.

BY TITRATION.

The precipitate is dissolved in nitric acid, and the solution is boiled for five minutes. The nickel is then determined by titration as described under the volumetric method. Since the solution is free from iron, the addition of the sulphuric-citric acid solution is unnecessary.

SOLUTION REQUIRED.

Dimethylglyoxime Solution.

Dimethylglyoxime	10 grams.
Alcohol (Ethyl or Methyl)	1000 cc.

DETERMINATION OF COBALT.

SULPHIDE PRECIPITATION METHOD.

ABSENCE OF COPPER.

One gram of the sample contained in a 400 cc. beaker is treated with 50 cc. of hydrochloric acid (2:1). Heat is applied until all action ceases and the contents of the beaker are diluted with an equal volume of water containing one half gram of sodium chlorate or with 100 cc. bromine water containing 5 cc. nitric acid (1.20 sp. gr.). The contents of the beaker are boiled until any metallic residue is dissolved, or the tungsten, if present, is converted to tungstic acid. The tungstic acid is removed by filtration and the filter and contents are washed with hydrochloric acid (ten per cent) until the washings are free from iron. To the filtrate in a 400 cc. beaker, 3 cc. of nitric acid (1.20 sp. gr.) are added and the solution is evaporated to a volume of approximately 40 cc. The solution is cooled and transferred to a separatory funnel with the aid of hydrochloric acid (1.11 sp. gr.), The volume of the solution should not exceed 50 cc. Forty cubic centimeters of ether (.72 sp. gr.) are added to the beaker and transferred to the funnel. The funnel is stoppered and the solution vigorously shaken. When the ethereal solution containing the iron has separated, the lower liquid is drawn off into the same beaker in which the steel was dissolved. The funnel is allowed to stand for five minutes and the small quantity of the acid solution which accumulates in the point of the funnel is added to the solution in the beaker. The beaker and contents are heated at a low temperature to expel the traces of ether. When the odor of ether can no longer be detected, 100 cc. of water containing 5 grams of citric acid are added, and the solution is neutralized with ammonia and 5 cc. are added in excess.

The solution is diluted to 200 cc. and saturated with hydrogen sulphide, which precipitates as sulphides the cobalt, the nickel, the manganese and traces of iron remaining from the ether separation. The precipitate is removed by filtration through an 11 cm. filter paper, and the filter and contents are washed three times with water containing hydrogen sulphide. The funnel should be kept covered as much as possible in order to exclude air. The paper and contents are transferred to a platinum crucible, dried and carefully roasted, finally ignited at a high temperature for twenty minutes and weighed as oxides.

The ignited residue is transferred from the crucible to a 250 cc. beaker, dissolved in 50 cc. of hydrochloric acid and diluted with water to a volume of 150 cc. An excess of 10 cc. of ammonia is added, followed by one half gram of ammonium persulphate and the solution is boiled for a few minutes. The precipitated oxides of iron and manganese are removed by filtration, washed with water, dried, ignited and weighed. The difference in weight between this weight and that of the total oxides is the weight of the cobalt and nickel oxides. To the filtrate, containing the nickel and cobalt in a 400 cc. beaker, 10 cc. of a solution of sodium chlorate (ten per cent) are added, and the solution is boiled for five minutes. Nitric acid (1:4) is carefully added until only a faint odor of ammonia can be detected. Ten to twenty cubic centimeters of dimethylglyoxime solution for each hundredth of a gram of nickel and cobalt are now added, and the solution is heated below boiling for fifteen minutes, then cooled in running water. It has been found that nickel may not be completely precipitated unless the solution is cooled. If no precipitate forms, ammonium hydroxide is added until a slight excess is present, which is necessary to precipitate the nickel. The precipitate of nickel is removed by filtration and the percentage of nickel determined by any of the previously described methods. The difference between the weight of nickel oxide ($Ni0$) and the combined weight of nickel and cobalt oxides is the weight of cobalt oxide (Co_3O_4), which multiplied by 73.43 gives the per cent of cobalt.

If copper is present, traces of this element will be precipitated by ammonium sulphide, hence the copper should be removed after the ether separation by saturating the solution with hydrogen sulphide. The filtrate is then boiled until the hydrogen sulphide is expelled, and the nickel and cobalt are determined as described above.

SOLUTION REQUIRED.

Hydrochloric Acid (1.11 sp. gr.).

Hydrochloric Acid (1.19 sp. gr.)	543 cc.
Water	457 cc.

NITROSO—β—NAPHTHOL METHOD.

Two grams of the sample are transferred to a 400 cc. beaker and treated with 50 cc. of hydrochloric acid (1:1). A gentle heat is applied until action ceases. The iron and any metallic residue is oxidized with 10 cc. of nitric acid (1.20 sp. gr.). The solution is evaporated until the salts just begin to separate. The contents of the beaker are slightly diluted in order to insure solution of all soluble salts, transferred to a graduated 500 cc. flask and cooled to room temperature. Zinc oxide emulsion is added in excess, which is shown when the supernatant liquid appears milky. The contents of the flask are diluted to the mark, mixed well, and the flask is set aside until the heavy precipitate has settled. Two hundred fifty cubic centimeters of the filtered solution (equivalent to one gram of the sample) are transferred to a 600 cc. beaker and, after the addition of 5 cc. of hydrochloric acid, diluted to a volume of 350 cc. The solution is heated to boiling, and for each hundredth of a gram of cobalt present 6 cc. of acetic acid solution of nitroso-β-naphthol are added. This solution is made by dissolving one gram of nitroso-β-naphthol in 15 cc. of glacial acetic acid.

The cobalt will be precipitated as a red compound, together with a portion of the excess of the reagent and, after stirring, the beaker is set aside until the precipitate has settled. The hot solution is filtered, the filter and contents are washed twice alternately with hydrochloric acid (1:1) and water and finally with hot water. The precipitate is transferred to a porcelain crucible, heated gently until the carbonaceous matter has disappeared and then at a high temperature for twenty minutes. The crucible is cooled, weighed, and the precentage of cobalt is found by multiplying the weight of the residue (Co_3O_4) by the factor 73.43.

VOLUMETRIC METHOD.

The filtrate obtained in the determination of tungsten is used for this determination. Fifty cubic centimeters of the sulphuric-citric acid solution are added, followed by ammonium hydroxide until 10 to 15 cc. are in excess. The solution is brought to a boil, one gram of sodium chlorate is added and boiling is continued for five minutes. The solution is cooled, diluted to 200 cc. and nitric acid (1:4) is carefully added until the solution is neutral, when 3 cc. of ammonium hydroxide are added. The solution is again cooled, if necessary. Two cubic centimeters of a solution of potassium iodide (ten per cent) are now added, followed by a few cubic centimeters of the standard silver nitrate solution. Standard potassium cyanide solution is now added until the opalescence disappears. Standard silver nitrate solution is added until a cloudiness appears and then standard potassium cyanide solution until the solution is clear. The difference is cubic centimeters between the two standard solutions used represents the sum of the cobalt and the ever-present nickel, which is determined as described under the dimethylglyoxime method for the determination of nickel and deducted as described below.

Solutions Required.

Standard Silver Nitrate Solution.

Silver Nitrate	7.2024 grams.
Water to make	1000 cc.

Standard Potassium Cyanide Solution.

Potassium Cyanide	5.6 grams.
Potassium Hydroxide	1.0 gram.
Water	1000 cc.

Sulphuric-Citric Acid Solution.

This solution is prepared as described under the volumetric method for nickel.

The silver nitrate solution is carefully prepared and the cyanide solution adjusted to exact agreement therewith. For this purpose, to a 400 cc. beaker, containing 100 cc. of water, 3 cc. of ammonia and 2 cc. of potassium iodide solution (ten per cent), there is added from a burette 30 cc. of silver nitrate solution. Standard potassium cyanide solution is then added until the solution is perfectly clear. Silver nitrate solution is then added until a faint cloudiness appears, which is dispelled by two drops of potassium cyanide solution. The volume of the cyanide solution required is noted, and the cyanide solution is adjusted so that the standard solutions are in exact agreement. With exactly agreeing solutions, each cubic centimeter excess of standard cyanide solution over the silver nitrate solution corresponds to .1 per cent of cobalt. The value of the solutions is then confirmed by titrating a standard cobalt steel, the cobalt content of which has been determined by one of the previously described gravimetric methods.

The percentage of nickel, as found by the dimethylglyoxime method, is multiplied by 8.04 and deducted from the difference in cubic centimeters between the cyanide and the silver nitrate solutions used; the difference is the cyanide equivalent to the cobalt, which divided by 10 gives the percentage of cobalt.

If desired, the cyanide and silver nitrate solutions described under the volumetric method for nickel may be used. In that case, the percentage of nickel multiplied by 10, is deducted from the difference in cubic centimeters of cyanide and silver nitrate solutions used; and this difference multiplied by .0804 gives the percentage of cobalt.

DETERMINATION OF COPPER.

THIOSULPHATE PRECIPITATION.

ABSENCE OF TUNGSTEN.

Five grams of the sample are transferred to a glazed porcelain dish, 65 cc. of the nitric-sulphuric acid mixture described under the determination of silicon are added, and the covered dish is heated until fumes of sulphuric anhydride are evolved. Ten cubic centimeters of sulphuric acid (1:1) are added, followed by 50 cc. of hot water, and a gentle heat is applied until the separated salts are dissolved. The solution is filtered and the filter is washed with hot water, the filtrate being retained in a 600 cc. beaker. The filtrate is diluted to 300 cc. and heated to boiling. Fifty to seventy cubic centimeters of a solution of sodium thiosulphate (fifty per cent) are then added, and the boiling is continued foı five minutes, or until the precipitate of copper sulphide has coagulated. The precipitate is collected upon an 11 cm. filter paper, washed with sulphuric acid (two per cent) and hot water; the copper is determined by the gravimetric or volumetric method described below.

If preferred, the sample may be dissolved with sulphuric instead of nitric-sulphuric acid mixture. In this case, 5 grams of the sample are transferred to a 600 cc. beaker, 150 cc. of sulphuric acid (1:5) are added and heat is applied until the sample is dissolved. The solution is diluted to a volume of 300 cc., and the copper is precipitated with 15 cc. of thiosulphate solution. The determination is then concluded as described above.

PRESENCE OF TUNGSTEN.

If tungsten is present, the tungstic acid is separated as described under the methods for the determination of tungsten. To the filtrate, 20 cc. of sulphuric acid (1:1) are added and the solution is evaporated to fumes of sulphuric anhydride. The residue is dissolved with 10 cc. of sulphuric acid (1:1) and 50 cc. of hot water. After the silica has been removed by filtration, the filtrate is diluted to a volume of 300 cc., and treated with thiosulphate for the precipitation of copper as in the absence of tungsten.

GRAVIMETRIC METHOD.

The filter containing the precipitate of copper sulphide is carefully ignited and weighed. Since copper oxide is somewhat hygroscopic, care should be observed that the residue in the crucible does not absorb moisture from the air.

The ignited copper oxide carries with it traces of iron. The impure oxide is dissolved in the crucible with nitric acid, the solution is transferred to a 250 cc. beaker and diluted to 100 cc. The iron is precipitated as hydroxide with ammonia, and the precipitate is collected upon a 9 cm. filter paper, washed with hot water and ignited in the crucible in which the previous ignition was made. The weight is noted and deducted from the weight of the impure copper oxide; the difference is pure copper oxide. The per cent of copper is calculated by multiplying the weight of pure copper oxide by the factor 79.89 and dividing the product by the weight of the sample used.

PRESENCE OF MOLYBDENUM.

If molybdenum is present, the impure oxides in the crucible are treated with hydrochloric acid until all soluble oxides are dissolved, when it is transferred to a beaker. Sodium hydroxide solution is then added to the crucible and the crucible warmed. The solution is transferred to the beaker and more sodium hydroxide is added until the iron and copper are precipitated. The solution is boiled and filtered from the precipitate of hydroxides of iron and copper, which are ignited and weighed. The precipitate is treated with nitric acid, and the iron precipitated by ammonium hydroxide, ignited and weighed as described.

VOLUMETRIC METHOD.

The nitric acid solution of the copper and iron oxides, molybdenum, if present, having been removed as described under the gravimetric method, is rapidly evaporated to the smallest volume possible in order to remove the greater portion of the free acid, and the solution is diluted with cold water to a volume of 150 cc. Ammonia is added from a burette until the addition of a final drop develops a permanent blue color in the solution, after which there is added by means of a pipette six drops of acetic acid. Ten cubic centimeters of a solution of potassium iodide (forty per cent) are added, then standard sodium thiosulphate solution is added until the color of the liberated iodine has almost disappeared. Ten cubic centimeters of the starch solution are now added, and the addition of the standard sodium thiosulphate solution is continued to the final disappearance of the blue color. The number of cubic centimeters of the sodium thiosulphate solution required, multiplied by its value in terms of copper and divided by the weight of the sample used, equals the per cent of copper in the sample.

The apparently large excess of potassium iodide is employed because of its relation to the 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 for the preliminary evaporation of the acid solution.

Solutions Required.

Sodium Thiosulphate Precipitating Solution.

Sodium Thiosulphate Crystals...............	500 grams.
Water (to make 1000 cc.)....................	720 cc.

Starch Solution.

See "Determination of Sulphur."

Standard Sodium Thiosulphate Solution.

Sodium Thiosulphate.........................	8 grams.
Water.......................................	1000 cc.

One cubic centimeter of the standard solution is equal to approximately .002 gram copper. The solution may be standardized by using a standard copper steel, the copper content of which has been determined by the gravimetric method. Or the solution may be standardized by titrating a nitric acid solution of approximately .05 gram of pure copper, accurately weighed.

HYDROGEN SULPHIDE PRECIPITATION.

ABSENCE OF TUNGSTEN.

Five grams of the sample are transferred to a 600 cc. beaker and treated with 125 cc. of sulphuric acid (1:4). If molybdenum is present, one half gram of ammonium persulphate is added, after all action has ceased, and the contents of the beaker are boiled. The solution is cooled, almost neutralized with ammonia, diluted to 250 cc., saturated with hydrogen sulphide and then boiled until the sulphides of copper and molybdenum coagulate. The precipitate is collected upon a filter and washed several times with cold water containing hydrogen sulphide. The determination is continued gravimetrically or volumetrically as described under the thiosulphate precipitation method.

PRESENCE OF TUNGSTEN.

If tungsten is present, the tungstic acid is separated as described under the methods for the determination of tungsten, and the filtrate is evaporated to fumes of sulphuric anhydride after the addition of 20 cc. of sulphuric acid (1:1). The contents of the dish are treated with 50 cc. of water, heated until the residue is dissolved and the solution is then treated as previously described.

THIOCYANATE PRECIPITATION METHOD.

Five grams of the sample are dissolved in 60 cc. of the nitric-sulphuric acid mixture, given under the methods for the determination of silicon, and the solution is evaporated to fumes of sulphur trioxide in a covered porcelain dish. Care must be taken that all nitric acid is expelled. The dish is removed from the heat and, when cold, 5 cc. of sulphuric acid (1:1) and 50 cc. of water are added. The solution is boiled, transferred to an 800 cc. beaker and diluted to 400 cc. with hot water. Seventy cubic centimeters of sodium sulphite solution are added while stirring, followed by 25 cc. of potassium thiocyanate solution (five per cent). The solution is boiled for five minutes and filtered through a very close 11 cm. filter paper, the precipitate and beaker being washed with cold sulphuric acid solution (two per cent). The paper and precipitate are transferred to the original beaker, and 20 cc. of hydrochloric acid (1:1) followed by standard potassium iodate solution (two cubic centimeters for each .1 per cent of copper) are added. The paper is well macerated with a glass rod and water added to a volume of 500 cc. Potassium iodide solution (ten per cent) is now added (one cubic centimeter for each cubic centimeter of iodate added), and the free iodine is titrated with standard thiosulphate solution. During this titration the thiosulphate should be added rather slowly and the solution vigorously stirred, care being taken that no part of the solution is bleached before the whole. When the yellow color of free iodine has nearly vanished, 5 cc. of starch solution are added, and the thiosulphate is added until the disappearance of the blue color. The difference between the iodate and thiosulphate used represents copper, one cubic centimeter being equal to .1 per cent.

SOLUTIONS REQUIRED.

Sodium Sulphite Solution.

Sodium Sulphite Crystals	500 grams.
Water to make	1000 cc.

Potassium Thiocyanate Solution.

Potassium Thiocyanate	50 grams.
Water	1000 cc.

Standard Potassium Iodate Solution.

Potassium Iodate	20 grams.
Potassium Hydroxide	1. gram.
Water	1000 cc.

Standard Sodium Thiosulphate Solution.

Sodium Thiosulphate Crystals	137.5 grams.
Water	1000 cc.

The copper thiocyanate is oxidized by the potassium iodate according to the following reaction:

$$4\ CuCNS + 7\ KIO_3 + 14\ HCl = 4\ CuSO_4 + 7\ ICl + 4\ HCN + 7\ KCl + 5\ H_2O.$$

Four atoms of copper being oxidized by 7 molecules of KIO_3 with the production of 7 molecules of ICl which, on dilution and addition of KI react thus: $7\ ICl + 7\ KI = 14I + 7\ KCl$.

The 14 atoms of free iodine liberated represent one-third of the oxidizing power of the iodate, which equals 42 atoms for the seven molecules of iodate. Therefore, four atoms of copper represent two-thirds of seven molecules of iodate or 28 atoms of iodine, and one atom of copper equals 7 atoms of iodine or hydrogen. Therefore, a liter of a normal solution of iodate, in this reaction, is equivalent to 9.08 grams of copper. As it is desired that one cubic centimeter should equal .005 gram copper, the solution is .5506 Normal, which requires 19.64 grams of potassium iodate and 136.7 grams of sodium thiosulphate per liter. Since the salts are not quite pure, larger amounts are dissolved and the solutions standardized by titration of the thiosulphate with potassium permanganate as described under the methods for the determination of sulphur. The solutions are diluted so that both are .5506 Normal, then one cubic centimeter equals .1 per cent copper on a five gram sample.

DETERMINATION OF MOLYBDENUM.

HYDROGEN SULPHIDE PRECIPITATION.

ABSENCE OF TUNGSTEN.

A weight of sample containing about 30 milligrams of molybdenum is transferred to an 800 cc. beaker and dissolved in a mixture of 100 cc. of water and 50 cc. of sulphuric acid (1:1). When effervescence ceases, a solution containing one gram of ammonium persulphate is added, and the solution is boiled; it is then cooled, and the sulphuric acid is nearly neutralized with ammonium hydroxide. The solution is heated nearly to boiling and hydrogen sulphide is added at a rapid rate for ten minutes. The solution is allowed to stand below the boiling temperature for several hours and filtered from the precipitate of sulphides, which are washed with a solution of sulphuric acid (two per cent) through which hydrogen sulphide has been passed.

As the filtrate may contain traces of molybdenum (.001, or less, up to .01 per cent), it is boiled to expel the excess of hydrogen sulphide and to reduce the volume to 500 cc., after which one gram of ammonium persulphate is added to oxidize the molybdenum and part of the iron. Hydrogen sulphide is passed as before, and the resultant precipitate removed by filtration and added to the main precipitate. The determination is completed by one of the following optional methods.

PRESENCE OF TUNGSTEN.

If tungsten is present, it is separated as described under the methods for the determination of tungsten, and the filtrate is evaporated to fumes of sulphur trioxide after the addition of 30 cc. of sulphuric acid (1:1). The contents of the dish are treated with 50 cc. of water and heated until the residue is dissolved. The solution is then ready for the precipitation as sulphide. The tungstic acid may contain a small amount of molybdenum. In this case, the tungstic acid is fused with sodium carbonate and dissolved in water. Two grams of tartaric acid are added, then an excess of sulphuric acid. The molybdenum is then precipitated as a sulphide with hydrogen sulphide.

WEIGHING AS MOLYBDENUM TRIOXIDE.

The paper and precipitate of sulphides are ignited at a temperature just sufficient to burn the paper. The residue is weighed as molybdenum oxide plus oxides of any contaminating metals. To the crucible, hydrochloric acid is added and heat is applied. The solution is transferred to a beaker, and the crucible is rinsed with sodium hydroxide solution, which is then transferred to the beaker. The solution is made alkaline with sodium hydroxide, boiled and filtered from the resultant precipitate. This precipitate is dissolved in hydrochloric acid, and a second precipitation by sodium hydroxide solution is made. The precipitate is collected on a paper, washed with water, ignited in the original crucible and weighed. The difference between the two weights is molybdenum oxide, 66.67 per cent of which is molybdenum.

WEIGHING AS LEAD MOLYBDATE.

The precipitate of sulphides is washed from the paper into a 400 cc. beaker. That part remaining on the paper is dissolved in 20 cc. of hot hydrochloric acid (1:1) and bromine water, the solution being received in the beaker with the precipitate. The solution is diluted to 100 cc., 20 cc. of hydrochloric acid and three grams of sodium chlorate are added, and the contents of the beaker are boiled until the molybdenum sulphide is dissolved. The solution is filtered, and the paper and residue are reserved and tested for molybdenum as follows: The paper containing the residue is transferred to a 150 cc. beaker and treated with 20 cc. of nitric acid, 5 grams of sodium chlorate and 10 cc. of sulphuric acid. The solution is heated until clear, then to fumes of sulphur trioxide, when it is allowed to cool. Thirty cubic centimeters of the sulphuric-hydrochloric acid mixture are added, and the color is developed by the addition of potassium thiocyanate and stannous chloride as described under the color method. If the color is not apparent, 10 cc. of ether are added, and the tube is shaken. The color-producing salt will be concentrated in the ether and can be compared with the color developed from a known quantity of molybdenum dissolved in 30 cc. of the sulphuric-hydrochloric acid mixture.

To the main filtrate obtained in this test, sodium hydroxide solution is added in excess and the solution is boiled and allowed to stand until the precipitate has settled, after which it is removed by filtration. If the precipitate is voluminous, it is dissolved in hot hydrochloric acid (1:1) and reprecipitated as before. If the precipitate is small, it is dissolved in 30 cc. of the sulphuric-hydrochloric acid mixture and tested for the presence of molybdenum by the color method as previously described.

To the filtrate. the volume of which should not exceed 250 cc., hydrochloric acid is added until an excess of 5 cc. is obtained. Fifty cubic centimeters of ammonium acetate (fifty per cent) are added. The solution is heated to boiling and stirred while the lead acetate precipitant solution is added. The lead acetate solution should be one-half cubic centimeter for each milligram of molybdenum present plus an excess of five cubic centimeters. The solution is boiled for ten minutes, allowed to stand until the precipitate has settled and filtered from the precipitate, which is washed with hot water. The paper and precipitate are ignited in a porcelain crucible, slowly at first and finally at a red heat and weighed as lead molybdate, 26.14 per cent of which is molybdenum.

SOLUTIONS REQUIRED.

Sodium Hydroxide Solution. (*Ten Per cent*).

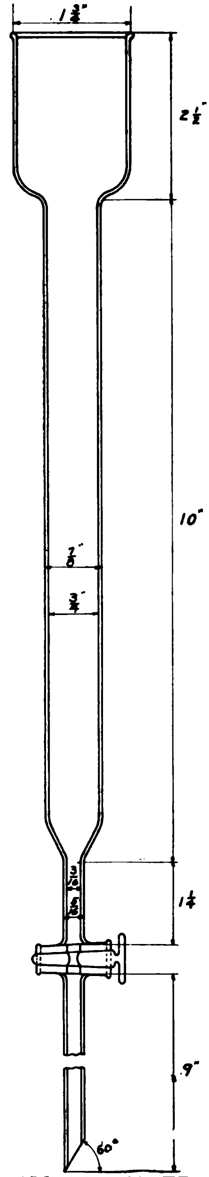
Sodium Hydroxide	100 grams.
Water	1000 cc.

Lead Acetate Solution.

Lead Acetate	10 grams.
Acetic Acid	10 cc.
Water	990 cc.

VOLUMETRIC METHOD.

The molybdenum sulphide precipitates and papers are transferred to a 250 cc. beaker. Twenty cubic centimeters of nitric acid, 5 grams of sodium chlorate and 10 cc. of sulphuric acid are added, and the liquid is boiled until fumes of sulphur trioxide are copiously evolved. After allowing it to cool, 5 cc. of nitric acid are added, and the evaporation is repeated. This evaporation with 5 cc. portions of nitric acid is repeated 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 cubic centimeters 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. Two grams of pure zinc, granulated to pass a twenty mesh sieve and containing less than .002 per cent iron are 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.



AMALGAMATED ZINC REDUCTOR FIGURE 7.

The reductor, the tube for which is shown in the accompanying cut, (Fig. 7), 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 two or three 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 twenty centimeters with amalgamated zinc in granulated form and of a fineness to pass a twenty mesh sieve. This zinc should not contain more than .002 per cent iron. Amalgamation of the zinc is effected by treating it with a solution of mercuric chloride (two per cent) for a few minutes and then washing it thoroughly by decantation with water. When not in use, the reductor should always be kept filled to above the top of the zinc with water.

The reductor, being clean and otherwise in good condition, is attached to the suction flask, and the filter pump is regulated so that twenty cubic centimeters of the solution will pass through the reductor per minute. The ferric sulphate-phosphoric acid solution is introduced into the suction flask (.2 cc. for each milligram of molybdenum present), and the solution is diluted until the end of the reductor tube dips into the ferric phosphate solution. One hundred cubic centimeters of warm sulphuric acid (two and five-tenths per cent) are introduced into the funnel which forms the top of the reductor tube, and the stopcock 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 sulphuric acid (two and five-tenths per cent) are added, followed by 50 cc. of hot 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 solution of potassium permanganate until a permanent faint pink color is obtained. Working under the conditions described, complete reduction from molybdenum trioxide to molybdenum sesquioxide is obtained, none of the molybdenum sesquioxide being reoxidized by the air after passage through the reductor. Since zinc always contains some iron, a blank determination is made on the total number of grams used for each determination which includes the zinc employed for the preliminary reduction and also that dissolved in the reductor. This is done by dissolving two grams of the zinc in 75 cc. of sulphuric acid (five per cent), filtering through 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 cubic centimeters of this solution used for the blank, multiplied by the molybdenum value of each cubic centimeter of standard permanganate and by 100, and divided by the weight of the sample taken, gives the percentage of molybdenum.

SOLUTIONS REQUIRED.

Potassium Permanganate Solution.

A normal solution is equivalent to 32 grams of molybdenum per liter or .032 gram molybdenum per cubic centimeter. The permanganate solution should be of such strength that one cubic centimeter is equivalent to not more than .1 per cent molybdenum, based upon the weight of the sample taken. Therefore, if two grams are used, the normality should not be greater than .0625; if five grams are used, the normality should not be greater than .15625. The solution is made as described under the persulphate method for chromium. The value of one cubic centimeter in terms of a fraction of a gram of molybdenum is found by multiplying the normality by .032.

Ferric Sulphate Solution.

Ferric Sulphate	100 grams.
Phosphoric Acid (1.75 sp. gr.)	150 cc.
Sulphuric Acid (1:1)	20 cc.
Water	830 cc.

COLOR METHOD.

ABSENCE OF COPPER.

One half gram of the steel is transferred to a 200 cc. casserole and dissolved in 10 cc. of nitric-sulphuric acid. The solution is evaporated until fumes of sulphur trioxide are evolved. The dish is cooled, and 30 cc. of sulphuric-hydrochloric acid are added and heat is applied until all is in solution. The solution is cooled and transferred to a comparison tube which is then placed in the bath for further cooling. From a burette 5 cc. of potassium thiocyanate (five per cent) are added and the solution is mixed; 10 cc. of stannous chloride are then added from a burette, and the solution is well mixed for ten seconds, when it is diluted with sulphuric acid (1:7) and compared with a standard treated in the same manner and at the same time as the sample. The standard is diluted to some convenient multiple of the percentage of molybdenum in the steel. (The thiocyanate and stannous chloride are added to both in equal amounts and as near the same time as possible.)

If the chromium is much over one per cent, difficulty may be encountered in obtaining complete solution after evaporation to dryness. In this case, one-half gram of the steel is transferred to a 200 cc. flask and dissolved in 15 cc. of sulphuric acid (1:1) and 30 cc. of water. When solution is complete, 15 cc. of ammonium persulphate solution (fifteen per cent) are added and the solution is boiled. Three cubic centimeters of hydrochloric acid (1:1) are added and the solution is boiled ten minutes to expel the excess of persulphate and to reduce the volume to 30 cc. It is then transferred to a comparison tube for comparison as described. If any residue remains undissolved, paper pulp is added and the residue is removed by filtration. The residue and pulp are transferred to a 150 cc. beaker, and 10 cc. of nitric acid, 5 grams of sodium chlorate and 5 cc. of sulphuric acid are added. The solution is evaporated until copious fumes of sulphur trioxide are evolved and the solution is colorless. The solution is cooled and added to the filtrate; the color is then developed on the combined solutions.

Instead of using a standard molybdenum steel for comparison, a solution containing a definite amount of molybdenum may be used. Such a one is made from standard ferro-molybdenum. The comparison is made as follows: To the standard tube is added 25 cc. of a solution of ferric sulphate containing .5 gram iron followed by one cubic centimeter of chromic sulphate solution for each per cent of chromium present. The standard molybdenum solution is then added—one cubic centimeter for each tenth per cent of molybdenum expected. The solution of the test is transferred to the other comparison tube, and the additions of thiocyanate and stannous chloride are made as directed. The amount of hydrochloric acid present must be carefully measured as more hydrochloric acid causes fading of the color.

SOLUTIONS REQUIRED.

Standard Molybdenum Solution.

One gram of standard ferro-molybdenum (over fifty per cent molybdenum) is accurately weighed and transferred to a platinum dish. Twenty cubic centimeters of nitric acid (1.20 sp gr.) and a few cubic centimeters of hydrofluoric acid are added and heat applied to dissolve the alloy; 20 cc. of sulphuric acid (1:1) are added and the solution evaporated until fumes of sulphur trioxide are evolved. The dish is removed and allowed to cool, then 50 cc. of water are added and the solution is boiled until all is dissolved. The solution is cooled, transferred to a liter flask, 100 cc. of sulphuric acid (1:1) are added and the solution is diluted to 1000 cc. This solution is then transferred to a larger flask or bottle and further diluted so that one cubic centimeter contains .0005 gram molybdenum. The total volume in liters is found by dividing the percentage of molybdenum by fifty.

Ferric Sulphate Solution.

Ferric Sulphate	70 grams.
Hydrochloric Acid (1:1)	120 cc.
Sulphuric Acid (1:1)	500 cc.
Water	380 cc.

Chromic Sulphate Solution.

Fifty grams of chromium potassium sulphate are dissolved in 100 cc. of sulphuric acid (1:1) and 200 cc. of water, and the solution is heated until the purple color changes to green. The solution is then diluted to 1000 cc. One cubic centimeter equals one per cent chromium on a half gram sample.

The standard molybdenum solution, the ferric sulphate solution and the chromic sulphate solution may be so combined that 25 cc. would contain the requisite amount of iron, chromium and molybdenum. When the chromium content is about one per cent and the molybdenum is .30 to .40 per cent, the following standard solution is useful.

Ferric Sulphate	70 grams.
Hydrochloric Acid (1:1)	120 cc.
Sulpuric Acid (1:1)	400 cc.
Water	150 cc.

Chromium Potassium Sulphate	2 grams.
Sulphuric Acid (1:1)	100 cc.

This solution is boiled until green.

Ferro-Molybdenum Solution	132 cc. (exactly).

The above solutions are mixed and diluted to exactly 1000 cc.

Sulphuric-Hydrochloric Acid.

Sulphuric Acid (1:1)	450 cc.
Hydrochloric Acid (1:1)	100 cc.
Water	450 cc.

Stannous Chloride Solution.

Stannous Chloride	250 grams.
Hydrochloric Acid	200 cc.
Water	800 cc.

The stannous chloride is dissolved in the hydrochloric acid and diluted to 1000 cc.

Nitric-Sulphuric Acid.

Nitric Acid (1.20 sp. gr.)	833 cc.
Sulphuric Acid (1:1)	167 cc.

DETERMINATION OF ALUMINUM.

ABSENCE OF TUNGSTEN.

Five grams of the sample contained in an 800 cc. beaker are treated with 50 to 60 cc. of hydrochloric acid. Heat is applied until the sample is dissolved and the solution is diluted to about 350 cc. Following the addition of two grams of sodium phosphate, ammonia (1:1) is added, a few drops at a time. until a slight turbidity appears. Three cubic centimeters of hydrochloric acid (1:1), followed by 10 grams (in solution) of sodium thiosulphate and 15 cc. of ammonium acetate (twenty per cent) are added, and the solution is heated to boiling and boiled for fifteen minutes. All the aluminum is precipitated as phosphate with small amounts of chromium, nickel, copper, iron and titanium, if these elements are present. The solution is filtered while warm and washed thoroughly with hot water. The residue is ignited in a platinum crucible and fused with two grams of sodium carbonate and two-tenths gram of sodium nitrate. The fusion is leached in water, and the insoluble residue collected on a filter paper, ignited and fused as before. This fusion is leached in water, the solution is filtered and the two filtrates, containing the aluminum and chromium are combined. The combined filtrates are acidified with hydrochloric acid and boiled to expel carbon dioxide. Ten cubic centimeters of a solution of sodium or ammonium phosphate (ten per cent) are added, the solution is heated to 60° to 70° C. and made just alkaline with ammonia, and allowed to stand at this temperature for one or two hours. The precipitate is removed by filtration, washed with hot water, ignited in a porcelain crucible and weighed as aluminum phosphate. This weight, multiplied by 22.19 and divided by the weight of the sample taken, gives the per cent aluminum. As the reagents often contain traces of aluminum, a blank determination should be made as outlined above and a correction applied to the percentage of aluminum found.

PRESENCE OF TUNGSTEN.

If tungsten is present, two grams of the sample are treated with 40 cc. of hydrochloric acid (1:1). When all action ceases, 5 cc. of nitric acid are added to oxidize the iron and tungsten and the solution is digested on a hot plate until the tungstic acid is a yellow color. The solution is filtered from the residue of impure tungstic oxide, and in the filtrate, the aluminum phosphate is precipitated as in the absence of tungsten. The residue of impure tungstic acid may contain alumina, and it is dissolved on the paper with ammonia (1:3). The residue is reserved for ignition with the impure aluminum phosphate precipitate obtained.

DETERMINATION OF TITANIUM.

THIOSULPHATE PRECIPITATION.

Five grams of the sample contained in a 400 cc. beaker are treated with 100 cc. of hydrochloric acid (1:1) and the solution in the beaker is boiled until all action ceases. One hundred cubic centimeters of water containing three grams of sodium chlorate are added in order to oxidize or dissolve any separated metallic residue, and the contents of the beaker are boiled until the tungsten (if present) is converted to yellow tungstic acid. The solution is diluted to a volume of 200 cc. and boiled for five minutes. The tungstic acid is separated by filtration and washed with hydrochloric acid (ten per cent) until the washings are colorless. The filtrate is retained in a 600 cc. beaker.

The tungstic acid may hold traces of titanium, which are recovered by treating the residue with ammonia (1:3). The tungstic acid is thus dissolved while the titanium will remain insoluble, and is separated by filtration. This residue is reserved to be added to the main precipitate of titanium obtained as follows:

To the main filtrate, diluted to 300 cc., a slight excess of ammonium hydroxide is added followed by 3 cc. of hydrochloric acid. Fifty cubic centimeters of a solution containing 25 grams of sodium thiosulphate are added and the solution is boiled for ten minutes, whereby the titanic acid is precipitated with probable traces of aluminum, chromium, iron and vanadium. The precipitate is removed by filtration and washed three times with hot water. This precipitate is combined with the one reserved as above described and ignited in a platinum crucible. The combined precipitates are fused with three grams of sodium carbonate and a few particles of sodium nitrate, which is added to oxidize the chromium. The fusion is leached with water and the insoluble residue of ferric oxide and sodium titanate is removed by filtration. The determination is continued gravimetrically or by the color method.

If tungsten, molybdenum and vanadium are absent, the oxidation with sodium chlorate is unnecessary and the method can therefore be considerably shortened by omitting this procedure, as well as the first filtration. In this case, the iron will not be oxidized and, consequently, 10 grams of sodium thiosulphate are sufficient, after the addition of which, the determination is completed as described.

GRAVIMETRIC METHOD.

The residue on the filter paper is dissolved in hot hydrochloric acid (1:1); the titanium is reprecipitated by sodium thiosulphate as above described, removed by filtration, and ignited and weighed in a platinum crucible. The increase in weight, multiplied by 60.05 and divided by the weight of the sample taken, is the per cent titanium.

COLOR METHOD.

The residue of sodium titanate obtained above is dissolved by placing the paper and precipitate in a beaker containing 50 cc. of warm sulphuric acid (1:4). After the paper is removed by filtration the solution is ready for comparison. It is placed in a comparison tube and 5 cc. of hydrogen peroxide are added. To a similar tube of the same volume containing 50 cc. of sulphuric acid (1:4) and 5 cc. of hydrogen peroxide, the standard titanium sulphate solution is added until the color matches. The number of cubic centimeters of the standard titanium solution used indicates the titanium present.

SOLUTIONS REQUIRED.

Hydrogen Peroxide Solution.

Sodium Peroxide	7 grams.
Sulphuric Acid (1:1)	250 cc.
Water	750 cc.

The sodium peroxide is added to the mixture of water and sulphuric acid in successive small portions. After each addition, the solution is cooled to room temperature.

Standard Titanium Sulphate Solution.

Twenty-six hundredths of a gram of ignited titanic acid is fused with six grams of sodium carbonate; the fusion is disintegrated in 50 cc. of water, contained in a 250 cc. beaker, and the crucible and lid are placed therein. One hundred cubic centimeters of sulphuric acid (1:4) are added and heat is applied until all is dissolved. This solution is transferred to a 250 cc. volumetric flask and diluted to the mark with water. The purity of the titanic acid may be found, and the solution thus standardized by precipitating the titanium in 50 cc. of the solution with sodium thiosulphate as described under the gravimetric method. One cubic centimeter of this solution should equal approximately .6 milligram of titanium.

DETERMINATION OF URANIUM.

Three grams of the steel are dissolved in 40 cc. of hydrochloric acid (1.13 sp. gr.) in a 400 cc. beaker. When solution is complete, 10 cc. of nitric acid are added, and the solution is evaporated to dryness on the sand bath. The residue is dissolved in 20 cc. of hydrochloric acid (1:1) and the solution is diluted with 40 cc. of water and boiled for five minutes. The silica and any tungstic acid present are removed by filtration and washed with hydrochloric acid (ten per cent). The solution is boiled until the volume is about 20 cc. and cooled. An ether separation is made, some iron being left with the aqueous portion or added after the separation, so that there is about five times more iron than vanadium present. The solution is concentrated to 10 cc. and 30 cc. of nitric acid are added. The solution is again concentrated to 10 cc. and another 30 cc. of nitric acid are added and the volume again reduced by boiling to 10 cc. Forty cubic centimeters of nitric acid are added, followed by 5 grams of sodium chlorate. The solution is boiled until a volume of 20 cc. is obtained. The chromium will be oxidized and the manganese precipitated as the dioxide, which is collected on an asbestos plug.

The filtrate is diluted to 200 cc., and the uranium, iron and vanadium are precipitated by the addition of ammonium hydroxide free from carbonate. The precipitate is removed from the solution, which contains the chromium, by filtration. If necessary, the precipitate is dissolved with nitric acid (1.20 sp. gr.) and the resultant solution boiled down with nitric acid and chlorate to oxidize the chromium, and a second separation is made as before.

The precipitate is dissolved in nitric acid (1.20 sp. gr.), the solution is neutralized with ammonium hydroxide and then an excess of 20 cc. is added. The solution is brought to a boil, removed from the heat, and two grams of sodium carbonate are carefully added while the solution is stirred briskly. The solution is boiled for one minute and two grams more of sodium carbonate are added. The solution is well stirred and boiled for one-half minute. The precipitate, composed of oxides of iron and vanadium, is allowed to settle and is removed by filtration. The precipitate is dissolved and reprecipitated to remove traces of uranium. The two filtrates are combined, acidified with hydrochloric acid and boiled to expel the carbon dioxide. Ammonium hydroxide, free from carbonate, is then added in slight excess and the solution