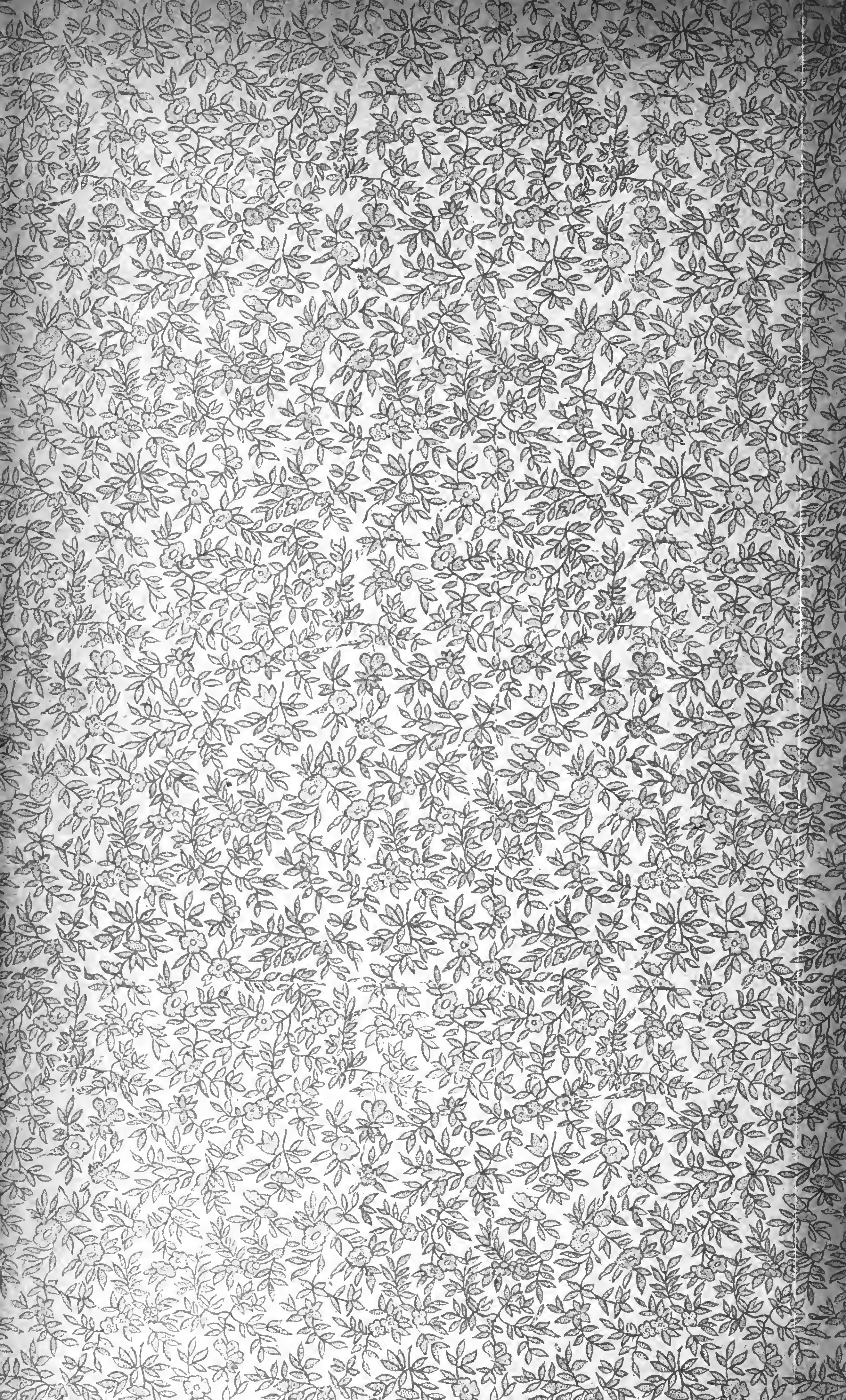

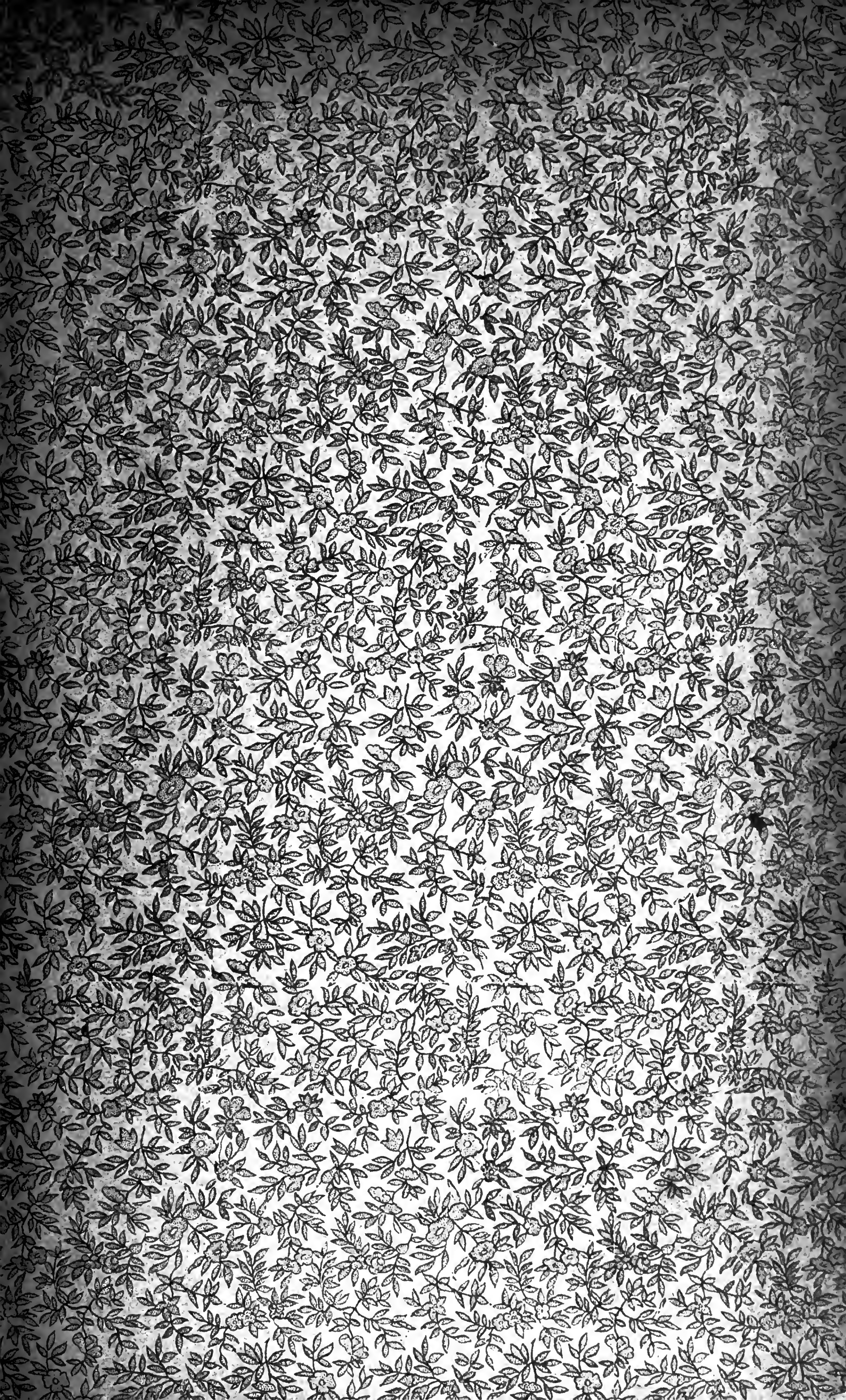

METHODS FOR THE ANALYSIS

—OF—

Ores, Pig Iron and Steel

IN USE AT THE

Laboratories of Iron and Steel Works

—IN THE—

REGION ABOUT PITTSBURG, PA.

TOGETHER WITH AN APPENDIX CONTAINING VARIOUS
SPECIAL METHODS OF ANALYSIS OF ORES
AND FURNACE PRODUCTS.

CONTRIBUTED BY THE
CHEMISTS IN CHARGE, AND EDITED BY A COMMITTEE OF
THE CHEMICAL SECTION, ENGINEERS' SOCIETY
OF WESTERN PENNSYLVANIA.

EASTON, PA.
CHEMICAL PUBLISHING CO.
1898.

PREFACE.

These methods in use in the iron and steel laboratories of the region near Pittsburg, Pa., were collected and published by the Engineers Society of Western Pennsylvania during 1896. The supply of copies having been exhausted, in response to a continuous demand the publication in more convenient form has been undertaken by the Chemical Publishing Company who have been authorized to do so by resolution of the Society at a meeting held March 13, 1897.

These methods were detailed by those using them in response to the following circular sent out by the committee in charge:

CHEMICAL SECTION.
ENGINEERS' SOCIETY OF WESTERN PENNSYLVANIA,
PITTSBURG, PA.

In accordance with a resolution of the Chemical Section of the Engineers Society of Western Pennsylvania, the undersigned wish to ask your cooperation in an effort to collect, for publication in the Proceedings of the Society, the method of analysis in use in the various iron and steel works laboratories of the region.

In calling the attention of chemists to the plan and asking their aid in its fulfilment, it should be mentioned that it is the aim of the Section to secure accurate statements of analytical processes, describing with minuteness and clearness the successive steps, in order that the proposed compilation may represent as correctly as possible the present status of analytical chemistry as applied to iron and steel.

A full presentation of the methods in general use is likely to prove of interest and value, but the completeness and promptness of the responses received from a large number of chemists must determine the success of the measure.

In case you are willing to cooperate, you are requested to send to any one of the undersigned a full description of the methods you use for the determination of the following substances:

In Ores—Silica, iron, phosphorus, manganese.

In Pig Iron—Silicon, sulphur, phosphorus, manganese.

In Steel—Carbon (by combustion), sulphur, phosphorus, manganese, nickel.

SUGGESTIONS:

1. If the method is described in a text-book or journal, a mere reference

will suffice, but any deviations from the published methods should be noted.

2. In writing a description of a method it is very desirable that minute details should be given (*e. g.*, weights taken, volume of solution, temperatures, etc., etc.).

3. If more than one method is used, please describe the one in everyday use on which the commercial transactions of the firm are based.

4. It is earnestly requested that a reply be sent at the earliest possible date.

Each method will be published over the name of the sender. The work of the committee will be confined to collecting and arranging for publication without comment or discussion.

F. C. PHILLIPS,
Western University, Allegheny, Pa.
A. G. MCKENNA,
Duquesne Steel Works, Duquesne, Pa.
E. S. JOHNSON,
Park Bros. & Co., Pittsburg, Pa.
Committee.

The methods which have been received in response to this circular may be considered to represent the general practice of the chief iron and steel works in the region of Pittsburg and Western Pennsylvania.

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APPENDIX.

I. METHODS USED AT THE LABORATORY OF THE CARNEGIE STEEL CO., HOMESTEAD, PA.

By John S. Unger.

DETERMINATION OF SILICA IN ORES OF IRON AND MANGANESE.

To 1 gram of the ground ore in an 8-oz. beaker add 35 cc. of hydrochloric acid (sp. gr. 1.20), cover with a watch-glass, and boil gently on a hot plate for twenty minutes. Remove and rinse watch-glass and sides of beaker with 15 cc. of water, filter off insoluble matter on an 11-cm. filter, catching filtrate in an 8-oz. beaker, and wash with water until soluble matter is removed. The filtrate, which should not exceed 90 cc., is placed on a sand-bath and allowed to go to dryness. The filter is ignited and the residue fused with 8 grams of sodium carbonate. The fusion is run up around the sides of the crucible and then the crucible is cooled by dipping cautiously in an 8-oz. beaker containing 35 cc. water, finally turning the crucible on its side and leaving it. Cover beaker with a watch-glass and add hydrochloric acid gradually until effervescence ceases. After the fusion dissolves out of the crucible, remove with a glass rod and wash the crucible with water. The solution should not exceed 90 cc. Evaporate on a sand-bath to dryness. When both solutions are evaporated, moisten the residues with 10 cc. hydrochloric acid (sp. gr. 1.20) and leave on the bath for a few minutes; then add 20 cc. hot water, and filter through an 11-cm. filter, the first into a 16-oz. Erlenmeyer flask, washing out the beaker carefully, then filter the second through the same filter. If the alkaline salts have not all dissolved in the second add 20 cc. hot water and stir until dissolved; filter, and rinse the beaker with hot water until filter is perfectly free from soluble salts. Ignite the filter in a muffle, cool, and weigh as pure silica. The filtrate, which is preserved for further use, should not exceed 150 cc.

DETERMINATION OF IRON IN IRON ORES.

To the filtrate from silica (given under silica) add 12 grams of Baker and Adamson's shot zinc and 10 cc. concentrated hydrochloric acid, and place in the neck of the flask a small funnel. Let the flask stand for about twenty or thirty minutes or until the iron is all reduced. Should the action on the zinc become feeble, add 10 cc. concentrated hydrochloric acid. When the iron is reduced test a drop of the solution with a drop of potassium thiocyanate on a white porcelain plate. If it shows no color or just a very faint pink, it is ready for titration. Have ready a 16-oz. wide beaker, a platinum triangle large enough to extend over the edges of the beaker, and a Gooch crucible with a tuft of glass wool $\frac{1}{4}$ inch thick at the bottom. Rinse the funnel into the flask with a wash-bottle and pour the solution through the Gooch crucible, receiving the solution in the beaker. Rinse the flask three times with about 10 or 15 cc. of water and wash the Gooch crucible once. To the filtrate in the beaker add 5 cc. concentrated hydrochloric acid and place on a hot plate for two minutes. The solution will now occupy 225 cc. Remove from the heat and titrate with standard bichromate solution, using 3 drops for each test toward the end, and adding the bichromate solution, 5 drops at a time, when almost done. Agitate each test drop by blowing gently, and continue the addition of the bichromate until the last test shows an absence of blue precipitate after agitating and standing thirty seconds. The bichromate used, multiplied by the factor, gives the metallic iron.

The potassium thiocyanate solution is made by dissolving 10 grams of the salt in 100 cc. water and is kept in a small bottle provided with a glass cap and a short piece of $\frac{1}{8}$-inch glass tubing to be used as a pipette in taking out the test drops. The potassium ferricyanide solution is made by dissolving 1 gram of the salt in 100 cc. water and test drops are removed as with thiocyanate. The solution must be made up each day. One drop is used for a test.

The potassium bichromate is made by dissolving 52 grams in 12 liters of water, then shaking well and keeping the stock bottle protected from light.

The porcelain plate is 6 by 6 inches with 12 depressions 1 inch wide by $\frac{1}{4}$ inch deep on its surface.

The bichromate solution is standardized by dissolving 3 portions of about 0.3 gram, 0.5 gram, and 0.7 gram, respectively, of perfectly clean, soft, iron wire of 99.80 per cent. pure iron in a 16-oz. Erlenmeyer flask (having a small funnel in the neck), in 40 cc. dilute hydrochloric acid, by the aid of gentle heat. When dissolved, rinse the funnel and sides of flask and make the solution up to 150 cc. Add 12 grams of zinc and when the iron is reduced, titrate exactly as in case of iron in ore. The weight of the wire taken, multiplied by 0.998 and divided by the number of cubic centimeters of bichromate solution used, gives the factor and these factors should agree to the third decimal place.

For iron in manganese ores, the basic acetate precipitate of iron spoken of under manganese is dissolved in 40 cc. dilute hydrochloric acid, the solution made up to 150 cc. and treated exactly as in the case of the determination of iron in iron ores.

DETERMINATION OF PHOSPHORUS IN STEEL, PIG IRON, AND ORES.

Dissolve 1.63 grams of steel in a 6-oz. Erlenmeyer flask in 30 cc. nitric acid (sp. gr. 1.20). Place the flask over a burner and evaporate over a naked flame to 15 cc., add to the boiling solution 20 cc. chromic acid solution, and again evaporate to 18 cc., remove from fire and wash down the sides of the flask with from 5 to 7 cc. water and cool to 40° or 45° C. Add 60 cc. molybdate solution, previously filtered and heated to 40° or 45° C., insert a stopper in the flask, and shake for five minutes. Leave stand in a warm place for fifteen minutes, then filter through a 7-cm. (Baker and Adamson, A grade) filter, previously dried and weighed at 110° C., and wash with a 2 per cent. nitric acid solution until free from iron, then twice with 95 per cent. alcohol. Dry twenty minutes at 110° C. and weigh. Each milligram corresponds to 0.001 per cent. phosphorus.

In case of pig iron dissolve 1.63 grams, in a 4½-inch evaporating dish, in 40 cc. nitric acid (sp. gr. 1.20), and evaporate to dryness on a sand-bath. Then place on a burner and heat over the naked flame until the mass ceases to evolve red fumes, allow dish to cool and add 25 cc. hydrochloric acid (sp. gr. 1.20). Cover with a watch-glass, and evaporate to 10 cc. Add cautiously 25 cc. nitric acid (sp. gr. 1.42) and evaporate to 12 cc., remove from burner, rinse the watch-glass and sides of dish with 12 cc. water, filter through an 11-cm. filter into a 6-oz. flask, and wash with water. The solution should not exceed 50 cc. Heat to 40° C., add 60 cc. molybdate solution previously filtered and heated to 40° or 45° C., shake, and finish as for steel.

In case of manganese ores dissolve 1.63 grams in 40 cc. hydrochloric acid (sp. gr. 1.20) in a 4½-inch evaporating dish, by gentle boiling, then evaporate to dryness on a sand-bath, add 25 cc. nitric acid (sp. gr. 1.42), and evaporate to 12 cc., dilute with 12 cc. water, and filter through an 11-cm. filter into a 6-oz. flask. The solution should not exceed 50 cc. Heat to 40° or 45° C., precipitate, and finish as in the case of steel.

In case of iron ores, if no phosphorus exists in the insoluble residue and the ore is easily decomposed, proceed exactly as for manganese ore. Should phosphorus exist in the insoluble residue, dissolve 1.63 grams in 40 cc. hydrochloric acid (sp. gr. 1.20) in an 8-oz. beaker by gentle boiling for twenty minutes, dilute with 20 cc. water, and filter into an 8-oz. beaker, washing with water; set filtrate on a sand-bath and evaporate to dryness. Ignite residue and then fuse with 8 grams of sodium carbonate and dissolve fusion as for iron in ore, evaporate the solution to dryness on a sand-bath, add to each beaker 25 cc. nitric acid (sp. gr. 1.42), and evaporate carefully to 12 cc.; dilute with 12 cc. water and filter both through an 11-cm. filter into an 8-oz. flask, using the same filter for both solutions. Wash with water, heat to 40° or 45° C., and proceed as for steel.

The chromic acid solution is made by dissolving 30 grams of pure chromic acid in two liters of nitric acid (sp. gr. 1.42) at a gentle heat. It must be made up fresh at least every two weeks.

The molybdic acid solution is made by mixing 100 grams molybdic acid to a paste with 265 cc. water, then adding 155 cc. ammonia (sp. gr. 0.90) and stirring until all is dissolved. To this solution add 66 cc. nitric acid (sp. gr. 1.42), stir and set aside for an hour. In another vessel make a mixture of 395 cc. nitric acid (sp. gr. 1.42) and 1,100 cc. water. Then pour the first solution into the second in a small stream, stirring constantly. Let stand for twenty-four hours when it is ready for use.

The filter-papers for weighing the yellow precipitate are Baker and Adamson's 7-cm. A grade. These retain the precipitate without its showing a tendency to pass through, and do not contain an appreciable amount of soluble matter, which might be extracted by the acid solution.

The stand for the evaporation over the burners is made of 1-inch angle iron bent and fitted with ¼-inch asbestos mill board, having a 2¼-inch hole over each burner; this supports the flask easily and prevents the solution from baking on the sides.

The drying bath is a copper drum with a coil of 1-inch steam pipe at bottom and fitted with a movable disk, near the top, having ½-inch holes, through which the stem of the funnel is inserted, the whole being covered by a lid. Steam is supplied at boiler-pressure and a temperature of 110° C. with very little fluctuation is constantly maintained.

DETERMINATION OF MANGANESE IN MANGANESE ORES.

To the filtrate from silica previously spoken of, add ammonia. When almost neutral, add it drop by drop until the solution assumes a reddish brown color. When the last drop produces a reddish brown precipitate, which does not dissolve on shaking, add 10 to 15 cc. of ammonium acetate and bring to a boil. Boil one minute. Then remove and let the precipitate settle; filter through a 12½-cm. filter, catching the filtrate in a 16-oz. beaker, and wash out the flask once with hot water. When the filter has run dry, place a funnel in the flask, and dissolve precipitate in 15 cc. dilute hydrochloric acid (1 : 1), wash iron out of paper, and repeat the precipitation with ammonia and ammonium acetate, combining the filtrates. Wash the precipitate three times with hot water and reserve for the estimation of iron. To the filtrate add three drops of solution of phenol-phthalein, then ammonia until pink, then 3 cc. in excess. Pass a current of hydrogen sulphide through the solution for ten minutes, rinse delivery-tube and set beaker on sand- or steam-bath for thirty minutes, filter through a double-pointed 7- and 11-cm. filter, and wash with dilute ammonium sulphide water. When washed place a clean 12-oz. beaker under funnel and pour over precipitate 40 cc. of a mixture of 20 cc. hot water and 20 cc. of 50 per cent. acetic acid, keeping the funnel covered with a watch-glass.

If the manganese sulphide does not all dissolve pour the solution through the filter again, wash filter four times with hot water, and place beaker on a hot plate. Boil for fifteen minutes, dilute to 150 cc; add 15 cc. ammonium phosphate, and if a precipitate forms, add a few cc. of hydrochloric acid until dissolved, bring to a boil, and then precipitate by adding ammonia, drop by drop, until the solution smells of ammonia. While precipitating, stir constantly to bring the precipitate down in a granular form, filter through a 12½-cm. filter, using suction, ignite in a muffle, and weigh as manganese pyrophosphate.

The ammonium acetate solution is made by dissolving 120 grams in 2,000 cc. water, then filtering.

The ammonium phosphate is a saturated solution of the salt in cold water, diluted with an equal bulk of water.

DETERMINATION OF SILICON IN PIG IRON.

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Weigh into a 4½-inch evaporating dish 0.9333 gram of sample, cover with a watch-glass, then add 50 cc. of a mixture of 10 cc. sulphuric acid (sp. gr. 1.83) and 40 cc. water. Place over a Bunsen burner, supporting the dish on a piece of ¼-inch asbestos board, having a 2¼-inch hole in the center, and evaporate until dense, white fumes escape, and the drop of water which condenses on the watch-glass falls back into the dish with a hissing sound. Remove the dish from the fire and let cool for two or three minutes. Then cautiously add 50 cc. of a mixture of 10 cc. hydrochloric acid (sp. gr. 1.20) and 40 cc. water, place over burner, and bring to a boil. Boil gently for one minute, remove from the fire, rinse the watch-glass, and filter the solution through an 11-cm. filter. Wash once with water, then with dilute hydrochloric acid (1 : 1) and finally with water until free from iron.

Ignite the precipitate in the muffle, cool, and weigh. To the residue in the crucible add from 4 to 10 drops pure hydrofluoric acid, depending on the amount of silica present. Drive off excess of acid by heating gently on a hot iron plate, then ignite for two or three minutes in a muffle, cool, and weigh.

The difference in weight is divided by 2, and a decimal point inserted two places from the right hand gives the percentage of silicon in the sample.

DETERMINATION OF SULPHUR IN PIG IRON AND STEEL.

Weigh 5 grams of the sample into a 16-oz. side-necked flask, fitted with a rubber stopper and thistle-tube. An 8-oz. beaker of the tall, narrow shape, containing 15 cc. of cadmium solution and filled to within one inch from the top with water, is placed under the delivery-tube. Then 90 cc. of a mixture of 40 cc. hydrochloric acid (sp. gr. 1.20) and 50 cc. water, are poured into the thistle-tube and the apparatus is placed on a stand made of ¼-inch asbestos mill board, having a 2¼-inch hole at one side and heated by a Bunsen burner. The heating is so regulated that the evolved gases are delivered at about 3 bubbles per second. As the action grows feeble, the heat is increased, until finally when all is dissolved, the solution is brought to a boil and kept boiling for one minute. The delivery-tube is then raised out of the beaker and the flask set aside.

The contents of the beaker are then poured into a 12-oz. wide beaker, the precipitate is washed out of the beaker with a wash-bottle, and 5 cc. of starch paste are added. 35 cc. of a mixture of 40 cc. hydrochloric acid (sp. gr. 1.20) and 50 cc. water are then poured into the absorption beaker and rinsed into the solution in the large beaker. The sulphur is then immediately titrated with standard iodine solution.

The iodine solution is made by dissolving 8 grams iodine and 30 grams potassium iodide in 200 cc. cold water and then diluting to about 1,850 cc. A standard steel is then tested by the method and the result noted, and from this the amount of water needed to dilute the iodine so as to bring it to the required strength, is calculated. After diluting, two determinations are made on the standard steel to see that the iodine solution is exactly right. The iodine solution is made of such strength that 1 cc. = 0.01 per cent. of sulphur in the sample. Two liters of standard iodine are made up at once and the solution is preserved in a dark cupboard. The amount actually in use is kept in a special burette having a blackened receiver to exclude light. The stock solution is standardized every week.

The cadmium solution is made by dissolving 300 grams cadmium chloride in 1 liter hot water in a large bottle and then adding 1.5 liters ammonia (sp. gr. 0.90), filtering through a fluted filter into a 12-liter bottle. 6.5 liters ammonia (sp. gr. 0.90) are then added to the solution and 3 liters of water. The whole is well shaken when it is ready for use.

The starch paste is made by heating 1 liter of water to boiling-point in a 1,200-cc. flask and adding gradually 10 grams of starch made into a cream with 50 cc. cold water. Keep the solution boiling constantly. When all the starch is added boil five minutes, then set aside to cool, decant the liquid, throwing the last 50 cc. away.

The solution is made up every three days.

DETERMINATION OF CARBON IN STEEL.

5 grams of the sample are weighed into a clean 8-oz. flask and 200 cc. of copper potassium chloride added; the flask is closed with a rubber stopper and shaken until the precipitated copper is completely redissolved, which is easily detected by the absence of copper-covered particles at the bottom of the flask. Remove and rinse the stopper, then filter through a perforated platinum boat, having a layer of asbestos $\frac{1}{8}$ inch thick at bottom and held in a platinum holder. Wash the residue twice with concentrated hydrochloric acid, then with water until all the soluble matter has been removed. Dry the boat for two hours at 90° C. when it is ready for burning. Introduce into the combustion-tube, pushing it against the roll of silver foil, and start a current of oxygen from the cylinder through the apparatus at 2 to 3 bubbles per second. In the meantime weigh the potash bulb and the small calcium-chloride tube filled with solid potassium hydroxide. Attach the bulb and tube to the apparatus and light first two burners and leave burning for five minutes to heat platinum gauze in a combustion-tube to redness, then light the next burner and leave burning two minutes, following this by the others in exactly the same way. When all are lighted leave burning five minutes. Then shut off the oxygen and start the air current, being careful to make the change without allowing any back-pressure from the air in the room. Aspirate air for forty minutes, using 1 liter, and weigh.

The copper potassium chloride solution is made by saturating 2 liters of cold water with the salt, adding to the solution 100 cc.

of hydrochloric acid (sp. gr. 1.20), then 1 gram of a high carbon steel, shaking until dissolved, then filtering the whole solution into a 2-liter bottle, through an asbestos filter.

The asbestos is prepared by rubbing the ignited fiber through a 20-mesh sieve by a gentle stream of water, receiving the water and pulp in a large vessel, allowing the pulp to settle and drawing the water off by a siphon. Cover the pulp with strong, hot hydrochloric acid and digest over night; draw off the acid with a siphon and wash with water by decantation until free from acid, pour into a bottle with water sufficient to cover it, and when needed shake the bottle before drawing out a portion.

The purifying of the air and oxygen is effected in an apparatus having one side fitted to the aspirator bottles supplying the air, while the other side connects directly with the oxygen cylinder. The wash-bottles are glass-stoppered, filled to $\frac{1}{2}$ height with potassium hydroxide (sp. gr. 1.30), the attached calcium-chloride jars filled to $\frac{1}{2}$ height with solid potassium hydroxide, and the balance with calcium chloride and a plug of glass wool on top; a Y-tube connects each side with the combustion-tube.

The combustion-tube is of platinum, $\frac{3}{4}$-inch bore, with a body 20 inches long, having $\frac{3}{16}$-inch platinum tubes 3 inches long extending from the body. The tube contains a roll of platinum gauze 4 inches long, filling the bore of the tube and pushed into the combustion-tube until the anterior end is over the first burner; this gauze is followed by a roll $1\frac{1}{2}$ inches long, of silver foil inclosed in a piece of platinum foil, which just fills the bore of the tube, and this is then followed by the boat, the tube being closed by a cone-shaped ground-joint which is reinforced by bands of nickel.

The combustion furnace is an ordinary 10-burner Bunsen furnace.

The absorbing train is made up of two U-tubes giving a total length in tubes of 44 inches; these are followed by a Geissler potash bulb containing potassium hydroxide solution (sp. gr. 1.30), (after a bulb has absorbed about $\frac{1}{2}$ gram carbon dioxide a fresh one is used), and a 4-inch calcium-chloride tube containing solid potash. The bulb and tube are weighed, and these are followed by an 8-inch calcium-chloride tube filled with solid potash to prevent any carbon dioxide from the outside air entering the apparatus. The first U-tube of the train is filled for the first 5 inches of its length with granulated silver. This silver is removed from time to time as it becomes dark-colored on the surface, ignited, and replaced in a tube. The silver is followed by 17 inches of calcium chloride. In the next U-tube there are 11 inches of calcium chloride, then 11 inches of anhydrous copper sulphate, followed by a plug of glass wool. The copper sulphate is renewed after every five combustions. When the U-tubes are first filled a combustion is made in the ordinary manner, but no weighings made, the object being to saturate any caustic lime which might be in the calcium chloride used. The entire train is supported on a special support which permits of adjustment in a vertical or horizontal direction.

DETERMINATION OF MANGANESE IN STEEL.

Weigh 200 milligrams of steel into a 2-oz. flask and add 20 cc. of 1.20 nitric acid. When dissolved, boil gently for five minutes, remove and pour the solution into a 100-cc. graduated cylinder. Wash out the flask three times with water. Finally dilute to the 100-cc. mark. Pour the contents into a 4-oz. precipitating jar and mix by pouring into a cylinder or jar at least three times, draw off 25 cc. with a pipette into the flask in which the solution was made, add 6 cc. nitric acid (sp. gr. 1.20) from a burette, place on a hot plate together with a standard in which the manganese is exactly known and which has been treated exactly like the steel, and when almost boiling add $\frac{1}{2}$ gram lead peroxide, measured approximately on a small glass spatula, and boil for three minutes. Remove, place in a cooling bath, and allow the lead dioxide to settle, which usually requires fifteen minutes. Decant the solution into a comparison tube and compare with the standard properly diluted as for color carbon determination.

DETERMINATION OF MANGANESE IN PIG IRON.

Dissolve as for steel, place a small funnel in the cylinder, and filter. Wash the residue thoroughly, being careful not to allow the washings to exceed 100 cc., and treat the filtrate as in the case of steel.

DETERMINATION OF NICKEL IN STEEL.

Dissolve 1 gram of steel in 25 cc. nitric acid (sp. gr. 1.20) and boil in a 100-cc. flask, until solution is complete. Wash contents of flask into a ½-gallon flask containing 700 cc. hot water, add 100 cc. sodium acetate solution, and bring to a boil for one minute. Remove from plate and let settle for three minutes, filter through a 38½-cm. fluted filter into a liter beaker, and allow the precipitate to run dry. To the filtrate, which should be perfectly clear and almost colorless, add 3 drops of phenol-phthalein, then ammonia until pink, place on a hot plate and pass a current of hydrogen sulphide gas through the solution for ten minutes; remove from the plate and add 12 cc. acetic acid (50 per cent.), stir and allow the precipitate to coagulate on a warm plate for ten minutes, filter through a 12½-cm. filter and wash with hydrogen sulphide water made slightly acid with acetic acid. Roast in a platinum crucible, carefully at a low red heat (usually at the front of a muffle) until the paper has just burned off. Take out crucible and break up the precipitate with a platinum rod to powder, then place in the muffle and ignite for fifteen minutes at a bright red heat, cool, and weigh. To the crucible add 3 cc. hydrochloric acid (sp. gr. 1.20), cover with a watch-glass and warm gently on a plate until the precipitate has dissolved. Wash into a 150-cc. beaker with water, add ammonia until the solution smells strongly of ammonia, and filter from the silica and ferric hydroxide. Redissolve precipitate in 3 cc. hydrochloric acid and repeat the precipitation with ammonia, wash with hot water, ignite in same crucible, and weigh. The difference in the weight gives the NiO. A correction of 5 per cent. on the quantity of nickel present is made to provide for the nickel remaining in the basic acetate precipitate.

The sodium acetate solution is made by dissolving 3,000 grams of sodium acetate in 12 liters of water.

II. METHODS USED AT THE LABORATORY OF THE MONONGAHELA FURNACE, McKEESPORT, PA.

By Frederick Crabtree.

DETERMINATION OF SILICA IN ORES.

0.5 or 1 gram of the ore (powdered to pass through a 100-mesh sieve) is fused with sodium carbonate, the fusion dissolved in dilute hydrochloric acid, and the solution evaporated to dryness in a 5½-inch or 6-inch R. M. evaporating dish. When the residue is thoroughly dry, dilute hydrochloric acid is added and the mixture boiled until the iron is dissolved. The solution is then filtered, the silica washed with hot water, ignited, and weighed.

DETERMINATION OF IRON IN ORES.

0.5 gram of the ore is placed in a 2-oz. beaker with about 35-40 cc. of strong hydrochloric acid, and allowed to stand on a steam-bath for several hours (usually over night). Sometimes several drops of stannous chloride are added to hasten the solution. When ready for titrating, the contents of the beaker are heated to boiling and examined to see if the residue is white; a slight excess of stannous chloride solution is added, the mixture placed in a 20-oz. beaker and diluted with about 300 cc. of cold water. About 25 cc. of cold saturated solution of mercuric chloride are then added and the solution titrated with a bichromate solution containing about 4.38 grams per liter.

DETERMINATION OF PHOSPHORUS IN ORES.

2 to 5 grams of the ore are digested with 75-150 cc. of strong hydrochloric acid and the solution evaporated to hard dryness. About 100 cc. of strong hydrochloric acid are poured on the residue and the mixture boiled until the solution is concentrated to about half that volume. Water is then added and

the diluted solution filtered, keeping the volume of the filtrate as small as is convenient.

The solution is then evaporated with nitric acid until the hydrochloric acid is driven off. The insoluble residue is ignited and the silica driven off by boiling with hydrofluoric acid. The residue is fused with sodium carbonate, the fusion dissolved in nitric acid, and the solution filtered into the main solution. To this ammonia water is next added (the fluid is now in a 16-oz. Erlenmeyer flask) until the solution becomes pasty and smells ammoniacal; the precipitate is dissolved in a slight excess of nitric acid and the solution brought to a temperature of 80° C., when 40 cc. of the molybdate solution are added.

A current of air is used to agitate the solution for about five minutes; the latter is filtered while still warm. After washing thoroughly with distilled water, the yellow precipitate is titrated according to the acidimetric method.[1]

Sometimes the method is varied by not evaporating with nitric acid to drive off hydrochloric acid after filtering from the insoluble residue; the insoluble residue may then be fused, the fusion dissolved in nitric acid, and the solution evaporated to dryness to get rid of silica.

DETERMINATION OF MANGANESE IN ORES.

The filtrate from the silica determination is nearly neutralized by ammonia, and then ammonium carbonate solution added until the iron is on the point of coming down, the solution still remaining clear. The addition of a solution containing about 2 grams of ammonium acetate and hot water enough to give a volume of about 400–500 cc., will cause the precipitation of the iron and aluminum. The contents of the beaker are heated to boiling and boiled for about one minute. The precipitate is filtered off and washed with hot water immediately. The manganese in the filtrate is precipitated by bromine and ammonia, and usually weighed as Mn_3O_4.

DETERMINATION OF SILICON IN PIG IRON.

1 gram of drillings is dissolved in 20 to 25 cc. of nitric acid

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[1] Hundeshagen: *Ztschr. anal. Chem.*, *1889*, p. 171; and Handy: *Proc. Engineers' Society W. Pa.*, *1892*, p. 78.

(1.20) and 8 to 10 cc. of dilute sulphuric acid (1:3) and evaporated in a 5-inch R. M. dish until the sulphuric fumes are given off copiously. The residue is treated with dilute hydrochloric acid and the mixture boiled; the residue is filtered off and washed with hot water and dilute hydrochloric acid, ignited, and weighed as SiO_2.

DETERMINATION OF SULPHUR IN PIG IRON.

The evolution method is ordinarily used, absorbing the sulphur in a dilute ammoniacal solution of cadmium chloride, and titrating with iodine solution without filtration.

DETERMINATION OF PHOSPHORUS IN PIG IRON.

5 grams of Bessemer pig iron are dissolved in 100 cc. of dilute nitric acid (30 per cent. of nitric acid of 1.42 sp. gr.); the loss due to evaporation is made good by diluting to just 100 cc., and the solution then filtered. Eighty cc. of the filtrate are boiled, oxidized by permanganate solution and the manganese oxide dissolved by the addition of hydrochloric acid. The solution is made ammoniacal and the precipitatere dissolved by nitric acid; to the solution, at a temperature of 75°–80° C., 40 cc. of molybdate solution are added, and a current of air used to agitate the liquid for about five minutes. The solution is filtered while warm, the precipitate being washed with cold water, and then titrated with a caustic potash solution, 1 cc. of which is equivalent to 0.0002 gram phosphorus.

DETERMINATION OF MANGANESE IN PIG IRON.

Titration by Permanganate.—One gram of the pig iron is dissolved in dilute nitric acid (25 cc. water, 15 cc. nitric acid of 1.42 sp. gr.); the solution is evaporated nearly to dryness, diluted with water, a slight excess of zinc oxide being mixed with the water added, and the volume made up to 500 cc. by addition of water. After thoroughly mixing, the precipitate is allowed to settle; 250 cc. of the supernatant liquid are decanted and titrated while hot.

DETERMINATION OF CARBON IN STEEL.

Chromic Acid Combustion Method.—Use the following train after the condenser: First, a small empty bottle; second, pyrogallic solution recommended by Committee on International Standards; third, silver sulphate solution; fourth, strong sulphuric acid; fifth, potash bulb; sixth, small weighed flask containing sulphuric acid to retain any moisture that might be carried over from potash bulb; seventh, a guard test-tube containing sulphuric acid.

For dissolving the steel use a solution of copper potassium chloride acidified with hydrochloric acid, and shake or agitate so as to have steel dissolved quickly.

DETERMINATION OF SULPHUR IN STEEL.

Iodine titration; the process described for pig iron.

DETERMINATION OF PHOSPHORUS IN STEEL.

4 grams are dissolved in 100 cc. of dilute nitric acid (sp. gr. 1.13), oxidized by permanganate, the precipitated manganese oxide dissolved by hydrochloric acid, etc., as in case of pig iron.

DETERMINATION OF MANGANESE IN STEEL.

Color Method.—0.2 gram of steel (our steel is soft and contains from 0.25 to 0.45 per cent. manganese, usually) is dissolved in 15 cc. of dilute nitric acid (sp. gr. 1.25). When the solution is clear, and nitrous fumes are all expelled, 15 cc. of water are added; the solution is brought to lively boiling, lead peroxide added, and the mixture boiled two minutes; a little more lead peroxide is then added, when the flasks are removed from the hot plate and placed in cold water for settling.

III. METHODS USED AT THE LABORATORY OF THE JUNCTION IRON AND STEEL COMPANY, STEUBENVILLE, OHIO.

BY JOSEPH M. WILSON.

DETERMINATION OF SILICA IN IRON ORES.

Weigh 1 gram of ore into a 5-inch flat dish, moisten with 10 cc. water, add 30 cc. concentrated hydrochloric acid, evaporate on a hot plate to dryness, and ignite. Moisten with hydrochloric acid, dry, and ignite again. Cool, moisten with hydrochloric acid, dissolve in 30 to 50 cc. boiling water, filter, wash with hot hydrochloric acid (1 : 1) and with cold water. Burn the filter wet. Mix with 5 to 6 parts sodium carbonate and fuse. Dissolve fusion in 50 to 60 cc. water, add hydrochloric acid till acid, evaporate to dryness, ignite till no further decrepitation occurs, cool, moisten with hydrochloric acid, dry and ignite (to render silica insoluble), cool, and moisten with hydrochloric acid; take up in boiling water, filter, and wash twice alternately with hot hydrochloric acid (1 : 1) and cold water; then five or six times with hot water. Burn and weigh as SiO_2.

If greater accuracy be desired, moisten the silica with hydrofluoric acid and add a few drops of sulphuric acid. Evaporate to dryness, ignite, cool, and weigh. The loss $= SiO_2$.

DETERMINATION OF IRON IN ORES.

The following solutions are employed: Potassium dichromate, 4.9 grams dissolved in one liter of water; 1 cc. = 0.005 gram Fe. Stannous chloride, 100 grams dissolved in 1 liter of hydrochloric acid (1 : 1). Mercuric chloride, 50 grams dissolved in 1 liter of water. Potassium ferricyanide, a piece one-fourth the size of a pea in 40 cc. water.

Weigh 0.25 and 0.5 gram ore into small unlipped beakers, moisten with water, add 30 cc. hydrochloric acid, cover, and place on a steam table; when solution is complete and residue appears white, boil on a hot plate, add stannous chloride from a pipette till the liquid becomes colorless, boil a few moments, remove to steam table till ready to titrate, wash into beaker, dilute to 300–350 cc., stir, pour in excess of mercuric chloride (30 to 40 cc.), stir, run in potassium dichromate *at once* until four drops fail to develop a blue color with ferricyanide indicator in one-half minute. Burette-reading on half-gram samples gives the per cent. of iron when 1 cc. potassium dichromate = 0.005 gram iron. Reading on $\frac{1}{4}$ gram doubled should vary not more than 0.2 cc. from that on $\frac{1}{2}$ gram.

Precautions.—Avoid large excess of stannous chloride; one or two drops more than is required to destroy yellow color is sufficient.

In adding mercuric chloride pour all in *at once.* If added slowly, metallic mercury is precipitated and the operation spoiled.

DETERMINATION OF PHOSPHORUS IN ORES.

Weigh 10 grams ore into a 5-inch (deep) dish, moisten with water, and add 100 cc. hydrochloric acid; let stand on steam table, evaporate to dryness, heat, cool, moisten with 100 cc. hydrochloric acid; boil down to a syrup, add 75 cc. water, filter, and wash with hydrochloric acid (1 : 1) and cold water. Ignite residue, fuse with 5 to 6 parts of sodium carbonate, dissolve the fusion in water and hydrochloric acid, evaporate to dryness and heat, moisten with hydrochloric acid, take up with water, filter, boil filtrate, and add a slight excess of ammonia. Filter, wash two or three times with hot water, dissolve in hot nitric acid of 1.2 specific gravity, add to main solution, which has in the meantime been evaporating to a syrup; add 75 cc. nitric acid and again evaporate to a syrup; transfer to a 16-oz. flask and add an excess of ammonia; redissolve the precipitate in nitric acid in very slight excess, warm to 87° C., add 50–75 cc. of molybdate solution, shake five minutes, and allow to settle; filter and wash with ammonium sulphate solution till free from iron.

The ammonium sulphate solution is made by diluting and mixing 48 cc. sulphuric acid and 55 cc. ammonia, and then making up to 2 liters.

The molybdate solution is prepared according to Woods' formula.[1]

A stream of air is blown through the liquid while adding the molybdate solution.

The yellow precipitate is dissolved in ammonia, 5 to 10 cc. magnesia mixture are added, the liquid well stirred and allowed to stand for two hours; filter and without washing redissolve the precipitate in hydrochloric acid. The bulk of the liquid must be kept below 25 cc. A piece of citric acid half the size of a pea is added and then ammonia in slight excess. After stirring, the liquid is set aside for fifteen to twenty minutes, stirring occasionally. The solution is now diluted with an equal bulk of ammonia and allowed to stand from twelve to twenty-four hours. Filter, using a Gooch crucible; wash with a solution of ammonium nitrate containing 50 grams ammonium nitrate in 2 liters nitric acid (1 : 3); burn and weigh. Or, the yellow precipitate is dissolved in sodium hydroxide and titrated with standard nitric acid, according to Hundeshagen,[2] or, the precipitate is dissolved in ammonia, the solution acidulated with sulphuric acid and the phosphorus determined volumetrically by permanganate, according to Emmerton.[3]

DETERMINATION OF MANGANESE IN ORES AND IN METALS.

Volhard's Method: This method was described by Emmerton[4] and is as follows: "Evaporate solution—peroxidized—with sulphuric acid, in excess, till copious fumes are evolved; cool, take up in water, filter into a 300-cc. graduated flask, add sodium carbonate till color is wine-red, but no precipitate forms; then zinc oxide suspended in water till color is light brown (or perhaps fawn), mix by pouring into beaker and back several times, filter through a 10-inch, dry, fluted filter, take 200 cc. of filtrate in a 16-oz. flask, to which add 2 drops nitric acid (sp. gr. 1.42), boil, run in potassium permanganate a little at a time, shake vigorously to make precipitate collect, allow to settle, and repeat till a permanent pink is obtained.

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[1] *Proc. Engineers' Society W. Pa.*, **8**, 80, *1892*.

[2] *Ztschr. anal. Chem.*, *1889*, 171.

[3] Blair's Analysis of Iron, Second Edition, p. 85.

[4] *Trans. A. I. M. E.*, 10, 204.

Notes.—This method is not applicable to substances containing less than 0.8 per cent. manganese owing to the difficulty in distinguishing the color of manganese dioxide, from the *pink* of potassium permanganate. When the substance contains more than 5 per cent., take 100 cc., or even less, instead of 200 cc.

Pig iron is to be treated as for silicon, then filtered, the filtrate evaporated a *second* time with sulphuric acid, proceeding then as above described.

The permanganate solution contains 1.27 grams potassium permanganate per liter.

1 cc. = 0.002262 gram Fe, or 0.000666 gram Mn, corresponding to 0.1 per cent. manganese when $\frac{2}{3}$ gram of the sample is used.

Color Method.—Weigh 0.2 gram of the sample into an 11-inch tube, add 20 cc. nitric acid (sp. gr. 1.20), boil till the escape of brown fumes ceases, add 10 cc. of water, boil, add about 3 grams lead dioxide, and continue boiling for two and one-half minutes. Place in cold water until the liquid has become clear; decant into the reading tube and compare.

Use pig iron or steel in which the manganese has been determined gravimetrically: (*a*) By Ford's method; (*b*) by acetate method, as a standard. (Weigh standard with each batch to be read.) Manganese is also determined by precipitation by bromine, and weighing as Mn_3O_4.

DETERMINATION OF SILICON IN PIG IRON.

Drown's method is used.

DETERMINATION OF SULPHUR IN PIG IRON.

By method described by Emmerton[1] absorption of hydrogen sulphide in potassium hydroxide (Powers and Weightman's white stick caustic is the only brand that will give uniformly correct results) and titration with iodine solution. 1 cc. = 0.0005 gram sulphur. Standardize by a *steel* of known sulphur content. Results check with those obtained by the *aqua regia* method. When solution is *complete*, boil till steam reaches the stopper of the first tube, remove flame, open the stop-cock in the funnel, and

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[1] *Trans. A. I. M. E.*, 10.

allow to stand till liquid in tube is cold. Wash into a beaker, making the volume up to 300–400 cc., add 3-5 cc. starch solution, then excess of hydrochloric acid, titrate with iodine solution, of which 1 cc. = 0.0005 gram sulphur. Standardize the iodine solution with steel or pig iron, the sulphur content of which has been determined as indicated.

Precautions.—Be sure that the metal is *entirely* dissolved. Pig irons high in sulphur frequently dissolve very slowly and *must be watched carefully.* The method for sulphur determination described by N. W. Lord[1] is to be highly recommended.

DETERMINATION OF PHOSPHORUS IN PIG IRON.

Follow Emmerton till the yellow precipitate is obtained, then Hundeshagen,[2] and Handy.[3]

DETERMINATION OF MANGANESE IN PIG IRON.

Color method, using a pig iron standard ; also Ford's method for the purpose of checking.

DETERMINATION OF CARBON IN STEEL.

Ullgren's method, as described by McCreath,[4] is followed, checking by combustion in a platinum tube. As the solvent, ammonio-cupric chloride, in saturated solution, is used.

The chromic acid solution contains 80 cc. concentrated sulphuric acid (previously purified by the addition of a little chromic acid) and 10 cc. of a saturated solution of chromic acid crystals. Not more than 20 cc. of water are used in rinsing the carbon into the combustion flask. Soda-lime is the absorbent for the carbon dioxide evolved.

The methods for the determination of sulphur and phosphorus are the same as in the case of cast iron.

Manganese is determined by color ; checking by Ford's method.

Nickel is determined according to the method of Eastwick.

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[1] Notes on Metallurgical Analysis, p. 52.

[2] *Loc. cit.*

[3] *Proc. Engineers' Society W. Pa., 1892*, p. 78.

[4] *Trans. A. I. M. E.*, 5, 575.

IV. METHODS USED AT THE LABORATORY OF THE CARNEGIE STEEL COMPANY, LUCY FURNACE, PITTSBURG, PENNA.

By Robert Miller.

DETERMINATION OF SILICA, IRON, AND PHOSPHORUS IN IRON ORES.

I use the methods described on pages 16, 19, 22–26, respectively, of "Notes on Metallurgical Analysis," by N. W. Lord.

DETERMINATION OF SILICON AND SULPHUR IN PIG IRON.

On pages 37 and 35, respectively, of the above work, will be found described the methods used by me for this purpose.

DETERMINATION OF MANGANESE IN PIG IRON.

Volhard's method, as described by Blair[1], is used for this determination.

DETERMINATION OF PHOSPHORUS IN PIG IRON.

Weigh off 1 to 5 grams of iron (according to the amount of phosphorus present), put into a 4-oz. beaker, and add cautiously 25–75 cc. nitric acid (sp. gr. 1.20). After the violent action has ceased, boil down to dryness, and bake for thirty minutes. Allow to cool, dissolve the mass in 20–40 cc. of concentrated hydrochloric acid, and evaporate the solution to 10 cc. Add 20 cc. of water and filter. Now add ammonia until ferric hydroxide separates out, and the mass becomes thick and smells of the precipitant. Redissolve the precipitate in strong nitric acid, adding the acid gradually and until the liquid has an amber color. Without previously heating the solution, add 40 cc. of molybdic acid and allow the yellow precipitate to settle. The phosphorus is all down in about ten minutes. Filter on a 9-cm. filter and wash with acid ammonium sulphate. Dissolve the precipitate in 5 cc. of strong ammonia (diluted with 25 cc. of water) and allow to run into the flask in which the precipitation was made.

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[1] Blair's Analysis of Iron, Third Edition, p. 118.

Wash the filter until the volume of the filtrate is 150 cc. Add 10 cc. of concentrated sulphuric acid, dilute to 200 cc. and filter through the reductor. The reduced solution is titrated with potassium permanganate.

The acid ammonium sulphate used in washing the yellow precipitate is made by adding 27.5 cc. of ammonia (sp. gr. 0.96) to 500 cc. of water, to this 24 cc. of strong sulphuric acid (C. P.), and making the whole up to 1 liter.

To prepare the molybdic acid solution, add to 100 grams of molybdic acid 200 cc. of water and then 160 cc. of ammonia. This dissolves all the acid. Pour the filtered solution into 1 liter of nitric acid (sp. gr. 1.20). Allow the mixture to stand a day or two before using.

V. METHODS USED AT THE LABORATORY OF THE BLACK DIAMOND STEEL WORKS, PITTSBURG, PA.

By Edward S. Johnson.

I. IRON ORES.

1. *Silica.*—1 to 3 grams of the finely pulverized ore are digested upon the water-bath in a covered beaker with 10 to 30 cc. of concentrated hydrochloric acid until decomposition is complete. The solution and silicious residue are then transferred to a porcelain dish, and the solution evaporated on the graphite-bath (substitute for the sand-bath) to dryness. The residue is taken up with concentrated hydrochloric acid and water, the solution evaporated as before, and, after redissolving the dry mass in concentrated acid and dilution with several volumes of water, the silicious residue is collected upon a Swedish filter, thoroughly washed, and ignited in a platinum crucible. After ignition the residue is subjected to a fusion with ten to fifteen times its weight of sodium carbonate. The fusion is dissolved in water and hydrochloric acid, the solution evaporated to dryness on the water-bath, and the separation of the silica further conducted as usual under the given circumstances. The insoluble residue remaining after the fusion, etc., is weighed ordinarily as SiO_2.

In still more accurate determinations, the silica thus obtained is treated with hydrofluoric and sulphuric acids. The loss after evaporation and ignition is silica.

2. *Iron.*—The process for the determination of iron in iron ores is the familiar one, consisting in the solution of the ore in the least possible quantity of concentrated hydrochloric acid, reduction of the resulting ferric or ferro-ferric to a ferrous solution, and titration of the highly dilute solution, in the presence of a large excess of sulphuric acid, with potassium permanganate.

0.4 to 0.5 gram of the sample is dissolved in a covered

10-inch by 1-inch test-tube in 4 to 5 cc. of concentrated hydrochloric acid. The tube is heated over a small gas flame, at first only warmed, and later, as the reaction proceeds, to gentle boiling. A small crystal (0.1 to 0.2 gram) of potassium chlorate is added to the solution to oxidize possibly present organic matter, and the boiling continued, with addition of more hydrochloric acid, if necessary, for some minutes in order to decompose an excess of chlorate.

When all but a flocculent silicious residue has been dissolved (the watch-glass covering the tube), the walls of the tube are rinsed down with water, and 3 to 4 grams of triturated zinc added to the solution. The resulting brisk evolution of hydrogen soon slackens; a few cubic centimeters of dilute sulphuric acid (1 : 1) are poured into the tube, and heat is applied, with addition of more dilute sulphuric acid as required, until the colorless condition of the solution indicates the complete reduction of ferric salt, and all zinc has dissolved. The remainder of 25 cc. of concentrated sulphuric acid (diluted with 1 volume of water) is next added, and the reduced solution transferred from the test-tube to a 600-cc. beaker. Sufficient cold, freshly-boiled distilled water, to make the volume of the solution 400 to 500 cc., is poured into the beaker. From a 50-cc. Gay-Lussac burette, a solution of potassium permanganate (1 cc. representing about 0.0068 gram of iron), standardized by oxalic acid, is run into the diluted ferrous solution until finally one drop imparts to it a permanent pink coloration. From the number of cubic centimeters used in the titration, a deduction is made for the volume of permanganate solution required to produce the above end-reaction with all materials present or applied in the operations just described, *i. e.*, acids, zinc, ferric chloride, water, etc. The remainder forms obviously the basis for the calculation of the percentage of iron.

3. *Phosphorus.*—This element is separated as ammonium phosphomolybdate and weighed in the same form.

1.63 grams of ore are weighed off into a small porcelain dish and ignited gently. When it has sufficiently cooled, the sample is treated with about 20 cc. of concentrated hydrochloric acid, and the mixture, with frequent stirring, is heated on the water-bath until all but silicious matter has dissolved. The solution is evaporated to dryness, and the residue redissolved in 20 to 30 cc. of hydrochloric acid. This second hydrochloric acid solution is evaporated until the separation of basic chloride of iron begins. With two or three drops of acid, the solution is restored; 30 to 40 cc. of water are added, and the insoluble silicious residue is filtered off. The filtrate, which should have a volume of about 60 cc., is ready for the precipitation which is effected as described for steel, p. 32.

4. *Manganese.*—According to the percentage of manganese present, the colorimetric or a gravimetric method is applied for its quantitative determination: for quantities up to about three per cent., the former; for higher percentages, the latter.

A. COLORIMETRIC METHOD.

From 0.05 to 0.10 gram of ore is placed in a 6-inch by ½-inch test-tube, and dissolved in 2 to 3 cc. of concentrated hydrochloric acid which is then expelled by boiling with an excess of concentrated nitric acid of 1.42 sp. gr. The nitric acid solution is poured into a 10-inch by 1-inch test-tube, rinsed out of the smaller tube with 32 per cent. nitric acid, and diluted with the same to a volume of about 35 cc. By the addition of lead peroxide and boiling the solution, manganese is oxidized to permanganic acid and determined in this form, as directed for the estimation of manganese in steel, p. 33.

B. GRAVIMETRIC METHOD.

For quantities over 3 per cent., the colorimetric method is as yet scarcely longer available[1]; a gravimetric determination is then resorted to. The usual practice is to separate the manganese from a nitric acid solution in presence of a large excess of strong nitric acid by precipitation with potassium chlorate as hydrated dioxide. The latter is separated by filtration, washed with strong nitric acid, and redissolved in sulphurous acid. The manganese in this solution is finally freed wholly from iron by a basic acetate precipitation. In the filtrate from the iron precipitate, manganese is precipitated in the form of ammonium manganese phosphate.

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[1] Experiments, with the object of determining the maximum percentage which may be estimated colorimetrically, are, however, in progress.

II. PIG IRON.

1. *Silicon.*—1 gram of metal is dissolved in a small, covered, porcelain dish in 10 cc. of dilute sulphuric acid (1 : 3) with the addition of an equal volume of water. The action of the acid is hastened by heating. When the evolution of hydrogen has ceased, the cover-glass is rinsed off into the dish, and the latter placed on the graphite-bath, where the contents of the dish are heated until dense white fumes of sulphuric anhydride form abundantly. The dish is removed from the bath, allowed to cool somewhat, and the residue treated with water. Heat and stirring are applied until all sulphate of iron has dissolved. The insoluble residue is filtered off, washed with water and dilute hydrochloric acid until free from iron, ignited, and weighed as SiO_2. If S represent the weight of metal taken for the determination, SiO_2 the weight of silica found, and Si the percentage of silicon, then

$$Si = \frac{SiO_2 \times 140}{S \times 3}.$$

2. *Sulphur.*—The method adopted for the estimation varies with the variety of iron and the accuracy required. For gray iron and "commercial" accuracy, the evolution-volumetric method is applied; for white iron and also gray varieties of pig iron, when the utmost accuracy is demanded, the aqua regia method is made use of.

A. EVOLUTION-VOLUMETRIC METHOD.

The details of the process are given below in the description of methods for the analysis of steel, p. 30.

B. AQUA REGIA METHOD.

The sample—about 5 grams—is dissolved in concentrated nitric acid of 1.42 sp. gr., with the addition of a small quantity of hydrochloric acid—a few cubic centimeters of concentrated acid at a time—and by the aid of heat, when necessary, to start the dissolving of the borings. When the action of the acid has ended, about 2 grams of sodium carbonate are added, and the solution is warmed until the escape of carbon dioxide has ceased. Silica is separated as usual by evaporation to dryness, solution of the residue in hydrochloric acid, and filtration. The slightly acid filtrate is diluted to 75 to 100 cc. for each gram of metal taken for the determination, and treated, while at a boiling temperature, with a hot solution of barium chloride in moderate excess. After the mixture has stood several hours, the precipitate of barium sulphate is collected on a washed Swedish filter, and washed as usual with hot water and dilute hydrochloric acid (1 : 20). Should the precipitate be contaminated with oxide of iron, a separation of the latter by fusion with sodium carbonate, etc., is undertaken after ignition.

3. *Phosphorus.*—The details of the method for the determination of phosphorus in pig iron are essentially the same as in the case of steel. 1.63 grams of borings are dissolved in 50 cc. of 20 per cent. nitric acid. The insoluble carbonaceous and siliceous matter is filtered off, and the filtrate—about 60 cc. in volume—is treated as directed on p. 32.

4. *Manganese.*—The same considerations and practice apply in the determination of manganese in pig iron as in the estimation of that element in steel, see p. 33.

III. STEEL.

1. *Carbon.*—In order to determine the carbon in steel, the separation is accomplished by decomposing the metal, as generally customary, by means of cupric potassium chloride. As is well known, a residue containing the whole of the carbon remains after the action of the double chloride. By combustion in a stream of oxygen, the carbon of the residue is converted for weighing into carbon dioxide.

According to the amount of carbon present, 1 to 10 grams of steel are treated with the above-mentioned solution (30 to 40 cc. for each gram of metal) of cupric potassium chloride which is made by dissolving 12 grams of a pure preparation of the salt in 3 liters of water and 50 cc. of concentrated hydrochloric acid, and filtration of the solution through ignited asbestos.

The mixture of chloride and steel borings is constantly stirred, warmed at first, and finally heated to about 100° C. until the metallic copper which separates in the reaction is redissolved. Sufficient dilute hydrochloric acid (1 : 1) is added to dissolve the basic chlorides of iron and copper, which may separate out toward the end of the above operation, and keep them in solution during the subsequent filtration. This is effected by Dr. Blair's familiar device for the purpose, consisting, as need scarcely be added, of a platinum boat, with a finely perforated bottom, and a funnel of the same metal, into which the boat may be tightly packed with asbestos to allow of the use of the filter-pump. The packing is done by means of asbestos in the form of pulp such as is also used in forming a felt filter over the perforations in the boat. The pulp for the felt may be conveniently made by heating asbestos wool to redness, cutting the fibers into short pieces with the scissors (a manipulation rendered much easier by the preparatory heating), and, after a second ignition, agitating with water.

When the carbonaceous residue has been collected in the boat, washed thoroughly with dilute hydrochloric acid and water, and dried at 100° C., it is ready for combustion.

The latter is carried out in a porcelain tube of the usual dimensions, heated in a ten-burner, Bunsen combustion furnace, and supplied with a slow stream of oxygen purified by passage over red-hot copper oxide and through absorbents for water and carbon dioxide, in the following order: Through potassium hydroxide solution (1 : 2), and over granulated calcium chloride and soda-lime.

The combustion-tube, projecting four or five inches beyond the furnace at either end, is filled, excepting the projecting ends and enough space in the rear for the reception of the boat, with coarsely granular, copper oxide which is kept in place by short, spiral rolls of copper gauze. Rubber stoppers at the rear and front ends of the tube connect, respectively, with the supply of oxygen and the apparatus for the purification and absorption of the carbon dioxide formed in the combustion-tube. The possible impurities which require removal are hydrochloric acid and chlorine. The gases issuing from the front end of the tube are, therefore, caused to pass first through a saturated solution of ferrous sulphate acidulated with a few drops of dilute sulphuric acid, where any chlorine in the mixture is converted into hydrochloric acid, and any of the latter substance in the gases is mainly absorbed. Should hydrochloric acid escape absorption in the ferrous sulphate solution, it is retained by the saturated solution of silver sulphate which follows. The gases leaving the silver solution are saturated with vapor of water. By passing them through concentrated sulphuric acid and over calcium chloride they are completely dried, and may enter the Geissler potash bulbs which immediately follow, and in which the absorption of their carbon dioxide takes place. The bulbs are filled with potassium hydroxide solution (1 : 2) ; to prevent loss of moisture from the solution by the continuous passage of gas through the apparatus, the bulbs are fitted with a cover-tube, with ground-joint, containing solid potassium hydroxide.

Connected with the exit-end of the potash bulbs, a 6-inch, straight, calcium-chloride tube, filled also with pieces of potassium hydroxide, protects them against the possibility of the entrance of moisture and carbon dioxide from the atmosphere. It concludes the train of apparatus attached to the front end of the combustion-tube.

After the familiar preliminaries of introducing the boat with its carbonaceous residue, weighing and attaching the potash bulbs, securing all connections, and starting a slow stream of oxygen through the apparatus, the combustion is begun by heating the front half of the porcelain tube to redness. The rest of the tube containing the boat is then gradually heated to the same temperature. For fifteen to twenty-five minutes a red heat is maintained and the passage of oxygen continued. The oxygen is then cut off, and air from an independent drying and purifying apparatus—a duplicate of that described for use with oxygen—is drawn during forty-five to sixty minutes slowly through the entire apparatus. By this manipulation all carbon oxide is brought into the potash bulbs, and the latter filled with air. To insure a complete displacement of the oxygen in the potash bulbs, after the main aspiration, air which has been freed from carbon dioxide is drawn for some minutes through the drying apparatus directly behind the bulbs, and the bulbs themselves.

The potash apparatus is detached and allowed to stand fifteen to twenty minutes in the balance case, where it had stood for at least the same length of time before the first weighing. The increase in weight is ascertained, and therefrom the percentage of carbon deduced according to the well-known formula.

2. *Sulphur.*—The determination is effected by separating the element as cadmium sulphide and estimating the sulphur in the latter volumetrically with iodine solution.

The metal is dissolved in dilute hydrochloric acid; the gases evolved are passed into a strongly ammoniacal solution of cadmium chloride in which the sulphur, entering as hydrogen sulphide, is precipitated. The precipitate is filtered off, dissolved in a large volume of dilute hydrochloric acid, and the hydrogen sulphide again set free, measured as indicated above.

The solution of the sample is carried out in a 250-cc. Florence flask.

Into the neck of the flask is fitted a rubber stopper with three perforations. One of the latter receives the stem of a separating funnel with a wide mouth and a bulb which should have a capacity of about 50 cc.; through another perforation passes the $\frac{1}{4}$-inch conduction-tube, connecting the evolution flask directly under the stopper with the absorption-tube; a third $\frac{1}{8}$-inch tube, the hydrogen tube, passes through the stopper to the bottom of the flask where it is drawn out to a point and bent upwards about $\frac{1}{8}$ of an inch. Above the stopper it is connected with a supply of hydrogen.

The conduction-tube, which is in one piece, rises perpendicularly to about $\frac{1}{2}$ inch from the stopper, bends away from the perpendicular about 60°, extending in this direction 5 or 6 inches, when it dips directly downward into the absorption-tube, a 10-inch by 1-inch lipped test-tube of stout glass. Between the first and second bends in the conduction-tube are blown two $\frac{3}{4}$-inch bulbs.

The evolution flask and absorption-tube are securely held in the required position by specially adapted racks—the flasks over Argand gas burners—during the precipitation of the sulphur.

In carrying out a determination with the above apparatus, 3 to 5 grams of the sample are placed in the flask, and about 50 cc. of cadmium chloride solution (80 grams of cadmium chloride dissolved in 1.5 liters of concentrated ammonia water and 2.5 liters of water) in the absorption-tube. Connections being made and the hydrogen tube closed, 50 cc. of dilute hydrochloric acid (1 : 1) are gradually or at once, according to the probable rate of evolution of gas, run into the flask through the separating funnel, and a brisk generation of gas is maintained, if necessary, by the aid of heat. When the sample has dissolved, hydrogen is turned on in a slow stream, and the solution boiled until the bulbs of the conduction-tube become hot. The flame under the flask is then turned out, and the passing of hydrogen continued moderately from ten to fifteen minutes.

The precipitated cadmium sulphide is next transferred to a rapid German filter. To this end, after disconnecting the absorption apparatus from the flask, the conduction-tube is withdrawn from the absorption-tube and laid aside, the adhering precipitate being beforehand washed down into the tube as completely as possible ; the portion adhering firmly to the latter, unless it be considerable, is not removed to the filter, but left to be dissolved off, together with that remaining on the conduction-tube, at the final solution of the precipitate. After several washings the filter and precipitate are placed in a 600-cc. beaker. According to the quantity of precipitate, 200–400 cc. of water are poured over it, 3 cc. of starch solution (1 : 150) added, and the mixture stirred until the filter and precipitate are well disintegrated.

Fifty cc. of dilute hydrochloric acid (1 : 1) are poured into the absorption-tube, and water is added to fill the tube to within about an inch of the top. The conduction-tube, which had been laid aside before the filtration, is quickly dipped into the diluted acid until its tip nearly touches the bottom, then raised and lowered in the liquid several times. By manipulating in this way, the precipitate left in the absorption- and conduction-tubes is almost instantly dissolved, the hydrogen sulphide formed absorbed in the surrounding liquid, and the comparatively strong solution of hydrogen sulphide, existing on their surfaces immediately after the contact of the precipitate with the acid, rinsed off. The contents of the absorption-tube are added to the water and precipitate in the beaker. The precipitate dissolves mainly at once and entirely on stirring. Without waiting until all cadmium sulphide has dissolved, the estimation of the sulphur is at once begun by titration of the liberated hydrogen sulphide with iodine solution.

The standard iodine solution is prepared by dissolving 1 gram of resublimed iodine in 50 cc. of an aqueous solution of potassium iodide (1 : 10), and diluting to 1 liter. While pure reagents and careful manipulation insure a solution of the desired strength, the latter is nevertheless confirmed by direct experiment before the solution is used. For this purpose sodium thiosulphate is applied. A preparation of the salt of requisite purity may be made by recrystallization of the chemically pure preparation of the trade. A saturated, warm aqueous solution is prepared and cooled to nearly 0° C. with constant stirring. The compound separates under these circumstances as a minutely crystalline mass. By decantation and the use of the filter-pump, the mother-liquor may be almost completely removed. The still moist preparation is perfectly freed from water of solution between sheets of filter-paper.

3. *Phosphorus.* This element is determined by weighing as ammonium phosphomolybdate.

1.63 grams of steel are dissolved in a covered beaker in 45 cc. of 20 per cent. nitric acid, the action of the acid being hastened by warming. When a perfect solution has been obtained and brought to the boiling-point, an excess of a saturated solution of potassium permanganate is added and the boiling continued for two or three minutes. While still boiling, the mixture is treated with sufficient ferrous sulphate in saturated, slightly acidified (5 cc. sulphuric acid per liter) solution to dissolve the precipitated manganese dioxide resulting from the action of potassium permanganate on the original nitric acid solution of the metal. The dioxide disappears, leaving usually a clear solution. If it should not, recourse must be had to filtration for the removal of the "scale," etc., sometimes unavoidably weighed off at the beginning of the determination. A clear solution having been produced, about 15 cc. of water are added, and the contents of the beaker again heated to boiling. The source of heat is removed, and the cover and walls of the beaker are rinsed down with water. The volume of the liquid at this stage of the operation should be about 60 cc. After stirring a few seconds, the temperature for precipitation, under 80° C., will exist in the solution. 45–50 cc. of molybdate solution are then added, and the mixture thoroughly and repeatedly stirred. The precipitant is prepared by dissolving 185 grams of pure ignited "molybdic acid" in 900 cc. of ammonia water (sp. gr. 0.96), adding this solution to 2,700 cc. of 32 per cent. nitric acid, and diluting the whole with water to 4 liters. The supernatant liquid is poured, with as little disturbance of the precipitate as possible, when it has become clear, through a washed Swedish filter. The latter is washed twenty-five times with 1 per cent. (by volume) nitric acid, when the precipitate is transferred to the filter, and the washing continued until the precipitate and filter are free from iron. The filter with its contents is dried for one hour at 100° C., and weighed between accurately-ground watch-glasses, the drying and weighing of the filter alone having before been conducted under similar conditions. The number expressing the weight of the precipitate in grams also represents the percentage of phosphorus.

4. *Manganese.*—In the determination of manganese, the colorimetric method is used almost exclusively, the quantities encountered rarely exceeding 3 per cent. For higher percentages, as in the case of ores also, a gravimetric method is used. For the latter, see p. 25, Gravimetric Method.

COLORIMETRIC METHOD FOR MANGANESE.

The process consists in converting the manganese present into permanganic acid and deriving colorimetrically, by means of a solution of potassium permanganate[1] containing a known quantity of manganese, the amount of manganese in the permanganic acid obtained from a given weight of steel.

0.1 gram of metal is dissolved in a 10-inch by 1-inch test-tube in 35–40 cc. of 32 per cent. nitric acid, and the solution heated to boiling over a small flame from a Bunsen burner. When the formation of nitrous fumes ceases, the heat is re-

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[1] The use of potassium permanganate in this connection was, I believe, first suggested by Mr. B. B. Wright, formerly chemist to the Black Diamond Steel Works.

moved, and 0.2 to 0.5 gram of lead peroxide are added. Heat is again applied, and the mixture boiled for three or four minutes. The tube is then stood aside, closely covered, and in the dark, in cold water until the excess of lead peroxide has settled down. When clear, the acid solution above the lead peroxide—now containing the manganese as permanganic acid—is decanted into a 50-cc. comparing tube, which is graduated to 0.5 cc., and is one of a set of three exactly similar tubes; the remaining two receive the solutions of potassium permanganate to be used in determining the quantity of manganese, in the form of permanganic acid, obtained by the process just described.

The permanganate solutions are prepared from a stock solution of such strength that 10 cc. of the same, when diluted to 250 cc., will produce a solution of which 1 cc. contains 0.00001 gram of manganese as permanganic acid. In practice this dilute solution is called the *normal* standard. From the normal, others are prepared (by dilution with water in the comparing tubes) having a simple ratio—1 : 2, 1 : 3, 3 : 4, etc.—to the normal. All of these solutions are adjusted directly before use from the stock solution. The latter is made 1 liter at a time, and may, with proper precautions, be kept for several weeks without appreciable change.

Equipped with this solution and its derivatives, the procedure in estimating the quantity of manganese in the permanganic solution, yielded by a sample of steel under the conditions above detailed, is obvious and simple. In one of the comparing tubes are placed 30–40 cc. of a standard permanganate solution of lighter tint than the permanganic solution. The latter is then diluted with water until the tints in both tubes cannot be distinguished one from another, the examination or "comparing" of the shades of color being carried out over a sheet of white paper in the diffuse light of a window. The ratio of the volumes of the two solutions is plainly equal to the ratio of the quantity of manganese contained in them. The volumes being read off from the graduated comparing tubes, and the quantity of manganese in one solution being known, the quantity in the other is readily calculated. If the normal permanganate be used, the number expressing the volume of the solution (in cubic centimeters) containing the unknown quantity of manganese divided by 100 is the required percentage when 0.1 gram of steel is taken for the determination ; if a standard of lighter tint be used, the volume must first be multiplied by the fraction showing its relation to the normal. For example, a volume of 35 cc. with the normal standard represents 0.35 per cent. manganese ; with a 3 : 4 standard, 0.26 per cent.

In the case of the higher percentages of manganese, which may still be determined colorimetrically with convenience and accuracy, some modifications of the general method already given are advisable or necessary. It is advisable to weigh off for the determination at least one gram of borings that a representative result may be obtained from the sample. A solution in 32 per cent. nitric acid is prepared and diluted in a 500-cc. flask to the mark. Aliquot parts equivalent to 0.05 to 0.1 gram are then taken for single determinations. After evaporation to 5 to 10 cc., transfer to a test-tube, and dilute to about 80 cc. with 32 per cent. nitric acid, when the solution will be ready for oxidation. Experiments thus far have shown that under the above conditions ten to twenty minutes boiling with 0.5 gram of peroxide suffices to oxidize at least 2.5 per cent. manganese in $\frac{1}{10}$ of a gram. The test of complete oxidation is made the obtaining, within the limits of error, of the same result, whether 0.1 gram or half that quantity be used for the determination, the conditions being in each case in all other respects the same.

Further, after the decantation of the permanganic solution, a slightly varying quantity of the latter is left adhering to the tube and the residue of peroxide. When higher percentages are concerned, the quantity of manganese represented by the liquid residue is not inconsiderable, and cannot be neglected in accurate determinations, as in the case of the lower percentages. The tube and residual peroxide should therefore be rinsed with a few cubic centimeters of water or 32 per cent. nitric acid. The rinsings are filtered through carefully washed asbestos into the decanted solution. The asbestos for the filtration is prepared by boiling with strong hydrochloric acid, washing with water, and ignition.

VI. METHODS USED AT THE LABORATORY OF THE OLIVER & SNYDER STEEL WORKS, PITTSBURG, PA.

By S. M. Rodgers.

DETERMINATION OF SILICON IN PIG IRON AND STEEL.

1 gram of pig iron, carefully separated with a magnet, is placed in a 4-inch evaporating dish and 30 cc. of nitrosulphuric acid, made by adding 60 cc. of concentrated sulphuric acid to 600 cc. of nitric acid (sp. gr. 1.20), are added. Cover with a watch-glass and place over a small flame. When the solution of the drillings is complete, remove the cover and rinse into the dish with water and continue the evaporation cautiously, until sulphuric acid fumes appear. Remove the dish from the heat, cool, add 15 cc. of concentrated hydrochloric acid, and 10 cc. of water and boil till all the sulphate of iron is dissolved. Dilute with an equal volume of cold water and filter through an ashless filter, using the filter-pump. Wash, first with cold water, then alternately with cold water and hot dilute hydrochloric acid (sp. gr. 1.10), and finally with hot water. Place the filter and contents in a platinum crucible and burn the filter-paper at a low temperature, finishing with the blast or muffle till the precipitate of silica is perfectly white. If colored red, add three drops of sulphuric acid and 5 to 15 drops of hydrofluoric acid and heat cautiously under the hood to dryness; then use the blast till the iron is completely oxidixed. Cool in a desiccator and weigh. The difference between the last two weights is the exact weight of the silica. Should the sample contain chromium, correct results can best be obtained by fusing the impure silica with about 2 grams of pure potassium bisulphate, and heating cautiously till white fumes of sulphur trioxide are given off. Cool, dissolve the mass in dilute hydrochloric acid, filter off the purified silica; treat as in the first operation, and calculate in the usual manner.

In steel, 2 to 5 grams are dissolved in 30 to 60 cc. of concentrated hydrochloric acid and treated in the same manner as pig iron.

DETERMINATION OF SILICON IN FERRO-SILICON AND SILICO-SPIEGEL.

0.5 gram of the finely pulverized sample are placed in a 4-inch evaporating dish and 50 cc. of dilute hydrochloric acid,[1] made by using three volumes of water to one volume of concentrated acid, are added. Cover with an inverted watch-glass just large enough to drop inside of the dish. Place over a small flame, and evaporate to dryness. Follow the directions given for the determination of silicon in pig iron, and purify with hydrofluoric and sulphuric acids. Hydrofluoric acid is very conveniently handled, by cutting a light groove in the inside of the neck of the bottle, beginning below the termination of the stopper and extending upward a little more than half way to the top. Then cut a similar groove in the stopper, beginning a little below the termination of the groove in the neck and extend same to the upper end of the stopper. When the grooves are communicating, one drop at a time can be added. To close the orifice, the stopper is slightly turned so that the grooves are no longer communicating.

DETERMINATION OF SULPHUR IN IRON AND STEEL.

Aqua Regia Method.—Weigh, into an 8-oz. beaker, 6 grams of iron or steel, cover with a watch-glass and add 10 cc. of bromine water, and 60 cc. of aqua regia, a little at a time. After the violent action of the acid has ceased, place the beaker over a small flame till solution of the drillings is complete. Then evaporate rapidly till the excess of acid is expelled. Dilute to 120 cc. with cold water, mix thoroughly and filter exactly 100 cc. (the equivalent of five grams), add 5 cc. of a saturated solution of citric acid, and 10 cc. of a 10 per cent. solution of barium chloride. Stir occasionally and set aside over night. Carefully decant the clear supernatant liquid into a platinum Gooch crucible, containing an accurately-fitting disk of filter-paper, using moderate suction. Discard the clear filtrate, and detach

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[1] The formula for mixing this solvent was first obtained from Mr. C. B. Murray, of Edgar Thompson Steel Works, Braddock, Pa.

from the pump. Now transfer the entire precipitate to the filter and wash with a dilute solution of hot hydrochloric acid, using a few drops of hydrofluoric acid to dissolve any silica that may have been carried down with the precipitate, continue the washing till the precipitate is entirely free from iron salts, and lastly use a little hot water. Place the cap on the crucible and dry over a small flame. Then burn off the carbon completely, cool in a desiccator, and weigh. Multiply the weight of barium sulphate by 13.7 and divide by 5. The result will be the per cent. of sulphur in the sample.

Evolution Method.—5 grams of iron or steel are placed in a 16-oz. ring-neck flask, carrying a 4-oz. funnel-tube and a delivery-tube, the latter terminating at the bottom of an 8-inch test-tube containing a solution of ammoniacal cadmium chloride. 4 oz. of hydrochloric acid (sp. gr. 1.10) are placed in the funnel-tube and allowed to flow into the flask. After the violent action of the acid has ceased, place the flask over a small flame and continue the evolution till the drillings are completely dissolved. Finally bring the solution to a boil for about two or three minutes. Disconnect the flask and remove from the heat. Transfer the contents of the tube to a white bowl and dilute with 200 cc. of cold water. Acidulate with hydrochloric acid by conducting it through a tube to the bottom of the solution. Add 3 cc. of starch solution and titrate with standard solution of iodine, 1 cc. of which is equivalent to 0.01 per cent. of sulphur in 5 grams of the sample, thus obviating the necessity for a calculation.

The *iodine solution* is made by dissolving 4 grams of resublimed iodine in 8 grams of pure potassium iodide dissolved in 10 cc. of water, and diluted to one liter, which makes approximately the strength desired. The solution is then accurately standardized by running the iodine solution against an exact weight of sodium thiosulphate, this weight having been previously determined, by first accurately standardizing the iodine solution by the bichromate and thiosulphate method, and then carefully determining, by numerous experiments, the exact weight of sodium thiosulphate equivalent to the iodine. This having been done on a large quantity of the thiosulphate and the weight noted on the container, makes the work of standardizing iodine both accurate and rapid.

DETERMINATION OF PHOSPHORUS IN PIG IRON AND STEEL.

Weigh into a 6-oz. casserole 1.63 grams of drillings, and cover with an inverted watch-glass just large enough to drop inside of the dish. Add 50 cc. of nitric acid (sp. gr. 1.20), and place over a small flame; when solution is complete, evaporate rapidly to dryness. Then increase the heat till the bottom of the dish is a dull red, and continue this heat till oxidation of the organic matter and phosphorus is complete, which may be indicated by holding the wet stopper of the ammonia bottle within the dish. The absence of white fumes indicates that this stage of the process is completed. The watch-glass need not be removed if care be taken not to cool the dish too rapidly. When cold, dissolve the mass in 15 cc. of a mixture of 390 cc. concentrated hydrochloric acid and 60 cc. concentrated sulphuric acid. Evaporate till the mass has the appearance of burnt sugar, or almost to dryness. Now add, drop by drop without cooling, 10 cc. hot dilute hydrochloric acid, and sufficient water to effect complete solution of the mass, concentrate, add 10 cc. strong nitric acid, and boil till the red fumes pass off. Dilute with 25 cc. of cold water, and filter under strong suction. Wash first with cold water, then with a few drops of hot hydrochloric acid, and then with hot water. To the filtrate add 10 cc. of strong ammonia, and then just enough strong nitric acid to dissolve the precipitated iron and render the solution a deep amber color. Heat or cool to exactly 80° C., add 40 cc. of molybdic acid solution, and shake. Set in a warm place till the precipitate settles, which should not be more than fifteen to thirty minutes.

Filter through a Gooch crucible containing an accurately-fitting disk of No. 0 Swedish filter-paper, using strong suction. The precipitate will not run through if the solution, before precipitation, is not too strongly acid. Otherwise it invariably runs through. The precipitate is thoroughly washed with a solution of 2.5 per cent. hydrochloric acid and 2.5 per cent. molybdic acid solution. The crucible and contents are transferred to the hot air-bath and dried at 120° C. Or the precipitate may be thoroughly dried in three minutes by drawing clean, dry, hot air through the crucible. If the disks are cut from carefully selected filter-paper, they will not vary in weight more than 1 milligram, and by noting this we can eliminate one weight in each determination. The solvent action of the solutions do not appreciably affect the weight of the paper disk as might be the case in using a whole filter.

If extreme accuracy be required, the precipitate may be dissolved off the disk with ammonia, neutralized with hydrochloric acid and let stand over night. Any iron or silica that may have been retained by the precipitate can be estimated by filtering through the same disk, washed, dried, and weighed. On subtracting this result from the previous weight, the difference between the two weights in milligrams, will be the per cent. of phosphorus in the sample.

In checking all results, the molybdate-magnesia method is used mainly, as described by Prof. N. W. Lord in his "Notes on Metallurgical Analysis," p. 22.

DETERMINATION OF MANGANESE.

Weigh 5 grams of iron or steel into a 6-oz. casserole and dissolve in 60 cc. of strong nitric acid. When solution is complete, add 10 cc. of concentrated hydrochloric acid and boil five minutes. Filter, if necessary, and concentrate the filtrate to a small bulk. Add 25 cc. of strong nitric acid and 5 grams of pure potassium chlorate, cover with a watch-glass, and boil ten minutes. Repeat this operation once, if the sample is low in manganese, and twice if high. Boil fifteen minutes after the last addition of potassium chlorate, filter through an asbestos plug, and wash with strong nitric acid. Transfer the plug and precipitate to the same beaker in which the precipitation was made, rinsing out the last particles with dilute hydrochloric acid, add a few crystals of oxalic acid, dilute with 25 cc. of hot water, and boil till the manganese dioxide is completely dissolved. Filter and wash thoroughly with hot water, and boil the filtrate a few minutes. Dilute to 250 cc., and cautiously add dilute ammonia water (1 : 1) till a faint permanent precipitate of iron is produced; add slowly 25 cc. of a concentrated solution of ammonium acetate with constant stirring. Cover the beaker and boil three minutes; allow the precipitate to settle, and decant the supernatant liquid through a filter, letting the filtrate run into a 24-oz. beaker, and wash the precipitate once or twice by decantation. Transfer the precipitate to the filter and wash once with hot water. Redissolve the precipitate with the least quantity of hot dilute hydrochloric acid, allowing the solution to run into the same beaker in which the precipitation was made, and make a second basic acetate separation in the same manner. Test this precipitate with sodium carbonate on a platinum wire, and if not free from manganese, make a third separation. Concentrate the filtrate to about 300 cc. and add 5 to 10 cc. of acetic acid, boil, and add 5 to 10 grams of ammonium phosphate, stirring till crystalline. Finally, add 15 to 25 cc. of strong ammonia and continue the stirring till the precipitate is completely crystalline in its characteristic silky form. Remove from the heat and let the precipitate settle. Filter through an ashless filter and wash thoroughly with water containing a few cubic centimeters of ammonia. Transfer the precipitate to a deep platinum crucible and heat cautiously till the filter-paper is charred. Then increase the heat slowly to the highest temperature of the blast, and continue this heat till the precipitate is perfectly white and constant in weight. Cool in a desiccator, weigh, multiply the weight by 0.3874, divide by the number of grams taken, and the result will be the per cent. of manganese in the sample.

DETERMINATION OF NICKEL IN STEEL.

Weigh into a large beaker 0.5 to 2 grams of steel, and dissolve in dilute hydrochloric acid (sp. gr. 1.12). Add 10 cc. bromine water and boil till iron is completely oxidized. Dilute to about 400 cc. with water. Precipitate the iron with concentrated ammonia, filter rapidly on a ribbed filter, and wash the precipitate three or four times with hot water. Suck the precipitate dry, puncture the filter, and wash the precipitate into the original beaker. Dissolve the last traces of the precipitate with hot dilute hydrochloric acid, add ten cc. strong hydrochloric acid, and, when solution is complete, dilute to 300 cc. with water and precipitate the iron as before, using a moderate excess of ammonia. Make at least four precipitations in this manner, using an excess of ammonia each time; combine the filtrates and concentrate till crystallization of the salts begins. Place on a steam-bath and dissolve any separated salts in 25 cc. of strong ammonia. Filter through a small filter and wash with dilute ammonia water till the filtrate measures 275 cc. in volume. Precipitate the nickel on a weighed platinum cylinder which is connected with the zinc plate of a battery of 2 or 3 Bunsen cells, keeping the solution at 80° C.

DETERMINATION OF NICKEL AND COBALT.

1 to 5 grams of the sample are placed in a small flask, and a mixture of 5 cc. of concentrated nitric acid, 5 cc. of concentrated sulphuric acid, and 3 cc. of concentrated hydrochloric acid added for every gram of the sample taken. Heat over a small flame till solution is complete and copious fumes of sulphuric anhydride are given off, adding more sulphuric acid if required to avoid going to dryness. Cool, dilute with water, filter, and wash thoroughly with hot water. If second group bases are present, the filtrate is heated to about 70° C., and a strong current of hydrogen sulphide gas is passed through the solution till the latter is cold. Filter out the precipitated sulphides, wash thoroughly with hydrogen sulphide water, and boil the filtrate. While boiling add hydrochloric acid and potassium chlorate, a little at a time, till oxidation of the iron is complete. Dilute with water and add ammonia, stirring constantly, till the iron is completely precipitated, and the solution decidedly alkaline. Filter and wash the precipitate once or twice with hot water. Dissolve the precipitate with dilute hydrochloric acid and add ammonium carbonate till a slight permanent precipitate is produced. Add one drop of hydrochloric acid to clear the solution, then 10 to 15 grams of ammonium acetate and bring to a boil. Remove from the heat a few minutes till the precipitate settles, and filter, using moderate suction. Wash with hot water, and dissolve the precipitate with dilute hot hydrochloric acid, letting the solution run into the original beaker, and make a second precipitation in the same manner as the first. Combine the filtrates, concentrate to 350 cc., and acidify slightly with acetic acid.

Boil and pass a current of hydrogen sulphide through the solution while boiling. Filter off the precipitated sulphides of nickel and cobalt, and wash thoroughly with hydrogen sulphide water. Acidify the filtrate slightly with acetic acid and boil. If any further precipitation takes place, collect on a filter and wash as above. Transfer the precipitates from the filters as completely as possible, ignite the filters, and add the ashes to the precipitates and dissolve the sulphides in aqua regia. Expel the excess of acid by evaporation, dilute with water, add a solution of moderately strong potassium hydroxide, and heat almost to boiling for some time. Filter, wash, and transfer the precipitate to a beaker as completely as possible, dissolving off the last traces with a solution of potassium cyanide, receiving the filtrate in the beaker containing the precipitate. Warm gently till the precipitate is dissolved, and heat to boiling to expel excess of hydrocyanic acid. Add to the hot solution finely pulverized mercuric oxide and boil. Filter off the precipitated nickel, wash, dry, and ignite in a weighed porcelain crucible. Multiply the weight of the precipitate by 0.78667 to obtain the weight of the nickel, from which the per cent. can be readily calculated.

In order to insure accurate results, boil the oxide in water, filter, wash, dry, and ignite as before. A decrease in weight is likely due to some adhering salt. Dissolve the nickel in aqua regia, dilute in water, and filter through an ashless filter. Ignite, weigh, and deduct from the oxide of nickel. Dilute the filtrate, add an excess of ammonia, and let stand over night. If a precipitate occurs, filter, wash, ignite, and deduct this weight also from the weight of the nickel oxide. From the remainder, calculate the per cent. of metallic nickel.

Carefully neutralize the filtrate from the precipitated nickel by mercuric oxide, with nitric acid, and add a solution of mercurous nitrate as long as a precipitate of mercury cobaltocyanide is formed. Filter, wash, and dry the precipitate, and reduce the cobalt to the metallic state in a current of hydrogen in a Rose crucible, and weigh.

DETERMINATION OF CHROMIUM IN CHROME ORE AND FERROCHROME.

Weigh into a platinum crucible, whose capacity is not less than 40 or 50 cc., 0.5 gram of fine ground ore, place on top of it 25 grams of potassium bisulphate, and fuse very cautiously over a very low flame. After the mass is in a liquid condition, increase the heat cautiously to dull redness. Carefully run the fusion up on the sides of the crucible to dislodge any stranded particles of ore. The mass must now be kept in a state of tranquil fusion at least forty or fifty minutes, or longer if the sample has not been finely pulverized. Cool the crucible, place it in a 5-inch casserole, cover the crucible with hot water, and invert a watch-glass over the solution and crucible just large enough to drop inside the edges of the dish. Place the dish in an air-bath at 120° C. till the contents are readily washed from the crucible. Wash off the watch-glass, add 35 to 40 cc. concentrated hydrochloric acid and 15 cc. of hot water, and boil gently till solution is complete. Remove from the heat and let the silicious matter settle. Decant the supernatant liquid into a 12-oz. beaker, add 15 or 20 cc. more hydrochloric acid to the residue, and boil gently fifteen minutes longer. Combine the two solutions and filter through an ashless filter, wash, ignite, and weigh the silica. The filtrate is made slightly alkaline with ammonia and heated on the steam-bath till the chromium, iron, and aluminum are completely precipitated and the excess of ammonia is volatilized. Filter without washing, dissolve the precipitate in dilute hydrochloric acid, and receive the filtrate in the original beaker. Reprecipitate in the same manner, filter, and wash the precipitate two or three times with hot water. Combine the two filtrates and determine the calcium and magnesium by any good method. Transfer the precipitate and filter to the 5-inch casserole, add 50 cc. of strong nitric acid, cover with a watch-glass, heat gently to boiling, and add, cautiously, potassium chlorate, little by little, till the iron and chromium are completely oxidized, which is indicated by the deep orange color of the chromic acid. Transfer to a beaker and dilute to 200 cc. with water. Precipitate the iron and aluminum with ammonia and filter into a 24-oz. beaker, without washing. Dissolve the precipitate with warm, dilute nitric acid, and receive the filtrate in the same beaker in which it was made. Reprecipitate as before and filter, receiving the filtrate in the same beaker as the first. Repeat these solutions and precipitations till the resulting precipitate of iron and aluminum gives no reaction for chromium when a small part of it is fused on a platinum wire with sodium carbonate. The iron and aluminum may be determined by any good method. To the filtrate containing the chromium, add acetic acid to slight acid-reaction, and add 10 cc. of a 20 per cent. solution of lead acetate. Cover and set aside for about four hours, stirring frequently. Filter on a Gooch crucible as in the determination of phosphorus, and wash with cold water till the washings give no reaction for lead with fresh hydrogen sulphide water. Dry in an air-bath at 100° C. till the precipitate ceases to lose weight. If pure, 16.181 per cent. of the weight is metallic chromium.

DETERMINATION OF CARBON IN IRON AND STEEL.

The determination of carbon is made according to the process described in Blair's "Chemical Analysis of Iron," Third Edition, p. 148.

DETERMINATION OF GRAPHITE IN PIG IRON.

1 to 3 grams of pig iron are carefully separated with a magnet and dissolved slowly in 30 to 60 cc. of nitric acid (sp. gr. 1.13) in an 8-oz. beaker. Set aside till the graphite settles. Dry and weigh accurately a platinum Gooch crucible containing an accurately-fitting disk of filter-paper. Place in the filtering tube, and filter the solution through the crucible, using strong suction. Wash alternately with hot dilute hydrochloric acid (sp. gr. 1.10) and cold water; then with a 10 per cent. solution of caustic soda, alternating with hot dilute hydrochloric acid and hot water, and finally with much acid and hot water till the last traces of soda are washed out; and lastly, with ether. Dry in an air-bath at 100° C. and weigh. Ignite the crucible in the blast till all the graphitic carbon is completely oxidized; cool and weigh. Any increase in weight over the

weight of the empty crucible will be the weight of retained silica. This subtracted from the previous weight of the precipitate, will give the true weight of graphite.

VII. METHODS USED AT THE LABORATORY OF THE HAINSWORTH STEEL CO., EDITH FURNACE DEPARTMENT, ALLEGHENY, PA.

By R. G. Johnston.

DETERMINATION OF SILICA IN IRON ORES.

Weigh out 1 gram of the finely ground ore, and transfer to a platinum crucible containing about 10 grams of sodium carbonate. Fuse for about fifteen minutes, or until a quiet fusion is obtained. Allow the crucible to cool, and place it in a beaker containing about 40 cc. of water; add about 15 cc. of hydrochloric acid to dissolve the fused mass out of the crucible. Remove the crucible, rinsing it with a fine jet of water. Stand the beaker on the sand-bath, and evaporate its contents to dryness over night. Moisten the mass with a few cubic centimeters of hydrochloric acid, and add about 30 cc. of hot water. When all has dissolved, filter, wash well with hot water, dry, ignite, and weigh as SiO_2.

The filtrate may be used for determining either iron or alumina.

DETERMINATION OF IRON IN IRON ORES.

Weigh off 0.5 gram of the finely ground ore into a beaker without lip. Digest with 30 cc. of hydrochloric acid over night on the sand-bath. A solution of stannous chloride is now added drop by drop until the ferric chloride solution is completely deoxidized. Dilute with about 100 cc. of hot water and add 30 cc. of a solution of mercuric chloride to oxidize an excess of stannous chloride.

Titrate with a standard solution of potassium bichromate, testing after each addition of the standard solution with a drop of potassium ferricyanide, on a white plate, for ferrous chloride.

The stannous chloride solution is made by dissolving 80 grams of the common salt in 500 cc. of water and an equal volume of hydrochloric acid.

To prepare the mercuric chloride solution dissolve 50 grams of the compound in 1 liter of water acidified with 15 cc. of hydrochloric acid.

DETERMINATION OF PHOSPHORUS IN IRON ORES.

Weigh out 5 grams of the sample (10 grams if very low in phosphorus) and digest in a beaker with boiling hydrochloric acid for about one-half hour. Filter, and fuse the residue with about 4 grams of sodium carbonate. Dissolve the fusion and evaporate the two solutions to dryness. Moisten with a few cubic centimeters of hydrochloric acid, take up with hot water and filter from the silica. Combine the two filtrates, and evaporate to a syrup. Add about 30 cc. of nitric acid (sp. gr. 1.42), and evaporate a second time to get rid of the last traces of hydrochloric acid. Dilute the solution to about 50 cc., and add 15 cc. of strong ammonia, which will form a thick paste. Dissolve the latter in about 30 cc. of nitric acid (sp. gr. 1.20). Heat the solution to 80° C., and add 100 cc. of molybdic acid solution. Stir for a few minutes and allow the precipitate to settle. After about one hour, filter, and wash with a one per cent. solution of nitric acid. Dissolve the precipitate on the filter with a solution of ammonia (1 : 2), allowing the solution to run into a small beaker containing a few crystals of citric acid and about 3 cc. of hydrochloric acid. The volume of the solution should now be about 100 cc. Add a few cubic centimeters of magnesia solution, stir well, and allow the mixture to stand over night. Filter and wash well with the above ammonia solution. Dry, ignite, and weigh. Dissolve the precipitate in the crucible in about 5 cc. of water and 3 cc. of nitric acid, and determine the weight of any residue insoluble in the acid. Deduct from the weight of the precipitate as obtained above. The difference is the weight of magnesium pyrophosphate derived from phosphate in the ore.

I have used this method for some three years and have always had good results.

DETERMINATION OF MANGANESE IN PIG IRON AND IRON ORE.

Weigh out 2 grams of the iron and dissolve in 40 cc. of nitric acid (sp. gr. 1.20). In a porcelain dish, 3.5 inches in diameter, evaporate to a syrup or until a further evaporation would cause iron to separate out as basic nitrate. Dilute and wash into a half-liter flask ; neutralize, and precipitate with oxide of zinc. Make the solution up to the mark, and shake well. Allow the precipitate to settle in a large beaker, decant off 250 cc. of the solution which correspond to 1 gram of iron, transfer to a flask, and heat to boiling. Titrate with a solution of potassium permanganate, shaking well after each addition of the standard solution. A pink coloration will show the end of the reaction.

For iron ores low in manganese, dissolve in hydrochloric acid of 1.20 sp. gr. If a hematite, add a few drops of nitric acid of 1.20 sp. gr. Magnetite will require more oxidizing agent. In other respects proceed as above.

DETERMINATION OF SILICON IN PIG IRON.

Ford's method is used for this determination. See Blair's "Chemical Analysis of Iron," Third Edition, p. 77.

DETERMINATION OF SULPHUR IN PIG IRON.

In determining sulphur, the evolution method is used. The hydrogen sulphide formed in dissolving the sample is absorbed in a solution of caustic soda (1 : 8), and, after acidification of the absorbent, titrated with iodine solution.

DETERMINATION OF PHOSPHORUS IN PIG IRON.

Emmerton's method as described by Blair's "Chemical Analysis of Iron," Second Edition, p. 95, is made use of.

DETERMINATION OF MANGANESE IN PIG IRON.

The method of Volhard as modified by O. Textor is used for the estimation of manganese. The details have already been given in the description of methods for the analysis of ores.

VIII. METHODS USED AT THE LABORATORY OF THE CARNEGIE STEEL CO., EDGAR THOMSON STEEL WORKS AND FURNACES, BRADDOCK, PA.

By C. B. Murray.

DETERMINATION OF SILICA IN IRON ORES.

1 gram of the dried ore is fused with 12 to 15 grams of sodium carbonate in a large platinum crucible. After thorough fusion the crucible and contents are cooled in a 12-oz. beaker containing about 200 cc. of water. About the same volume of strong hydrochloric acid is now added and the fusion is dissolved. The solution is evaporated to dryness on a steam table, the residue taken up with 50 cc. hydrochloric acid diluted with water, the silica filtered, ignited, and weighed.

In the case of manganese ores, 1 gram of the ore is dissolved in 50 cc. hydrochloric acid, boiled, filtered, and the residue fused. The fusion is added to the original solution. Then proceed as above. This is to avoid the action of chlorine on the crucible.

DETERMINATION OF IRON IN ORES.

0.5 gram of the ore is dissolved in 50 cc. hydrochloric acid. In case the residue left is not white the solution is filtered, the residue fused with sodium carbonate, dissolved out in hydrochloric acid, the iron precipitated as hydroxide, dissolved in dilute hydrochloric acid (1 : 1), and the solution added to main solution. As a rule there is no iron left in the residue, and then a fusion is not necessary.

To the hot solution of the ore, stannous chloride is added from a burette drop by drop, stirring all the while, till the solution is colorless. Three drops in excess are then added. After allowing a few minutes for the stannous chloride to complete the reduction of any iron adhering to the silica, dilute to about 400 cc. with cold water, add *all at once* 20 cc. mercuric chloride solution, and stir vigorously. Now add from a burette potassium bichromate enough to nearly oxidize all the iron. Place on a white tile several drops of the ferricyanide solution. Take out a drop of solution from the beaker and let it fall into a drop of the ferricyanide. Continue adding bichromate and testing as above till blue color is faint. Then take two drops for every test. Wait one-half minute at each test for color to develop. When no blue color appears at the end of one-half minute, take the burette reading, which gives directly the percentage of iron in the ore.

SOLUTIONS EMPLOYED.

The potassium dichromate solution contains 4.4 grams of the salt in 1 liter of water.

1 cc. corresponds to 0.005 gram iron, or to 1 per cent. when 0.5 gram of ore is employed.

The mercuric chloride solution contains 50 grams of the salt in 1 liter.

The stannous chloride solution contains 50 grams in 1 liter.

The potassium ferricyanide solution contains two or three pieces of the size of pin heads in 50 cc. of water. Prepare every other day.

DETERMINATION OF PHOSPHORUS IN ORES.

Dissolve 10 grams of the ore when the phosphorus is under 0.070 per cent., or 5 grams when it is above 0.070, in 150 cc. hydrochloric acid. Filter by suction. Treat the residue in the same manner as for silica and evaporate main solution to dryness on the steam table. Take up main solution and fusion of residue each with 100 cc. nitric acid. Heat on the sand-bath till all is in solution. Filter and unite the filtrates. To this liquid, which should not exceed 300 cc., add ammonia till the solution becomes a pasty mass. Add nitric acid till the iron is redissolved and the solution an amber tint.

Heat to 70° C. and add 60 cc. of the molybdate solution. Cork and shake thoroughly for five minutes. Let stand at a temperature of 40° to 50° C. for an hour. Filter through a 12.5-cm. filter. Wash thoroughly with a 2 per cent. nitric acid solution. Dissolve the yellow precipitate on the filter in strong ammonia and let the solution run through into a 5-oz. beaker containing about 1 gram citric acid dissolved in 10 cc. strong hydrochloric acid. After all the precipitate has been dissolved and run through the filter, stir the solution in the beaker and add 10 cc. magnesia mixture and fill up the beaker with strong ammonia. Stir a little and set in cold water till the solution is cold. Then stir vigorously until the precipitate comes down. Let stand over night. Filter through a 9-cm. filter. Wash thoroughly with dilute ammonia (1 : 3). Ignite, first at a low temperature, then at a higher. Weigh as $Mg_2P_2O_7$. Dissolve the weighed precipitate in dilute nitric acid (sp. gr. 1.20), heating crucible till all is in solution. Filter, ignite, and weigh the residue, which is mainly silica. Subtract this weight from the first and the difference is pure $Mg_2P_2O_7$.

SOLUTIONS USED IN PHOSPHORUS DETERMINATIONS.

Molybdic Acid Solution.—100 grams of molybdic acid are dissolved in 400 cc. of ammonia (sp. gr. 0.96). This is poured into 1 liter of nitric acid (sp. gr. 1.20), thoroughly stirred, and 1 cc. of a solution of sodium phosphate, containing 5 grams to the liter, added. The mixture is well shaken and allowed to stand twelve hours. The solution should be perfectly colorless.

Magnesia Mixture.—110 grams magnesium chloride and 280 grams ammonium chloride are dissolved in 1,300 cc. of water and 700 cc. ammonia (sp. gr. 0.96). The solution should stand at least a week before using.

DETERMINATION OF MANGANESE IN ORES.

Dissolve 1 gram of the ore dried at 100° C. in 25 cc. strong hydrochloric acid. When all is in solution, dilute with an equal bulk of water and filter. Wash twice with hot water. Ignite the residue till the filter-paper is destroyed. Cool, add to the crucible two or three drops of sulphuric acid and a little hydrofluoric acid, and evaporate to dryness to expel silica. Fuse the residue with about 3 grams sodium carbonate. Dissolve fusion in the original filtrate from first solution, and evaporate this to dryness in the sand-bath. Take up in 150 cc. strong nitric acid. Boil for about twenty minutes, and then add, a little at a time, 5 to 8 grams potassium chlorate. When enough has been added to oxidize all the manganese, the solution will give a little puff and the green fumes will disappear. Now add about 1 gram more potassium chlorate and boil the solution for two minutes. Cool and filter through a prepared asbestos filter or "plug." Wash beaker and plug twice with strong nitric acid. The filtrate should then be boiled and more potassium chlorate added to ascertain if all the manganese has been precipitated. The manganese dioxide on the plug, together with the asbestos, is now returned into the same beaker in which the precipitation was made, dissolved in 25 cc. hydrochloric acid and boiled a few minutes. The asbestos is filtered off and a few drops of sulphuric acid are added to precipitate any barium which is generally found in manganese ores. Let stand about two hours. Now add ammonia till a faint precipitate appears, then 25 cc. of ammonium acetate solution. Boil for one minute, remove from the heat, and, as soon as settled, filter. Wash three times with hot water. Dissolve precipitate on filter in hydrochloric acid (1 : 1) and let run into beaker in which first basic acetate separation was made. Make a second basic acetate separation just as the first. Combine the filtrates and dilute to about 400 cc. Add 40 cc. ammonium phosphate solution and then acidulate with hydrochloric acid. Boil and add ammonia, drop by drop with constant stirring, until all the manganese is precipitated and the precipitate is in the well-known crystalline form. Let the solution cool, filter with suction, wash three times with hot water, ignite, and weigh as $Mn_2P_2O_7$.

SOLUTIONS EMPLOYED.

Ammonium Acetate Solution.—Dissolve 450 grams of the salt in 8 liters of water.

Ammonium Phosphate Solution.—Dissolve 560 grams of the salt in 2.5 liters of water.

DETERMINATION OF MANGANESE IN MANGANIFEROUS IRON ORES.

Dissolve 1 gram of iron ore in 50 cc. hydrochloric acid. Evaporate to dryness on the steam-bath. Take up in 20 cc. nitric acid, and evaporate to about 10 cc. Wash into a 500-cc. flask, dilute to about 200 cc., and add a solution of zinc oxide in water till all the iron is precipitated. Dilute to 500 cc., make acid, shake well, let settle, and decant off 250 cc. into a flask. Boil for about five minutes. Titrate with a standard solution of potassium permanganate.

DETERMINATION OF SILICON IN PIG IRON.

Dissolve 1 gram of iron in 20 cc. strong hydrochloric acid in a platinum dish. Evaporate to dryness over a bare flame. Heat for one minute after it is dry. Remove flame, add 10 cc. hydrochloric acid and about 25 cc. water. Boil, filter, ignite, and weigh as SiO_2.

DETERMINATION OF SULPHUR IN PIG IRON.

Dissolve 5 grams in 100 cc. hydrochloric acid (1 : 1) in a 500-cc. flask. Pass the gas evolved through two U-tubes containing each 25 cc. potassium hydroxide solution. After the evolution of gas has ceased, heat the flask to boiling and boil till inlet-tube to first U-tube is hot. Remove the tube and draw off the potassium hydroxide solution from the U-tubes by means of a stop-cock at bottom into a large porcelain dish. Dilute to 500 cc. Titrate with a standard solution of iodine.

SOLUTIONS EMPLOYED.

The potassium hydroxide solution contains 1 pound caustic potash in 17,000 cc. of water. The starch solution is prepared by dissolving 4 grams starch in a liter of boiling water and decanting the clear liquid for use.

The iodine solution is standardized by using a standard steel and also a "shot" sample. The factor varies considerably between the two. For pig-iron drillings and steel, the steel factor is used. For "shot" samples the shot factor.

DETERMINATION OF PHOSPHORUS IN PIG IRON.

Dissolve 1.63 grams in 25 cc. nitric acid (sp. gr. 1.20) in a 4½-inch dish. Evaporate to dryness over a lamp and bake for one-half hour. Take up in 20 cc. hydrochloric acid and evaporate till the volume of the solution is about 4 cc. Add about 5 cc. nitric acid and heat till red fumes cease to come off. Dilute twice with water and filter into an 8-oz Erlenmeyer flask. Add ammonia till a paste is formed, then nitric acid till the solution shows an amber color. Heat to 40° C. and add 50 cc. molybdate solution. Shake for five minutes and let stand one-half hour. Filter and wash five times with 2 per cent. nitric acid and twice with strong alcohol. The filters are then placed in a water-bath and heated one hour, removed, and weighed in a "clip." Of course the filter-papers should have been heated one hour and weighed previously. Since we started with 1.63 grams, calling the percentage of phosphorus in yellow precipitate 1.63, every milligram equals 0.001 per cent. phosphorus.

The solutions are the same as used in an ore analysis.

DETERMINATION OF MANGANESE IN PIG IRON.

1 gram of iron is dissolved in 25 cc. nitric acid (sp. gr. 1.20), evaporated to about 10 cc.; then proceed as in case of manganese in manganiferous iron ores.

DETERMINATION OF CARBON IN STEEL.

In case of steels of over 0.50 per cent. carbon take 1 gram; for steels under 0.50 take 2 grams. Dissolve in 100 cc. in first case, or 150 cc. in second, of the double chloride of copper and potassium solution. The process may be hastened by stirring and heating to about 80° C. After all is in solution filter into a platinum boat, wash four or five times with dilute hydrochloric acid (1 : 1) and with hot water. For the combustion a platinum tube is used containing six inches of copper oxide held in place by platinum gauze.

The oxygen used in the combustion is purified by passage, first through a bottle of potash solution, and second through a jar of solid potash, upon which a layer, one inch deep, of calcium chloride rests. A ten-burner Bunsen furnace is used.

Two burners are lighted under the copper oxide in the platinum tube. When this point is red hot all the burners are lighted and oxygen passed through for half an hour. The carbon dioxide is caught in a solution of barium hydroxide in a Meyer tube containing six bulbs. For carbon under 1 per cent., 25 cc. of a saturated solution of barium hydroxide is sufficient. This amount will about fill four of the bulbs in the tube. At the end of half an hour the oxygen is shut off and air passed through the same train for fifteen minutes. The Meyer bulb is then detached and the solution filtered through a 9-cm. filter using suction. By means of a rubber tube connected with the train a jet of air is forced into the funnel during filtering, keeping an atmosphere free from carbon dioxide surrounding the filter-paper. The tube is easily washed clean. The filter-paper with precipitated barium carbonate is put into a platinum crucible and the crucible subjected to gentle heat until the filter-paper is burnt, then placed in a muffle furnace and heated till white. It is weighed as $BaCO_3$ and carbon calculated.

SOLUTIONS EMPLOYED.

Double Chloride of Copper and Potassium.—2,250 grams of the double salt are dissolved in 6.5 liters of water and 0.5 liter hydrochloric acid added.

The barium hydroxide solution contains 20 grams of the commercial baryta dissolved in 1 liter of water.

DETERMINATION OF SULPHUR IN STEEL.

5 grams of steel are dissolved in 100 cc. hydrochloric acid (1 : 1). From this point on, the method employed is the same as in the case of pig iron.

DETERMINATION OF PHOSPHORUS IN STEEL.

Dissolve 1.63 grams of steel in 25 cc. nitric acid (sp. gr. 1.20), and proceed in the same manner as in the case of pig-iron, except that it is not necessary to filter off graphite.

DETERMINATION OF MANGANESE IN STEEL.

Dissolve 1 gram in 25 cc. nitric acid (sp. gr. 1.20) and proceed as in the case of pig iron.

DETERMINATION OF NICKEL IN STEEL.

Use the method given by Blair, in "Chemical Analysis of Iron," Third Edition, p. 184.

IX. METHODS USED AT THE LABORATORY OF THE CLINTON IRON AND STEEL CO., PITTSBURG, PA.

By A. B. Harrison.

DETERMINATION OF SILICA IN IRON ORES.

The ore is treated according to the directions given in Blair's "Analysis of Iron," Third Edition, p. 239.

DETERMINATION OF IRON IN ORES.

The sample is dissolved in concentrated hydrochloric acid, the insoluble residue fused with sodium carbonate, and the fusion dissolved in dilute hydrochloric acid. Ths solution of ferric chloride obtained is reduced with stannous chloride, the excess of the latter being oxidized with mercuric chloride. The reduced iron solution is titrated with potassium bichromate.

DETERMINATION OF PHOSPHORUS IN ORES.

The sample is dissolved in hydrochloric acid, the insoluble residue fused with sodium carbonate, and the fusion dissolved in dilute sulphuric acid. The filtrate from the insoluble residue and the filtrate from the solution of its fusion are combined, precipitated with ammonia (sp. gr. 0.96), and the precipitate dissolved in nitric acid (sp. gr. 1.13). The determination is then proceeded with as in the case of steel.

DETERMINATION OF MANGANESE IN ORES.

See the method described for determination of manganese in pig iron, p. 58.

DETERMINATION OF SILICON IN PIG IRON.

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Drown's method somewhat modified is used. Dissolve 0.4667 gram of drillings in "silicon mixture" in a covered porcelain dish, and evaporate the solution to dryness without removing the cover. When the dish is sufficiently cool wash off the watch-glass into the dish, and rinse down the sides of the dish with hot dilute hydrochloric acid (1 : 1) until the volume of the liquid is

50 cc. Boil until all iron salts are dissolved, filter with the aid of suction, and wash alternately with hot water and dilute hydrochloric acid until all iron is washed out. Burn and weigh. Ashless filters being used, no calculation beyond " pointing off" will be necessary, as can readily be seen.

The silicon mixture is made as follows: Mix 1,500 cc. of water, 500 cc. of nitric acid of 1.40 sp. gr., and 150 cc. of sulphuric acid of 1.84 sp. gr.

DETERMINATION OF SULPHUR IN PIG IRON.

The determination of sulphur is carried out according to the " iodine method" as given in Blair's "Analysis of Iron," Third Edition, pp. 68–71. In this form the method is the iodine method as modified by Mr. E. T. Wood.

DETERMINATION OF PHOSPHORUS IN PIG IRON.

For this purpose I use Emmerton's method as described by Dr. Dudley.

DETERMINATION OF MANGANESE IN PIG IRON.

Manganese is determined according to a modification of Volhard's method. One gram of drillings is dissolved in 100 cc. of silicon mixture in a porcelain evaporating dish. After solution 5 cc. of concentrated hydrochloric acid are added, and the contents of the dish evaporated to dryness. The cover of the dish is washed off with hot water and the residue taken up with 100 cc. of water. Boil till all iron salts are dissolved. Transfer the solution without filtering to a liter flask, and dilute with water to 300 cc. Bring the contents of the flask to boiling, and add pure zinc oxide suspended in water till all iron is precipitated and zinc oxide is present in slight excess. Titrate the contents of the flask while boiling hot and without filtering with potassium permanganate solution.

DETERMINATION OF SILICON, SULPHUR, PHOSPHORUS, MANGANESE, AND NICKEL IN STEEL.

Silicon is determined as described in Blair's " Analysis of Iron," Third Edition, p. 72.

Sulphur is estimated by the method given for pig iron. The aqua regia method is used for checking.

Phosphorus is determined as in pig iron. Results are checked by the " magnesia method."

For nickel determinations the method of A. T. Eastwick is used. See *Proceedings of the Engineers' Society of Western Pennsylvania*, 9, 170.

Manganese is determined by the method described for pig iron.

X. METHODS USED AT THE LABORATORY OF THE ISABELLA FURNACE CO., ETNA, PA.

By F. G. Brinker.

DETERMINATION OF SILICA IN IRON ORES.

Dissolve 1 gram finely powdered ore in hydrochloric acid, dilute, filter, wash, and fuse residue with a mixture of sodium and potassium carbonates. The fusion is dissolved in a beaker in hydrochloric acid. Evaporate to dryness and bake. Dissolve in hydrochloric acid, dilute the solution, filter, wash the residue with hot water, dilute hydrochloric acid, and again with hot water. Burn and weigh.

DETERMINATION OF IRON IN IRON ORES.

Dissolve 1 gram of ore, finely pulverized, in a flask in 40 cc. hydrochloric acid, at a gentle heat. Add 1 gram of potassium chlorate. Place a funnel in the neck of the flask and boil gently till chlorine is expelled. Dilute to 50 cc., heat nearly to boiling, and deoxidize with a solution of stannous chloride measured by means of a burette. Cool, and titrate back the excess of stannous chloride with a solution of iodine.

If greater accuracy be required filter and fuse the insoluble residue, dissolve in acid, and add to the main solution before deoxidizing.

In preparing the standard iron solution, fine iron wire is used and treated as above described. The first factor is found by standardizing the stannous chloride and iodine solutions. Take 2 cc. of stannous chloride solution, dilute, add a little starch solution, and titrate with iodine solution. Divide the number of cubic centimeters of iodine into the number of cubic centimeters of stannous chloride. Multiply the number of cubic centimeters of iodine used to titrate back the excess of stannous chloride used by this factor, and subtract from the total volume of stannous chloride used for the reduction. The second factor is found by dividing the number of cubic centimeters of stannous chloride, used for the standard after the excess has been subtracted, into the weight of pure iron in the iron taken.

Multiply the number of cubic centimeters of stannous chloride solution by this and by 100. This gives the per cent. of iron in the sample.

SOLUTIONS EMPLOYED.

Stannous Chloride Solution.—Dissolve 60 grams of crystals in 125 cc. hydrochloric acid and 125 cc. water. To this solution there are added 650 cc. hydrochloric acid and 1,650 cc. water.

Iodine Solution.—This contains 8 grams iodine dissolved in potassium iodide solution and diluted to 1 liter.

I use also the permanganate method as described by Blair, deoxidizing by zinc. When titanium is present, I use acid ammonium sulphate.

DETERMINATION OF MANGANESE IN IRON ORES AND PIG IRON.

I use Williams' method and also Volhard's as described in Blair's "Chemical Analysis of Iron," Third Edition, pp. 112–117.

DETERMINATION OF PHOSPHORUS IN IRON ORE.

I use the molybdate-magnesia method as described by Blair in "Chemical Analysis of Iron," Third Edition, p. 89.

DETERMINATION OF SILICON IN PIG IRON

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Dissolve 0.9333 gram of drillings in a casserole in hydrochloric acid, and evaporate to dryness. Cool and take up with hydrochloric acid, heating the mixture to boiling. Dilute, filter, wash with dilute hydrochloric acid, and finally with hot water. Ignite cautiously until the filter has been burned off. The ignition is then continued for fifteen minutes at the highest heat of a gas blast-lamp. Cool and weigh. The weight of the silica found divided by 2 and multiplied by 100 gives the percentage of silicon.

DETERMINATION OF PHOSPHORUS IN PIG IRON.

Weigh 1.63 grams of well-mixed borings into a 500-cc. beaker and add cautiously 35 cc. nitric acid of 1.20 sp. gr. Boil down to dryness, and bake on a hot plate at 200° C., for thirty minutes. Redissolve in hydrochloric acid. Add 35 cc. of concentrated nitric acid and evaporate until the volume of the liquid is reduced to about 15 cc. Remove from hot plate, dilute with hot water, filter, and to the filtrate add ammonia until a precipitate forms which does not disappear on stirring. The neutralized solution is treated with 3 cc. of concentrated nitric acid, which should suffice to redissolve the precipitate and give a clear, amber-colored liquid, not red in tint. The solution is then heated to about 70° C., the molybdate solution added, and the mixture shaken for five minutes. Let the precipitate settle, collect it on a weighed filter, and wash with water containing 2 per cent. of nitric acid. Dry in the air-bath at 120° C. for thirty minutes after all visible moisture has disappeared, and weigh.

XI. METHODS USED AT THE LABORATORY OF THE SHENANGO VALLEY STEEL CO., NEW CASTLE, PA.

By Warren R. Clifton.

DETERMINATION OF SILICA AND IRON IN ORES.

Weigh 1 gram of the sample into a No. 2 beaker, add 25 cc. of strong hydrochloric acid, cover with a watch-glass, and digest at a temperature just short of boiling until the ore is decomposed; dilute with 25 cc. of water and filter into a No. 4 beaker. The residue is then burned and fused with sodium carbonate, the fusion dissolved in the filtrate from the residue, and the whole allowed to go to hard dryness. Redissolve the mass in about 15 cc. of strong hydrochloric acid, dilute, filter into a 300-cc. flask, and wash the residue three or four times with hot water; ignite and weigh as SiO_2. In the filtrate the iron is deoxidized by granulated zinc and determined by titration with a standard bichromate solution ; the addition of the standard is continued until a drop of the iron solution added to a drop of potassium ferricyanide solution no longer produces a blue coloration on standing one-half minute. The number of cubic centimeters of bichromate solution used multiplied by one hundred times the value of 1 cc. in iron, gives the percentage of iron.

Potassium Bichromate Solution.—Dissolve 17.570 grams of the fused salt in water, dilute to 2 liters, and standardize with iron wire.

DETERMINATION OF PHOSPHORUS IN ORES.

Digest 5 grams of the samples dried at 100° C., in a No. 2 beaker, covered by a watch-glass in 50 cc. of strong hydrochloric acid. When the ore appears to be perfectly decomposed, dilute, and filter into a No. 5 beaker. The residue is burned and fused with sodium carbonate, the fusion dissolved in hot water, the solution acidified with strong hydrochloric acid, added to the original filtrate, and the combined solutions allowed to go to hard dryness on the hot plate. The mass is then moistened with a little hydrochloric acid, diluted with a sufficient amount of water to dissolve the sodium salt, and filtered into a 400-cc. Erlenmeyer flask. The process is then carried on as in the case of steel.

DETERMINATION OF MANGANESE IN IRON ORES.

2 grams of ore are dissolved and further treated in the same manner as for phosphorus and the solution filtered into a 500-cc. flask. The solution is neutralized with ammonia until a slight permanent precipitate forms. Redissolve this with a few drops of hydrochloric acid, and add ammonium carbonate, drop by drop, until a faint precipitate is formed. Add about 4 grams of sodium acetate, boil one minute, and allow the precipitate to settle. Filter into a 500-cc. flask, and wash two or three times with hot water. The precipitate is washed back into the same flask in which the precipitation was made, and dissolved in the least possible quantity of hydrochloric acid. The precipitation is repeated exactly as before. Unite the filtrates and proceed as in the case of steel.

DETERMINATION OF SILICON IN PIG IRON.

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Twice the factor-weight—0.9340 gram of drillings—is weighed off into a No. 5 beaker. Add 50 cc. of water, and then pour into the mixture 20 cc. of sulphuric acid (sp. gr. 1.85), directing the acid to the center of the beaker. Evaporate until copious fumes of sulphur trioxide are given off. Cool the beaker over a cold blast jet. Add 100 cc. of water and 4 or 5 cc. of hydrochloric acid. Boil until all sulphate of iron has dissolved, filter hot, wash at first with dilute hydrochloric acid (1 : 1), and then with hot water; ignite and weigh. One-half the weight in decimilligrams is the per cent. of silicon in hundredths.

DETERMINATION OF SULPHUR IN IRON AND STEEL.

Dissolve 5 grams of drillings in a No. 5 beaker, covered by a watch-glass, in 50 cc. of strong nitric acid. When the violent action has ceased, add 15 cc. of strong hydrochloric acid, and, when solution is complete, about one-half gram of sodium carbonate. Evaporate the solution to hard dryness. Remove the beaker from the heat; when cold add 40 cc. of strong hydrochloric acid, and heat gently at first, until the oxide of iron is dissolved; evaporate again to syrup, and, if any ferric chloride separates, add a few drops of strong hydrochloric acid; dilute, and filter, washing with the least possible amount of dilute hydrochloric acid to remove the last trace of iron. Heat the filtrate, which should have a volume of about 400 cc., to boiling, add 5 cc. of a saturated solution of barium chloride, and allow to stand at about 40° C. over night. Filter through a 9-cm. Munktell's No. 1 filter; wash with a little dilute hydrochloric acid (1 : 1), and finally with hot water; dry, ignite, and weigh as $BaSO_4$.

DETERMINATION OF SULPHUR IN PIG IRON AND STEEL.

Evolution Method.—Place 3 grams of drillings in a dry 500-cc. flask, provided with a doubly perforated rubber stopper; the stopper carries a one-bulb thistle-tube, and a small piece of glass tubing bent at right angles; the latter is connected by a short piece of rubber tubing to a glass tube running to the bottom of an intervening bottle; the exit-tube of the bottle is connected by rubber tubing to a delivery-tube, also bent at right angles, reaching to the bottom of a one-inch by eight-inch specimen-tube. Connected by a rubber stopper and delivery-tube with this is a second specimen-tube. The whole apparatus is suitably supported. Dilute 15 cc. of an ammoniacal cadmium chloride solution to 100 cc. with cold water, and pour one-half into each of the specimen-tubes. About 100 cc. of boiling water is added to the 500-cc. flask, and the flask connected with the apparatus above described. Introduce, through the thistle-tube, 50 cc. of strong hydrochloric acid. When the sample has dissolved, boil the solution until the steam reaches the first specimen-tube, then disconnect at the latter, turn out the light, and allow the flask to draw back the acid and water which has distilled into the intervening bottle. Transfer the contents of the specimen-tubes to a 400-cc. Erlenmeyer flask, rinsing the tubes with a little hydrochloric acid and water. Now add a few cc. of starch solution, acidulate with strong hydrochloric acid, and immediately run in the iodine solution from a burette, agitating the contents of the flask at the same time, until the proper blue color is obtained. The volume in cubic centimeters of iodine solution used multiplied by the value of 1 cc., is the percentage of sulphur in the sample.

Cadmium Chloride Solution.—Dissolve 120 grams of cadmium chloride in 1,500 cc. of water, and add 600 cc. of strong ammonia.

Iodine Solution.—Weigh out into a half-liter flask 8 grams of iodine, and 20 grams of potassium iodide. Add about 100 cc. of water. Allow to stand over night and dilute to 2 liters. The solution is standardized with an iron of known sulphur-content. The known percentage of sulphur divided by the number of cubic centimeters of solution required is the strength of the iodine solution.

DETERMINATION OF PHOSPHORUS IN PIG IRON AND STEEL.

3 grams of drillings are dissolved in a No. 5 beaker in 40 cc. of nitric acid (sp. gr. 1.20) and the solution evaporated to hard dryness. Allow the beaker to cool, dissolve the precipitate in 30 cc. of strong hydrochloric acid, dilute with cold water, filter into a 400-cc. Erlenmeyer flask, and wash the filter with cold water. Add 10 cc. of strong ammonia and agitate the mixture until the precipitate formed is all dissolved. The solution is heated or cooled to 60° C., and 50 cc. of molybdate solution are added by aid of a pipette; the flask is shaken for two or three minutes and then allowed to stand till the precipitate has settled. Filter, collect the precipitate on a 7-cm. S. & S. No. 589 filter, and wash with dilute molybdate solution (water containing 5 per cent. of its volume of the above). Pour 3 or 4 cc. ammonia on the precipitate, stir it up with a fine jet of water, and allow the solution to run into the flask in which the precipitation was made. Add drop by drop enough strong hydrochloric acid to cause the separation of the yellow precipitate, and then ammonia until it redissolves. Pour the solution back through the filter, allowing it to run into a 120-cc. Erlenmeyer flask, and wash two or three times with cold water. To the cold solution add very slowly 10 cc. of magnesia mixture, agitating constantly, and, after the precipitant is all in, 5 cc. of strong ammonia. Shake vigorously. Stand the flask in cold water for about one hour; filter on a 7-cm. S. & S. No. 589 paper, and wash with 5 per

cent. ammonia. Ignite over the blast-lamp at a low heat, and weigh as $Mg_2P_2O_7$.

Molybdate Solution.—Dissolve 100 grams of molybdic acid in 450 cc. of strong ammonia. Pour 1,250 cc. of nitric acid (sp. gr. 1.20), into a 2.5-liter bottle, and place the bottle in a pail of cold water. Now add, in small portions, the molybdic acid and ammonia, taking about thirty minutes in the operation. The mixture is kept in a warm place for forty-eight hours and is then ready for use.

Magnesia Mixture.—Dissolve 280 grams of ammonium chloride together with 110 grams of magnesium chloride in 1,300 cc. of water, and add 700 cc. of strong ammonia. Allow the solution to stand four or five days before using.

DETERMINATION OF MANGANESE IN STEEL AND PIG IRON.

Dissolve 3 grams of drillings in a No. 5 beaker in 50 cc. of nitric acid (sp. gr. 1.20), evaporate until the solution is almost of a sirupy consistence, add 100 cc. of strong nitric acid, heat the solution to boiling, and while boiling add 5 grams of potassium chlorate in small portions. Continue the boiling for ten minutes. Cool the solution rapidly by standing the beaker in a pan of cold water; filter by aid of a pump through purified asbestos supported by a small piece of pumice stone in the stem of the filtering tube; wash two or three times with strong nitric acid. Transfer the precipitate, with the asbestos filter, to the beaker in which the precipitation was made. The filtering tube is washed off with water and a little hydrochloric acid; add about 5 cc. of hydrochloric acid, and agitate the contents of the beaker until the asbestos is all suspended. Heat the mixture till the precipitate is dissolved; filter from the asbestos into a No. 2 beaker, and wash with hot water. To the filtrate add enough ammonium acetate to precipitate the last traces of iron, boil, and filter into a 400-cc. Erlenmeyer flask.

To the filtrate add an excess of strong ammonia, and then, with a vigorous shake, a few cubic centimeters of bromine. Heat gradually to boiling, allow the precipitate to settle, filter, and wash with cold water. The washing of the precipitate is easily accomplished by means of cold water, there being no fixed alkali present. Ignite over a blast-lamp at a low heat and weigh as Mn_3O_4.

In the case of pig iron, dissolve in 50 cc. of dilute hydrochloric acid. Dilute and filter into a No. 5 beaker, evaporate down nearly to a sirup, being careful not to heat too strongly. Redissolve in 50 cc. strong nitric acid, and evaporate to total expulsion of hydrochloric acid. Add 100 cc. of strong nitric acid, heat to boiling, add 5 grams of potassium chlorate, and proceed as described for steel.

Determination of Manganese by the Color Method.—In case of steel 0.1 gram of each sample and of the standard, is measured off into 1-inch by 8-inch test-tubes. Pour into each test-tube 15 cc. of nitric acid (sp. gr. 1.20). When the violent action has ceased boil over an Argand burner till nitrous fumes are driven off. While boiling, add about five-tenths of a gram of lead peroxide, and boil each sample and the standard exactly one minute. The tubes thus filled are immediately placed in cold water and set aside in a dark place. When cool, and the excess of peroxide has settled out leaving the supernatant liquid perfectly clear, the standard solution is decanted into one of the comparing tubes. The solution is then diluted with water to as many cubic centimeters as the standard contains hundredths of 1 per cent. of manganese, and mixed thoroughly with the water. The test sample is decanted in the same manner, and diluted with cold water until it has the same shade as the standard solution. The reading in cubic centimeters represents the percentage of manganese in hundredths.

In the case of pig iron it is preferable to dissolve one gram each of the sample and of a pig iron standard in a No. 2 beaker in 75 cc. of nitric acid of 1.13 sp. gr. Dilute to 100 cc. with cold water and filter a portion through a dry filter. Draw out 10 cc. of this solution with a pipette and let it run into a test-tube. Add 5 cc. of nitric acid of 1.20 sp. gr., and proceed as in the case of steel.

DETERMINATION OF MANGANESE IN IRON ORES.

2 grams of ore are dissolved as in the case of a determination of phosphorus, and filtered into a 500-cc. flask. The solution is

neutralized by ammonia, and a slight permanent precipitate produced. Redissolve this precipitate in a few drops of hydrochloric acid, and add ammonium carbonate, drop by drop, until a precipitate begins to form. Then add 4 grams sodium acetate, and boil for one minute. Allow the precipitate to subside. Filter into a 500-cc. flask and wash two or three times with hot water. The precipitate is washed back into the flask in which it was formed, by breaking the filter with a glass rod, and dissolved in the least possible quantity of hydrochloric acid. Repeat the precipitation exactly as before, unite the filtrates, and proceed as in the case of steel.

DETERMINATION OF NICKEL IN STEEL.

Dissolve one gram of drillings in a No. 4 beaker in 25 cc. of nitric acid (sp. gr. 1.20), and evaporate to hard dryness. Redissolve in 15 cc. of strong hydrochloric acid and separate the iron exactly as directed in the determination of manganese in ores. Unite the filtrates and boil down until their volume is reduced to about 300 cc. Acidulate with a few drops of acetic acid, heat to boiling, and pass hydrogen sulphide till the solution smells strongly of the gas. Boil a few minutes until the precipitate has a flocculent appearance. Filter and wash with hot water, ignite the filter and precipitate, and transfer them to a No. 2 beaker. Dissolve in 3 or 4 cc. of strong hydrochloric acid with a few drops of strong nitric acid, evaporate to dryness, redissolve in a few drops of strong hydrochloric acid, dilute to about 100 cc., heat to boiling and pass hydrogen sulphide through the solution, let the precipitate subside, filter if necessary, wash with hot water and, if desired, burn and weigh as Cu_2S. To the filtrate add an excess of ammonia, pass hydrogen sulphide, allow the precipitate to settle, filter, wash, ignite in a porcelain crucible, and weigh as NiO.

XII. METHODS USED AT THE LABORATORY OF THE PENNSYLVANIA RAILROAD COMPANY, ALTOONA, PA.

By C. B. Dudley and F. N. Pease.[1]

"Method of Determining Carbon in Iron and Steel." By C. B. Dudley and F. N. Pease. *American Engineer and Railroad Journal*, July, *1893*, p. 347.

"Method of Determining Carbon in Iron and Steel." By C. B. Dudley and F. N. Pease. *American Engineer and Railroad Journal*, August, *1893*, p. 391.

"The Need of Standard Methods for the Analysis of Iron and Steel, with Some Proposed Standard Methods." By C. B. Dudley and F. N. Pease. *Journal of the American Chemical Society*, September, *1893*, p. 501.

"Method of Determining Sulphur in Steel." By C. B. Dudley and F. N. Pease. *American Engineer and Railroad Journal*, September, *1893*, p. 443.

"Standard Methods for the Analysis of Iron and Steel." By C. B. Dudley. *Proceedings Chemical Section, Engineers' Society, W. Pa.*, October, *1893*.

"Method of Determining Sulphur in Pig and Wrought Iron." By C. B. Dudley and F. N. Pease. *American Engineer and Railroad Journal*, December, *1893*, p. 579.

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[1] In publishing in the Proceedings of the Chemical Section of the Engineers' Society of W. Pa., the methods of chemical analysis in use at the different iron and steel works laboratories, it has been the practice heretofore, to print the methods in detail as described by the senders. In the case of the methods of Dr. C. B. Dudley and Mr. F. N. Pease, of the Pennsylvania Railroad Laboratory at Altoona, an exception has been made. Dr. Dudley, in charge of the Altoona Laboratory, has kindly placed at the disposal of the Committee, the details of the admirable methods so fully and clearly described in the publications of the Pennsylvania Railroad Laboratory. These methods have, however, been repeatedly reproduced in technical journals, and in the transactions of various scientific societies, and they are already so well known to chemists that a detailed account of them seems hardly necessary. In place of complete details, therefore, a list of references to the papers of Dr. Dudley and Mr. Pease is here given.

Some of the papers do not deal with single methods of determination of the constituents of iron and steel, but are of such general interest that it seems eminently proper that they should be included among the papers upon methods.

" Method of Determining Manganese in Steel." By C. B. Dudley and F. N. Pease. *American Engineer and Railroad Journal*, April, *1894*, p. 176.

" An Attempt to Find the Amount of Phosphorus in Three Samples of Steel." By C. B. Dudley and F. N. Pease. *Journal of the American Chemical Society*, April, *1894*, p. 217.

" On Some Points in the Determination of Phosphorus in Steel by the Volumetric Method." By C. B. Dudley and F. N. Pease. *Journal of the American Chemical Society*, April, *1894*, p. 224.

"Method of Determining Silicon in Steel." By C. B. Dudley and F. N. Pease. *American Engineer and Railroad Journal*, July, *1894*, p. 321.

" Method of Determining Phosphorus in Steels." By C. B. Dudley and F. N. Pease. Separate paper published by the Pennsylvania Railroad Company.

The methods above mentioned for the determination of carbon and of sulphur in steel are also published and distributed by the Pennsylvania Railroad Company.

XIII. METHODS USED AT THE LABORATORY OF McINTOSH, HEMPHILL & CO., PITTSBURG, PA.

By J. P. M'Kelvey.

DETERMINATION OF SILICA IN IRON ORES.

Fuse with sodium carbonate, dissolve in hydrochloric acid and evaporate to dryness, moisten the residue with hydrochloric acid, take up with water, filter, wash, ignite, and weigh.

DETERMINATION OF IRON IN IRON ORES.

The filtrate from the silica serves for the iron determination. Reduce in a 600-cc. Erlenmeyer flask with tested zinc, and titrate with bichromate as usual, using potassium ferricyanide as an indicator.

DETERMINATION OF MANGANESE IN IRON ORES.

Dissolve 1 gram of ore in hydrochloric acid and evaporate to dryness. Redissolve in 50 cc. of nitric acid (sp. gr. 1.42), and proceed as in Ford's method.

DETERMINATION OF PHOSPHORUS IN IRON ORES.

Dissolve 5 to 10 grams of ore in hydrochloric acid and evaporate to dryness. Take up in a small amount of hydrochloric acid, dilute, filter, and proceed as in the acetate method, separating arsenic by hydrogen sulphide.

DETERMINATION OF SILICON IN PIG IRON.

Dissolve 1 gram of drillings in 30 cc. of dilute hydrochloric acid and evaporate to dryness. Moisten the residue with hydrochloric acid, dilute, filter, wash, ignite, and weigh.

DETERMINATION OF SULPHUR IN PIG IRON.

As given in Blair's "Analysis of Iron," Third Edition, p. 65, under the heading " By Oxidation and Solution."

DETERMINATION OF PHOSPHORUS IN PIG IRON.

The acetate method is used.

DETERMINATION OF MANGANESE IN PIG IRON.

This determination is made by the color method as given in Blair's "Analysis of Iron," Third Edition, p. 126, with the exception that, after solution of the drillings and before diluting to 100 cc., the solution is filtered.

DETERMINATION OF SULPHUR, PHOSPHORUS, MANGANESE, AND NICKEL IN STEEL.

Sulphur and phosphorus are determined according to the methods already detailed for pig iron; manganese by the colorimetric method described in Blair's "Analysis of Iron," Third Edition, p. 126; for nickel determination see Blair's "Analysis of Iron," Third Edition, p. 184.

XIV. METHODS USED AT THE LABORATORY OF THE W. DEWEES WOOD COMPANY, McKEESPORT, PA.

By Theo. Tonnele and R. B. Carnahan, Jr.

DETERMINATION OF SILICA IN IRON ORES.

The sample, which has passed through a 100-mesh sieve, is dried thoroughly at 100° C. just previous to analysis.

Fuse 1 gram of the ore with 5 grams sodium carbonate and 0.25 gram potassium nitrate in a platinum crucible. Acidify with hydrochloric acid and evaporate to dryness. Redissolve in sufficient water and hydrochloric acid, filter, wash with dilute hydrochloric acid (sp. gr. 1.10) and hot water, ignite, and weigh. Treat the ignited residue in the usual way with hydrofluoric acid and a few drops of sulphuric acid; the loss in weight represents the quantity of silica in the ore.

DETERMINATION OF IRON IN ORES.

Dissolve 0.75 gram in concentrated hydrochloric acid, heating on the steam-bath over night. Deoxidize the ferric iron of the solution with stannous chloride, adding the latter gradually. When the solution is entirely colorless, cool somewhat, and then add 10 cc. of mercuric chloride solution. Titrate in the regular way with standard potassium bichromate, using a very dilute solution of potassium ferricyanide to determine the end-reaction.

Solutions.—The mercuric chloride is a saturated aqueous solution. The stannous chloride solution contains 150 grams of the salt dissolved in 1 liter of hydrochloric acid (1.10 sp. gr.). To prepare the standard bichromate, dissolve 7 grams of the salt in 1 liter of water, and dilute so that 1 cc. is equivalent to 0.0075 gram of iron. The solution is standardized from a steel of known composition.

DETERMINATION OF PHOSPHORUS IN ORES.

From 3 to 5 grams of ore (according to the percentage of phosphorus) are dissolved in strong hydrochloric acid, and the solution evaporated to dryness; the residue is redissolved in a few cc. of strong hydrochloric acid and water; and the silicious matter remaining filtered off and ignited. The latter is fused with a little sodium carbonate, the fusion dissolved in nitric acid and water, and the nitric solution added to the original filtrate, which is again evaporated to dryness. After dissolving in a little hydrochloric acid and water, the silica is removed by filtration. The filtrate is made slightly alkaline with ammonia, and then slightly acidified with nitric acid. The solution, which measures about 100 cc., is heated to 80° C.; 50 cc. of molybdate solution are added, and, after standing for about one minute, the mixture is agitated for five minutes by passing a stream of air or natural gas through it. The yellow precipitate is filtered by the aid of suction and washed with pure water. It is then titrated with standard alkali, the solution being standardized by steels and pig irons in which the phosphorus has already been determined by the molybdate-magnesia method, according to Blair's "Analysis of Iron," Third Edition, p. 89.

Solutions.—The molybdate solution is made by dissolving 1 pound of molybdic acid in 1,000 cc. of strong ammonia, and 1,000 cc. of water, and pouring this solution into 6½ liters of nitric acid (sp. gr. 1.20).

DETERMINATION OF MANGANESE IN ORES

From 3 to 5 grams of ore are dissolved in strong hydrochloric acid, and the solution evaporated to dryness. The dry mass is redissolved in hydrochloric acid and water, and the insoluble residue filtered off and ignited. The residue is fused with sodium carbonate and the fusion dissolved in hydrochloric acid and water. The solution, after separating the silica, is added to the main solution; potassium chlorate is then added, care being taken to expel the chlorine generated in excess. The iron is precipitated as basic acetate, the precipitate being redissolved and reprecipitated twice. For each gram of ore 2 grams of ammonium acetate are used. The combined filtrates are then concentrated and the manganese precipitated by bromine as dioxide. The precipitate is filtered off and dissolved in hydrochloric acid, the solution neutralized with ammonia, and the manganese again precipitated as ammonium manganese phosphate, according to Blair. Ignite and weigh as manganese pyrophosphate, $Mn_2P_2O_7$. When the percentage is less than 0.5, the manganese dioxide is converted for weighing into protosesquioxide.

DETERMINATION OF SILICON IN PIG IRON.

Dissolve 1 gram of borings in 35 cc. of "silicon mixture," and evaporate until the formation of fumes of sulphur trioxide begins. When sufficiently cool, dissolve in a little water and about 10 cc. of strong hydrochloric acid. Filter, using suction, wash with hot water and dilute hydrochloric acid (1.10 sp. gr.), ignite, and weigh as silica.

Solutions.—The "silicon mixture" is made by adding 100 cc. of strong sulphuric acid to 900 cc. of nitric acid (1.20 sp. gr.).

DETERMINATION OF SULPHUR IN PIG IRON.

Weigh into a 500-cc. flask, 5 grams of drillings, add 50 cc. of water, and, after connecting the flask with the absorption apparatus, add 50 cc. of strong hydrochloric acid. Without delay light a small flame under the flask, and dissolve as rapidly as desired. The evolved gas bubbles through 50 cc. of ammoniacal cadmium chloride solution contained in a 7-inch foot test-tube. When the drillings have dissolved, boil the solution to expel the last traces of hydrogen sulphide from the flask. Rinse out the contents of the test-tube into a shallow porcelain dish, made slightly acid with hydrochloric acid, add starch solution, and titrate to a decided blue color with a standard iodine solution.

Solutions.—Ammoniacal cadmium chloride solution is made by dissolving 30 grams of cadmium chloride in 5 liters of water and 1 liter of strong ammonia. The iodine solution is prepared by dissolving 8.5 grams of iodine and about 25 grams of potassium iodide in a small quantity of water, and diluting to 2 liters. This solution is then exactly standardized by a standard steel (rather high in sulphur) in which the percentage of sulphur has been exactly determined by the aqua regia method, as described by Blair in his "Chemical Analysis of Iron," Third Edition,

p. 65. Except only in a very few cases, all pig irons are tested for sulphur by the evolution method.

DETERMINATION OF PHOSPHORUS IN PIG IRON.

Dissolve 3 grams of the sample in 50 cc. of nitric acid (1.20 sp. gr.), evaporate to dryness, and heat the residue over a bare flame for five minutes. Cool, dissolve in a few cc. of strong hydrochloric acid, and evaporate until the solution measures about 10 cc. Then add about 20 cc. of strong nitric acid, and boil for about four minutes. Dilute with water and filter. The solution should have a volume of about 75 cc. Complete the determination as in the case of ores.

For the sake of rapidity we use the following method for several grades of Bessemer pig iron: Dissolve 3 grams of the metal in 100 cc. of nitric acid (sp. gr. 1.13). When the borings have completely dissolved add a saturated solution of potassium permanganate till a decided precipitate remains. Boil three minutes and then add 10 cc. of strong hydrochloric acid. Filter off the carbonaceous residue and proceed further as described for ores.

DETERMINATION OF MANGANESE IN PIG IRON.

Dissolve 3 to 5 grams of the sample in 50 cc. of nitric acid (sp. gr. 1.20), evaporate to dryness, and ignite for five minutes. Cool, redissolve in a few cc. of hydrochloric acid, evaporate the excess of acid, and filter. Make the basic acetate separation, etc., as described under iron ores.

The color method is also used largely for pig irons; *viz.*, dissolve 0.5 gram of pig iron in 15 cc. of nitric acid (sp. gr. 1.20) in an 8-inch test-tube, filter, and dilute the filtrate to 50 cc. Draw off 10 cc. with a pipette and place the solution in an 8-inch test-tube. Add 3 cc. of nitric acid (sp. gr. 1.20). Heat to boiling, add about 0.2 gram of lead peroxide, and boil the mixture for two minutes. Add about 15 cc. of cold water, and allow the tube to stand in cold water till the lead peroxide settles completely. Compare the color of the sample for analysis with that of a standard pig iron treated similarly. Standards are always made by the basic acetate method, the manganese being weighed as pyrophosphate.

DETERMINATION OF SULPHUR IN STEEL.

See Pig Iron.

DETERMINATION OF PHOSPHORUS IN STEEL.

See Pig Iron. The permanganate oxidation method is generally used; filtering off the silica becomes unnecessary in this case.

DETERMINATION OF CARBON IN STEEL.

Dissolve 3 grams of steel in 200 cc. of a saturated solution of cupric potassium chloride, containing 10 cc. of strong hydrochloric acid, at 60° C., with constant stirring.

Filter off the carbonaceous residue on an asbestos plug, and wash with dilute hydrochloric acid and hot water.

Transfer the residue to a 500-cc. flask and burn with a mixture of chromic and sulphuric acids, absorbing, for weighing, the carbon dioxide evolved.

The combustion train is as follows:

1. A 500-cc. flask.
2. An empty tube.
3. A tube containing:

   0.2 gram pyrogallic acid,
   5 grams potassium oxalate,
   3 grams sodium chloride,
   0.2 gram sulphuric acid, and
   water sufficient to make the volume 20 cc.

4. A tube containing silver sulphate and strong sulphuric acid.
5. A tube containing sulphuric acid.
6. An empty tube.
7. Geissler potash bulbs containing caustic potash (sp. gr. 1.27); and a guard U-tube containing strong sulphuric acid.

After the combustion, pure air is aspirated through the apparatus for twenty minutes.

Blanks are made, and the apparatus frequently checked by steels of known carbon content. The various minute details are carried out about as given in Blair's work above quoted.

DETERMINATION OF MANGANESE IN STEEL.

See Pig Iron. The silica filtration is not generally necessary, however.

DETERMINATION OF NICKEL IN STEEL.

Make the basic acetate separation, using 1 gram of steel, and to the filtrate add 10 grams of ammonium acetate and 6 drops of acetic acid. Precipitate with hydrogen sulphide, filter, burn, and weigh as NiO (and CuO, should copper be present).

Dissolve the ignited precipitate in hydrochloric acid, and a few drops of nitric acid, dilute with water, and precipitate any copper in the solution with hydrogen sulphide.

Ignite and weigh as CuO ; subtract the weight from the first weight. The difference represents the quantity of NiO derived from the sample.

XV. METHODS USED AT THE LABORATORY OF THE OHIO STEEL COMPANY, YOUNGSTOWN, OHIO.

By J. C. Barrett.

DETERMINATION OF SILICA IN ORES.

Weigh off 5 grams ore which has been dried at 100°, dissolve in 75 cc. strong hydrochloric acid, evaporate to dryness, add 30 cc. strong hydrochloric acid, and when dissolved dilute and filter, washing with dilute hydrochloric acid and water. The residue is then burned and fused. The fusion is dissolved in water, made acid with hydrochloric acid, and evaporated to dryness. Take up with hydrochloric acid and water, filter, and wash well with water. Place in crucible wet, heat gently until dry and the paper is well charred, then heat in a muffle until white. Weigh as soon as cold. Observe precautions for titanic acid and barium sulphate.

DETERMINATION OF IRON IN ORES.

The ore is dried at 100° for one hour and cooled in a desiccator. Weigh quickly 5 grams of the ore, dissolve in a dish with 75 cc. concentrated hydrochloric acid and evaporate to dryness on a sand-bath. Redissolve in 30 cc. strong hydrochloric acid, and when all is in solution evaporate to a very small bulk or near sticking-point. Dilute with hot water and filter, washing with as little dilute hydrochloric acid as possible. Wash well with hot water. Burn silicious residue and, if colored at all with iron, fuse. Dissolve and make acid with hydrochloric acid and evaporate to dryness to separate the silica. Take up with as little hydrochloric acid as possible and filter into the main solution, which should be in a graduated 500-cc. flask, calibrated accurately with a 100-cc. pipette. Keep at room temperature, fill with water of same temperature to mark, and mix well. Take 100 cc., with same pipette you have checked flask with, and put into a clean flask of 500-cc. capacity, fitted with a rubber stopper having a Bunsen valve. Add 100 cc. sulphuric acid

(1 : 4), and then 15 grams of zinc. Keep cool for a time, then add 10 grams more of zinc if necessary. When all action is over, raise to a good heat, but not to boiling. Cool, pour into a No. 5 beaker into which 50 cc. of sulphuric acid (1 : 4) has been poured; wash out flask well, decanting from residue caused by the zinc, filling the beaker to a little more than half full; and titrate with a standard solution of potassium permanganate, making allowance for a blank on zinc which is carried along side by side with the ore, using the same weight of zinc in blanks as for ore. In presence of titanium reduce with hydrogen sulphide. Remove the hydrogen sulphide and titrate.

DETERMINATION OF PHOSPHORUS IN ORES.

Dissolve 5 grams of ore in 75 cc. of strong hydrochloric acid and treat in the same way as for iron, except that there is added a little nitric acid on the first evaporation. When the second evaporation reaches the sticking-point add 3 or 4 drops of hydrochloric acid, dilute and filter into a 16-oz. flask, wash, and then burn the residue and fuse. Dissolve the fusion in water, make acid with hydrochloric acid, and evaporate; take up with as little acid as possible, dilute with water, and filter into the flask with first solution. Add 25 cc. ammonia, then 25 cc. concentrated nitric acid which should just redissolve the precipitate and leave the liquid slightly acid. Heat the solution in the flask to 85° exactly, and add 75 cc. ammonium molybdate solution and shake for five minutes. When it has stood for one-half hour, or until settled, filter through a 9-cm. Munktell paper, which has been dried for one hour at 110° and weighed between watch-glasses, as soon as taken from oven. In presence of arsenic or titanium follow Blair's acetate method after getting the main filtrate and that from the fused residue united, down to the basic acetate precipitate carrying the phosphorus. This is put into a small beaker, paper and all, and dissolved in a mixture of dilute nitric and hydrochloric acids, at a gentle heat. Filter from paper and evaporate to expel hydrochloric acid; now filter into a 16-oz. flask and precipitate phosphorus as above with ammonium molybdate solution at 85°. When necessary or desirable the yellow precipitate and paper are put into a small beaker, treated with dilute ammonia, the paper and silica separated, and phosphorus precipitated with magnesia mixture.

The yellow precipitate is washed well with 2 per cent. nitric acid solution, excess of moisture removed with blotting-paper and dried in an oven at 110°, taking from oven and weighing at once between the watch-glasses.

The ammonium molybdate solution is made by dissolving 200 grams molybdic acid in 500 cc. water with 500 cc. ammonia, and adding 2,500 cc. of nitric acid (sp. gr. 1.20), and keeping in a warm place for twenty-four hours.

DETERMINATION OF MANGANESE IN ORES.

Dissolve 5 grams of ore in 75 cc. concentrated hydrochloric acid, evaporate to dryness, take up with hydrochloric acid, and when in solution evaporate to a small bulk. Filter into a 500-cc. flask. Burn residue after washing, fuse, dissolve fusion in water, make acid, and evaporate to dryness. Take up with a small quantity of hydrochloric acid, dilute with water, and filter into main solution. If little manganese is present, evaporate the whole in a No. 4 beaker to sirupy consistency with concentrated nitric acid twice. If manganese be in large quantity, fill flask to mark and take a measured quantity after shaking up well, and evaporate as above. Then add 100 cc. concentrated nitric acid, heat to boiling and precipitate manganese dioxide with potassium chlorate and boil for a few minutes. Remove from the lamp and cool. Filter through asbestos filter and wash once with colorless nitric acid. When dry, transfer asbestos and precipitate to original beaker and wash filtering tube with concentrated hydrochloric acid and hot water, washing down the sides of the beaker with same, using about 18 cc. hydrochloric acid. Heat, while shaking, over a lamp, until manganese dioxide is entirely dissolved. Filter off asbestos receiving the solution in a 16-oz. flask. Wash well and make a basic acetate precipitation. Filter from this precipitate into a No. 6 beaker. Redissolve the precipitate with hydrochloric acid and repeat the basic acetate, filtering into the original solution. Make solution in beaker acid with acetic acid, heat to boiling, and precipitate manganese as phosphate with ammonium phosphate; boil until the precipitate is crystalline, stirring if necessary; then add 25 cc. ammonia, boil for a few minutes, remove from heat, and, when settled, filter and wash five times with water. Absorb excess of water on blotter and put precipitate in crucible. Char with lid on, then remove it and ignite until white. Weigh as $Mn_2P_2O_7$.

Use precautions for lead or barium.

DETERMINATION OF SILICON IN PIG IRON.

Weigh off 0.9404 gram of iron, dissolve in 25 cc. of a mixture of 28 parts of nitric acid (sp. gr. 1.20) and 12 parts of dilute sulphuric acid (1 : 1). As soon as solution is complete, evaporate over burner. Use a 4½-inch evaporating dish. When dry, raise the heat until copious fumes of sulphur trioxide escape. Cool, add a few cc. of dilute hydrochloric acid (3 : 5) and 25 cc. of hot water. Replace over the lamp until solution is complete. Filter, wash paper once with hot water, then once with dilute hydrochloric acid, and three or four times again with hot water; absorb excess of water from paper and residue with blotting-paper. Place in crucible and burn in a muffle, cool, weigh, and divide by 2. Result = silicon.

DETERMINATION OF SULPHUR IN PIG IRON AND STEEL.

Evolution Method.—Weigh 5 grams, place in a 16-oz. flask, closed with a funnel-tube and exit-tube for gas which is connected with a tube extending to the bottom of a 1-inch by 10-inch test-tube. This test-tube is filled two-thirds full of a cadmium chloride solution. In the bottom of the tube is placed about 1 inch of ammoniacal solution of cadmium chloride. (This is made by dissolving 100 grams in 500 cc. water and adding 500 cc. ammonia; filter into a 2-gallon bottle and add enough water to make 3 liters and enough ammonia to make 5 liters.) After adding 1 inch of this cadmium chloride solution, fill tube two-thirds with water. To drillings in flask add 80 cc. dilute hydrochloric acid (3 : 5), place over an Argand burner and heat until quite warm; lower the heat until solution is complete, then increase the heat until steam drives all gas from flask. Disconnect flask and pour the solution from the hot tube with the yellow sulphide into a No. 4 beaker. Wash out the tube with water and enough dilute hydrochloric acid to make solution in beaker acid and dissolve the sulphide. This is titrated immediately with a standard solution of iodine which has been standardized with a sulphur standard so as to read percentage. Each 0.1 cc. = 0.001 per cent. sulphur. While titrating be sure that all sulphide is dissolved. The beaker should be two-thirds full.

Aqua Regia Method.—Weigh 5 grams, place in a No. 4 beaker, add a mixture of 5 cc. strong hydrochloric acid and 40 cc. strong nitric acid to drillings at once. Heat until solution is complete, add 40 cc. strong hydrochloric acid, transfer to a No. 2 beaker or a 4½-inch dish, and evaporate to hard dryness. Do not ignite. Cool, add 30 cc. concentrated hydrochloric acid, dissolve and evaporate to formation of a crust, add 10 or 12 drops of hydrochloric acid, dilute, and filter into a No. 2 beaker. Wash well and fill beaker three-fourths full, heat to boiling and precipitate with 3 cc. barium chloride solution (25 grams to 500 cc. water). Allow to stand over night on a warm plate or sand-bath, then evaporate to formation of scum, add a few drops of hydrochloric acid and dilute with water to about one-half beaker full, evaporate again to scum, add a few drops of hydrochloric acid to redissolve and dilute to two-thirds full with cold water and allow to stand at room temperature over night. Filter through a double filter No. 589, 7 cm., wash well with hydrochloric acid and water, and burn in an open crucible. Purify this precipitate if necessary.

DETERMINATION OF PHOSPHORUS IN PIG IRON AND STEEL.

Dissolve 5 grams in a 4½-inch dish, using 60 cc. of nitric acid (sp. gr. 1.20) for steel, and 70 cc. for pig iron. When the solution is complete, which will take a few minutes for steel and about twenty minutes to a half hour for pig-iron, evaporate over Argand burner with watch-glass cover, having flame as high as possible without smoking. When nearly dry lower the heat so that any iron that may have splashed up on the watch-glass may be redissolved and carried down into the dish. As soon as dry, remove the watch-glass and heat over the lamp until all acid fumes are gone. Cool and add to pig iron 35 cc. strong hydrochloric acid, and to steel 30 cc.; replace the watch-glass and place over a low heat until solution is complete; then raise the heat and evaporate as rapidly as possible withc over on, until the solution is of a very dark color, and about to adhere to the dish. Remove from lamp, add 5 cc. strong nitric acid, shake about until well mixed and any that adheres to the sides may be dissolved; dilute with hot water to about 100 cc., washing off the watch-glass. Filter into a 16-oz. flask, washing paper and residue with two per cent. nitric acid and hot water. Add 25 cc. strong ammonia, shake up, and then redissolve with 25 cc. of strong nitric acid, leaving solution but slightly acid. Heat to 85° and add 75 cc. ammonium molybdate solution. Shake for five minutes. When well settled, filter through a 9-cm. Munktell filter, which has been dried at 110° for one hour, and weigh between watch-glasses. Wash well with 2 per cent. solution of nitric acid and dry at 110° for one hour. Weigh between watch-glasses. If arsenic or titanium be present, follow Blair's acetate method after filtering from residue down to the basic acetate precipitate carrying phosphorus. This precipitate is dissolved in a dilute solution of nitric and hydrochloric acids in a small beaker and warmed. Filter from paper, remove hydrochloric acid by evaporation, filter into a 16-oz. flask, and precipitate with ammonium molybdate solution.

If desirable and thought necessary dissolve yellow precipitate in dilute ammonia, by putting paper and all in beaker. Remove paper and silica and make magnesium precipitate.

MANGANESE IN IRON AND STEEL.

Color Method.—Weigh 2 grams iron or steel, place in a 1-inch by 10-inch test-tube, add 25 cc. nitric acid (sp. gr. 1.20). When solution is complete and all nitrous fumes are expelled, add about ½ gram lead dioxide and boil for two minutes, cool in water, and when settled compare color with that of a standand which has been treated in just the same way, the manganese in the standard being determined gravimetrically. Dilute the standard to twice as many cubic centimeters as percentage of manganese and divide cubic centimeters of all compared with it by 2. It takes some time for solution of pig iron and the solution should be kept over a very low flame so as not to concentrate bulk of solution until solution is complete before adding the lead dioxide.

Gravimetric Method.—Dissolve 5 grams of steel in 60 cc. nitric acid (sp. gr. 1.20), evaporate to a pasty consistency in a No. 4 beaker, then add 100 cc. concentrated nitric acid, heat to boiling, and precipitate manganese dioxide with potassium chlorate; filter on asbestos and proceed as with manganese in ores. Pig iron is treated in the same way as for phosphorus until filtering into a 16-oz. flask. For manganese it is filtered into a No. 4 beaker and evaporated twice with concentrated nitric acid to a pasty consistency; then 100 cc. of concentrated nitric acid are added, manganese dioxide precipitated with potassium chlorate, and the manganese dioxide treated in the same way as in the case of steel or ores.

DETERMINATION OF CARBON BY COMBUSTION.

The steel or iron is dissolved in double chloride of potassium and copper which is dissolved in the proportion of 5 pounds to 6 liters of water, and has been filtered first through paper and then through asbestos. 5 per cent. of hydrochloric acid is added to this solution as it is used. For 3 grams of steel use 180 cc. solution. If no stirring machine is at hand add solution to steel and stir frequently at first and allow to stand over night at room temperature. Then warm on sand-bath, stirring frequently until all copper is in solution. Cool and filter through a boat lined with asbestos, made by burning and grinding up in water, decanting away the murky part, leaving the fine asbestos, which by shaking up in a bottle with water can be easily transferred to a boat to make the felt. The solution of steel is filtered on felt, carefully washed with hydrochloric acid, then warm water until free from hydrochloric acid and copper. The boat with carbon is dried at 80° or 90° for one hour, then burned in oxygen in a platinum tube which contains a coil of platinum gauze and copper oxide.

The combustion train is made up as follows:

Drying and purifying jars filled with potash through which oxygen passes to combustion-tube; following the combustion-tube is a U-tube filled on one side with anhydrous cuprous chloride and on the other with anhydrous copper sulphate; then a U-tube filled with concentrated sulphuric acid to close the lower part of the U. Following these are the absorption bulbs (Geissler's potash with drying tube between the bulbs). The bulbs are filled with potash (sp. gr. 1.35 or 1.40) and the drying tube with calcium chloride. Connected with this is a Liebig bulb filled with sulphuric acid to trap. Then comes a calcium-chloride tube used as a protection, but not weighed. Great care is used in always keeping the potash bulb and the calcium-chloride tube filled with fresh material. A blank is always run before each day's series is begun, and this must agree with the first weight to within 0.0005 gram. Where a number of combustions are to be made the Geissler and Liebig bulbs are weighed and then placed in train for the next combustion, using the weight from the last one done until the series is finished. Test the joints each time the apparatus is put together. One of the essential requirements for good results is cleanliness.

The tube is heated up by lighting the burner nearest the absorption bulbs and then, with oxygen flowing so that bubbles go at the rate of 3 per second, each burner slowly in succession, until the whole tube is red hot, taking about ten minutes. Keep red hot for fifteen minutes. Then cut off oxygen and apply suction with bubbles going at the same rate; lower the flames for a few minutes, then extinguish them. After suction has run for a half hour the bulbs are ready to weigh.

DETERMINATION OF SILICON IN STEEL.

5 grams are dissolved in 50 cc. nitric acid (sp. gr. 1.20) and 35 cc. dilute sulphuric acid (1 : 1). Evaporate in a $4\frac{1}{2}$-inch dish over an Argand burner with watch-glass cover until bumping begins; remove cover and stir with rod until it grains or cakes. Dry until copious fumes escape. Cool, add about 20 cc. dilute hydrochloric acid and 100 cc. water. Heat until solution is complete, filter and wash well with hydrochloric acid and hot water, burn, and weigh.

XVI. METHODS USED AT THE LABORATORY OF THE CARNEGIE STEEL CO., DUQUESNE, PA.

By James M. Camp.

DETERMINATION OF PHOSPHORUS IN PIG IRON AND STEEL.

5 grams pig iron or steel are dissolved in 60 cc. nitric acid (sp. gr. 1.20) in a 12-cm. porcelain dish, with watch-glass cover, evaporated to dryness while covered, and heated over a lamp without cover till all acid fumes are driven off. When cool, dissolve in 30 to 35 cc. strong hydrochloric acid and evaporate with watch-glass cover till excess of free acid is driven off, as indicated by the first appearance of insoluble ferric chloride on the bottom of the dish. This is dissolved by adding 2 or 3 cc. of strong nitric acid and the solution diluted with warm water to about 75 cc., filtered, and washed into a 500-cc. flask, using the 2 per cent. nitric acid wash water used in washing the yellow precipitate, to remove the last trace of iron. A slight excess of strong ammonia is then added (about 25 cc.), and then a slight excess of strong nitric acid (about 28 cc.), till the solution is a clear amber color.

The solution is heated or cooled to 85° C. and 75 cc. ammonium molybdate are blown in by aid of a pipette ; the flask is shaken for five minutes and allowed to stand till the supernatant liquid is clear. It is then filtered through a weighed filter that has been dried at 100° to 130° C. and weighed between watch-glasses. The precipitate is washed with water containing 2 per cent. strong nitric acid, dried for one hour, or, till weight is constant, at above temperature, and weighed between watch-glasses. 1.63 per cent. of weight is taken for phosphorus.

Ammonium Molybdate Solution.—This is made by dissolving 225 grams molybdic acid in a mixture of 600 cc. water and 400 cc. strong ammonia, and adding this solution to 2.5 liters nitric acid of 1.20 specific gravity. This is kept in a warm place over night and is then ready for use.

DETERMINATION OF PHOSPHORUS IN ORES.

The agate-mortar sample is dried at 100° C. for one hour, allowed to cool, and 5 grams weighed off into a 12-cm. porcelain dish with watch-glass cover, 50 cc. strong hydrochloric acid added, and the solution allowed to go to dryness on the sand-bath; 30 to 35 cc. strong hydrochloric acid are added, warmed, and when all is in solution evaporated till the first appearance of insoluble ferric chloride. This is dissolved by adding one or two drops of strong hydrochloric acid and the solution diluted with hot water to about 75 cc., and filtered into a 500-cc. flask.

The residue is burned and fused with the mixed carbonates of potassium and sodium, dissolved in hot water, acidified with hydrochloric acid and evaporated to dryness; then moistened with dilute hydrochloric acid (1:2), diluted, and filtered into the same flask with original filtrate, keeping as concentrated as possible. (This gives the silica, perfectly pure, of the five grams of ore, on the filter-paper ready for burning and weighing.)

A slight excess of strong ammonia is now added and then a slight excess of strong nitric acid, and the process continued in the same manner as for pig iron or steel.

To save time, the above process is modified as follows: 5 grams of the dried ore in a 12-cm. covered porcelain dish are boiled with 50 cc. strong hydrochloric acid for about thirty minutes, or, till the ore is apparently all in solution, diluted with an equal volume of water, and filtered into another dish of the same size. The residue is burned and fused with the mixed carbonates, dissolved in hot water, acidified with hydrochloric acid in the same dish in which the original solution was made, and both solutions allowed to go to dryness on the sand-bath.

30 cc. strong hydrochloric acid are added to the dish containing the original filtrate, and heated till the excess of hydrochloric acid is driven off; dilute and filter into a 500-cc. flask. The fusion is moistened with dilute hydrochloric acid, diluted, and when in solution filtered into the same flask with the last filtrate. The process is then carried on as before.

DETERMINATION OF IRON IN ORES.

1 gram of the agate-mortar sample dried at 100° C. is weighed

off into a No. 0 beaker with watch-glass cover, 20 cc. of strong hydrochloric acid added, and for a 60 per cent. ore 5 cc. of the stannous chloride solution, heated on the sand-bath till all is in solution and the residue is white. While still hot in the same beaker, add cautiously, drop by drop, more stannous chloride solution till the color due to the presence of ferric chloride, has entirely disappeared and then one drop in excess. Transfer to a No. 4 beaker containing about 300 cc. cold water, add 10 cc. mercuric chloride solution, and stir; allow to stand about one minute, and then titrate with potassium bichromate solution, until a drop of the solution added to a drop of potassium ferricyanide solution on a porcelain plate shows no green color on standing one-half minute. The number of cubic centimeters bichromate solution used gives the percentage of iron.

In case the residue shows presence of iron it is filtered, burned, and fused with mixed carbonates, dissolved in water, and filtered; the oxide of iron on the filter is dissolved in dilute hydrochloric acid and allowed to run into the original solution.

SOLUTIONS.

Stannous Chloride Solution is made by dissolving 300 grams of the salt in 500 cc. strong hydrochloric acid and 500 cc. water; 1 cc. will reduce about 0.1 gram iron.

Mercuric Chloride Solution is made by dissolving 50 grams of the salt in 1 liter of water.

Potassium Ferricyanide Solution is made by dissolving about 0.05 gram of the salt in 50 cc. water.

Potassium Bichromate Solution is made by dissolving 8.9 grams of salt per liter of water and standardizing with iron wire, standard steel or ore, and diluting so that 1 cc. equals one per cent. iron; proving strength of solution after dilution with the standard steel or ore.

DETERMINATION OF MANGANESE IN ORES.

The agate mortar sample is dried for one hour at 100° C., allowed to cool, and five grams weighed off into a 12-cm. porcelain dish with watch-glass cover; 50 cc. strong hydrochloric acid are added and the solution allowed to go to dryness on the sand-bath.

The residue is moistened with dilute hydrochloric acid (1 : 2), diluted, heated till all is in solution and filtered into a 500-cc. graduated flask. The residue is burned and fused with five to ten times its weight of the mixed carbonates of potassium and sodium. If fusion shows presence of manganese it is dissolved in hot water, acidified with hydrochloric acid, evaporated to dryness, taken up as before, and filtered into the same flask with the original filtrate.

The solution is cooled, diluted to the mark, and, with the aid of an exactly agreeing pipette, 100 cc. (equal to 1 gram of ore) are taken as many times as desired into No. 4 beakers. 30 cc. strong nitric acid are added, and the solution evaporated to small bulk (10 to 15 cc.). 75 cc. strong nitric acid are now added and the solution heated to boiling, and, while boiling, an excess of potassium chlorate is added in small portions and boiled a few minutes after the final puff.

The solution is cooled and filtered through a purified asbestos plug with the aid of suction. Beaker and plug are washed twice with strong nitric acid and plug blown back into beaker in which precipitation was made. The filtering tube is washed off with water and dilute hydrochloric acid, to dissolve any adhering precipitate; 25 cc. strong hydrochloric acid are added; and then 1 to 2 cc. dilute sulphuric acid added to precipitate any barium that may be present.[1] The solution is heated to boiling, keeping the beaker constantly agitated to avoid bumping and when all the manganese dioxide is dissolved, filtered into a 500-cc. flask from the suspended asbestos.

The solution is neutralized with ammonia till a faint permanent precipitate of ferric hydroxide is formed, 10 to 15 cc. of a 25 per cent. solution of ammonium acetate added, and the solution heated to boiling and set aside to settle. It is next filtered into a 500-cc. flask with the aid of suction, and flask and funnel washed once with hot water. The precipitate is dissolved in dilute hydrochloric acid, into the same flask in which the precipitation

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[1] At this stage of the analysis, if there is baryta in the ore, which is usually the case, the nitrate being very insoluble in strong nitric acid, may be precipitated; consequently it will be filtered off with the manganese dioxide, and will ultimately go into solution in the subsequent dilution and boiling with hydrochloric acid. This must be separated by addition of sulphuric acid, and sufficient time allowed to precipitate, or it will be weighed with the manganese as pyrophosphate.

was made, and a second basic acetate precipitation, made as before, filtered into the same flask containing the first basic acetate filtrate, and the flask and funnel washed twice with hot water.

The subsequent precipitation can be made in the flask, or the united filtrates are transferred to a No. 6 beaker, carefully rinsing out the flask, and 10 cc. acetic acid added. The solution is heated to boiling, 5 to 10 grams ammonium phosphate crystals added, and the solution stirred till the precipitate assumes the well-known crystalline form. 25 cc. strong ammonia are now added and the solution stirred for a few minutes till the precipitate is all crystalline, and set aside to settle. It is now filtered through an 11-cm. filter-paper by aid of suction and washed with hot water, burned, and weighed as $Mn_2P_2O_7$. 38.74 per cent. of its weight is manganese.

When only a single determination is required, one gram can be weighed off and treated as directed for five grams. But if several are to be made and the residue fused, which should be done in all cases, unless absolutely certain that it contains no manganese (as a silicate of manganese exists that looks and burns perfectly white), then it is preferable to start with five grams as directed.

DETERMINATION OF MANGANESE IN STEEL AND PIG IRON.

From 2 to 5 grams of the steel or pig iron are weighed off into a No. 4 beaker with watch-glass cover, the least amount necessary of nitric acid of 1.20 specific gravity for complete solution added, and heated to boiling. When all is in solution the watch-glass cover is removed and the solution evaporated over the lamp till the excess of nitric acid is driven off, as indicated by the first appearance of the insoluble nitrate of iron in the solution; 75 cc. strong nitric acid are added, the solution heated to boiling, and while boiling an excess of potassium chlorate is added in small portions and boiled a few minutes after the final puff. Cool, and filter through a purified asbestos plug with the aid of suction; the beaker and plug are washed twice with strong nitric acid and the washings returned to the beaker in which the precipitation was made. The filtering tube is washed off with water and dilute hydrochloric acid, to dissolve any adhering precipitate, an excess of strong hydrochloric acid added, and the solution heated to boiling till the manganese dioxide is all in solution. It is then filtered from the suspended asbestos and the analysis finished in the same manner as for manganese in ores.

In case of a pig iron high in silicon, it is preferable to dissolve in hydrochloric acid, evaporate to dryness to separate silica, moisten with dilute hydrochloric acid, dilute, and filter. To the filtrate, add an excess of strong nitric acid (at least 75 cc., if 5 grams of iron were taken), and evaporate to total expulsion of hydrochloric acid. 75 cc. strong nitric acid are added and the solution heated to boiling. While boiling, an excess of potassium chlorate is added, and the analysis finished in the same manner as for manganese in steel.

DETERMINATION OF MANGANESE BY COLOR.

0.2 gram pig iron or steel, and standard steel of known manganese content, are weighed off in 1-inch by 10-inch test-tubes; 30 cc. nitric acid of 1.20 specific gravity are added to each, the tube heated over an Argand burner till dissolved, and boiled till all the nitrous fumes are driven off. While boiling, about one gram lead peroxide is added, boiling continued for one minute, and test-tubes set in a cold water-bath to settle. When cool, and the supernatant liquid is clear, the tube containing the standard solution is decanted into one of the comparing tubes; this can be very safely done without losing more than a drop of the solution, and without a particle of the lead peroxide entering the comparing tube. The solution is then diluted to twice the number of cubic centimeters, the standard steel contains hundredths per cent. manganese, and mixed thoroughly. The test pig iron or steel is decanted in like manner into the other comparing tube, and diluted with cold water to like colors. One-half the reading in cubic centimeters represents hundredths per cent. manganese.

In case the manganese is high in the sample—0.75 per cent. and upwards—the test and standard are each boiled two minutes after the addition of the lead peroxide,—otherwise the treatment is the same.

DETERMINATION OF SILICON IN PIG IRON.

Twice the factor weight (0.9404 gram of the drillings) is weighed off into a 12-cm. porcelain dish, and 25 cc. of the mixed acids, nitric and sulphuric, mixed in the proportion of 18 cc. nitric acid (sp. gr. 1.20) and 7 cc. dilute sulphuric acid (1 : 1) added, heated over an Argand burner till all is in solution, and afterwards to dryness, and finally until dense white fumes of sulphur trioxide are given off. It is then allowed to cool, moistened with dilute hydrochloric acid (1 : 2), diluted with hot water, and warmed till all is in solution; filtered, washed with hot water and dilute hydrochloric acid till free from iron, burned, and weighed. One-half the weight in decimilligrams is hundredths per cent. of silicon.

DETERMINATION OF SULPHUR IN PIG IRON AND STEEL.

Aqua Regia Method.

5 grams of pig iron or steel are weighed off into a No. 5 beaker, with a watch-glass cover, and 50 cc. aqua regia added at one time. This is freshly made up, by mixing 45 cc. strong nitric acid to 5 cc. strong hydrochloric acid. When the violent action has ceased, heat is applied till all is in solution, and the solution evaporated, still covered, until its bulk is considerably reduced. An excess of strong hydrochloric acid is then added (about 40 cc.) to displace all the nitric acid, and the solution after continued evaporation is finally transferred to a 12-cm. porcelain dish, and allowed to go to dryness on the steam-bath. 35 cc. strong hydrochloric acid are added and warmed till all is in solution and evaporated till the free hydrochloric acid is driven off, as indicated by a film of ferric chloride floating on the surface. This is dissolved by a drop or two of strong hydrochloric acid, diluted to about 75 cc., and filtered into a No. 2 beaker, washing with hot water and the least amount necessary of dilute hydrochloric acid to remove the last trace of iron. Heated nearly to boiling, 10 cc. of a 5 per cent. solution of barium chloride are added, and the solution set on a sand-bath and evaporated to the separation of the insoluble ferric chloride as before.

This is dissolved with a drop or two of strong hydrochloric acid, and with a wash-bottle a strong stream of cold water is blown into the beaker, thoroughly stirring up the solution till its volume is about 175 cc. and set aside in a cool place over night. The solution is filtered through a double 7-cm. filter, washed with hot water and dilute hydrochloric acid till free from iron, burned in an open crucible, and weighed. 13.756 per cent. of its weight is sulphur.

DETERMINATION OF SULPHUR IN PIG IRON AND STEEL.

Iodine Method.

5 grams of pig iron or steel are weighed off into a dry 500-cc. flask, provided with a doubly perforated rubber stopper, with a long-stem 4-oz. funnel-tube with a stop-cock, and a delivery-tube bent at right angles, on which a short piece of ¼-inch rubber tubing is placed, making connection with a delivery-tube also bent at right angles, reaching to the bottom of a 1-inch by 10-inch test-tube, suitably supported. About 10 cc. of the ammoniacal solution of cadmium chloride are introduced into the test-tube, which is diluted with cold water until the tube is about two-thirds full. 80 cc. of dilute hydrochloric acid (1 : 2) are poured into the funnel-tube, a file mark on the bulb indicating this amount, which is allowed to run into the flask. The stop-cock is then closed and a gentle heat applied, till the drillings are all in solution, and the flask is then strongly heated until nothing but steam escapes from the delivery-tube.

The apparatus is then disconnected, and the delivery-tube is placed in the No. 4 beaker in which the titrations are made; the contents of the test-tube are then poured into the beaker, the test-tube filled to the top twice with cold water, the sides of the tube rinsed down with about 25 cc. dilute hydrochloric acid, and filled again with cold water. The total volume of the solution equaling about 400 cc. (both acid and water are supplied from overhead aspirator bottle and suitable rubber connections with pinch-cocks), the delivery-tube is now rinsed off inside and out with dilute hydrochloric acid, and about 5 cc. starch solution added to the beaker.

Without waiting for complete solution of the cadmium sulphide, the iodine solution is run in from a burette, stirring gently, till a blue color is obtained. The solution is then stirred vigorously, keeping a blue color by fresh additions of the iodine solution, till the precipitate of cadmium sulphide is all dissolved, and the proper permanent blue color is obtained. The amount of iodine solution used in cubic centimeters represents hundredths per cent. sulphur.

The Iodine Solution is made by placing in a dry 500-cc. flask about 35 grams potassium iodide, 16 grams iodine, and 50 cc. water; shake, and dilute cautiously until all is in solution; and finally dilute to 3.5 liters. This is standardized with steels of known sulphur content, so that 1 cc. equals 0.0005 gram sulphur.

The Cadmium Chloride Solution is made by dissolving 100 grams cadmium chloride in 1 liter of water, adding 500 cc. strong ammonia, and filtering into an 8-liter bottle. Two liters of water are now added, and the bottle filled to the 8-liter mark with strong ammonia.

The Starch Solution is made by adding to one-half gallon boiling water, in a gallon flask, about 25 grams pure wheat starch, previously stirred up into a thin paste with cold water; this is boiled ten minutes and about 25 grams pure granulated zinc chloride dissolved in water added, and the solution diluted with cold water to the gallon mark. The solution is mixed, allowed to settle over night, and the clear solution decanted into a glass-stoppered bottle for use.

This solution will keep indefinitely.

DETERMINATION OF NICKEL IN STEEL.

Our determinations of nickel are made exclusively in machinery steel, pinions, and rolls; the amount ranges from 2.5 to 3.5 per cent. No attempt is made to separate cobalt, as it seldom occurs in the steel, and when present is derived from the nickel ores in inconsiderable amounts. The method is as follows:

Dissolve 1 gram of steel in 15 cc. nitric acid (sp. gr. 1.20), in a No. 3 beaker, transfer to a liter flask and dilute with hot water to about 700 cc. Neutralize the excess of acid with ammonia, and add about 15 grams sodium acetate in crystals. Heat to boiling and boil one-half minute; allow precipitate to subside, and filter through an 11-inch fluted filter, into a large beaker. Drain precipitate thoroughly, perforate filter, and wash precipitate back into flask in which precipitation was made, wash filter with dilute hydrochloric acid and water till free from iron; add a slight excess of hydrochloric acid to flask to dissolve all the precipitate, and dilute to about 700 cc. Neutralize and make second basic acetate precipitation and filtration as before.

Unite filtrates, make faintly ammoniacal, and heat nearly to boiling. If traces of iron separate, filter, and in filtrate pass hydrogen sulphide till the solution smells strongly of the gas. Make slightly acid with acetic acid, testing with litmus paper, and set on steam-bath till the precipitate of nickel sulphide subsides. Filter, wash with hot water, burn in the hottest part of the muffle, and weigh as NiO. 78.58 per cent. of its weight is nickel.

In case copper is present in any appreciable amount, dissolve the precipitate of nickel sulphide in hydrochloric acid with the aid of potassium chlorate, filter from the paper, dilute, warm, precipitate the copper with hydrogen sulphide, let subside, filter, wash, and if desired burn and weigh. To the filtrate add ammonia in slight excess, pass hydrogen sulphide, let precipitate subside, filter, wash, burn, and weigh as NiO, as before.

DETERMINATION OF CARBON IN STEEL BY COMBUSTION.

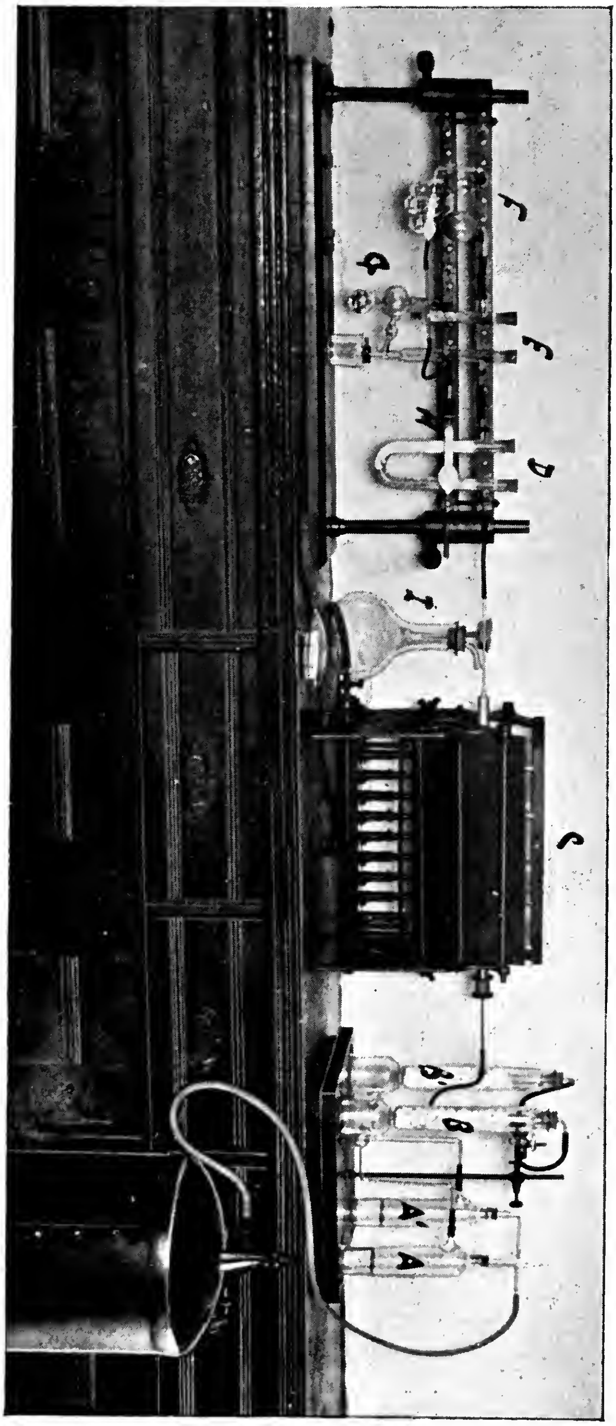
From 1 to 10 grams of steel are weighed off into a dry beaker of suitable size, and from 100 cc. to 500 cc. of the double chloride of copper and potassium solution added. This is made by dissolving 5 pounds of the double chloride of copper and potassium in five liters of water, filtering through a purified asbestos plug, and adding 250 cc., or 5 per cent., strong hydrochloric acid. The beaker is placed on a suitably arranged stirring apparatus, making about 250 revolutions per minute, and kept at a temperature of about 50° C. till all is in solution. When permissible it is preferred to allow the solution to cool, and the carbonaceous residue to subside before filtering. The solution is then filtered through a perforated platinum boat, with suitable asbestos blanket, and washed once with dilute hydrochloric acid, and then with warm water, allowing all the washings to run from the beaker into the boat. The boat is then dried at about 85° C. and is finally transferred to the platinum combustion-tube.

The accompanying photograph shows the arrangement of the apparatus. In front of the combustion furnace C is the double purifying train for oxygen and air; the first tubes, A and A′, contain a strong solution of caustic potash of 1.4 specific gravity. Solution of this strength is also used in the potash bulbs. Tubes B and B′ are filled to the top with stick caustic potash in short pieces. These tubes are connected by means of a three-way tube, with suitably arranged stop-cocks and rubber tubing, with the platinum combustion-tube, resting in a 10-burner furnace C. The tube is $\frac{5}{8}$ of an inch in inside diameter and 17 inches long, provided with a gas-tight joint, and prolongations 6 inches long and $\frac{3}{16}$ inch internal diameter. 2 inches from the rear end of the tube is placed a coil of platinum gauze 2 inches long completely filling the tube, then 2 inches of coarse lump oxide of copper, and 2 inches more of platinum gauze.

Next to the combustion-tube comes the 6-inch purifying U-tube D, the first half of which is filled with granulated anhydrous cuprous chloride and the second half with anhydrous copper sulphate. After this comes the special U-tube E, containing about 10 cc. strong sulphuric acid. The last half of the tube contains broken glass rods to diminish the air space. Then comes the potash bulb E, with a drying tube with ground-glass joint, and filled with freshly burned calcium chloride. After this a potash bulb G, containing strong sulphuric acid, and lastly the safety-tube H, filled with calcium chloride.

It will be observed that sulphuric acid is used as a drying medium both before and after the potash bulb, as the writer doubts the practicability of constantly moistening the gases to the proper degree with a plug of moist cotton, and prefers rather to dry the gases perfectly before entering the absorption-tube, and by means of the sulphuric-acid tube to catch any moisture taken up from the potash bulb, which will be weighed and its gain added to the gain of the potash bulb.

The combustion is proceeded with as follows: After the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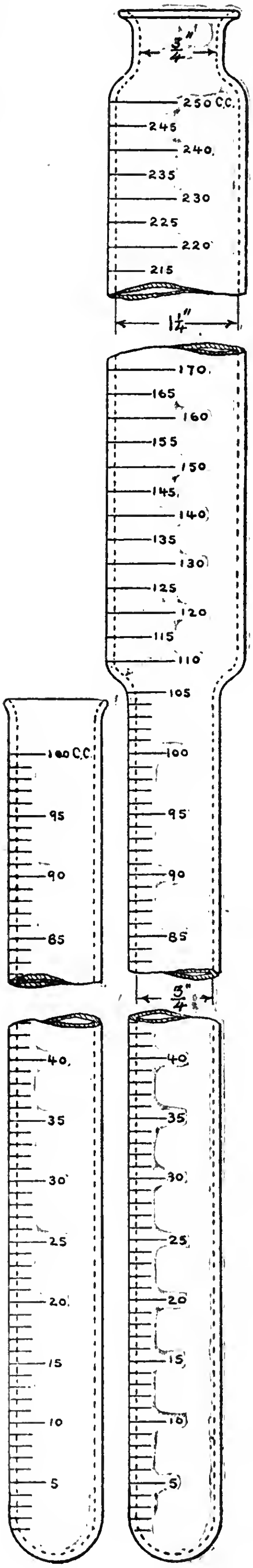
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introduction of the boat into the combustion-tubes, the oxygen is started flowing through the apparatus at the rate of three bubbles per second in the potash bulb. The burners under the platinum gauze and copper oxide are ignited, and, after the tube has acquired a full red color, the burners in front of the boat are turned on, and finally those under it until the tube throughout is a full red. This is continued for fifteen minutes, then the oxygen is shut off, the burners extinguished, and air is aspirated or forced through the apparatus, at the same rate as the oxygen, for fifteen minutes. The two tubes are then disconnected, the small caps placed on the ends, and each of them weighed, the gain in the tube containing the sulphuric acid being added to the gain of the potash bulb. Three-elevenths of the total gain is carbon. These weights are taken as the first weights of the succeeding combustion. At the beginning of a series of combustions, a blank analysis is run to get the first weights.

APPENDIX.[1]

BLAST-FURNACE CINDERS AND THEIR ANALYSIS.[2]

By James M. Camp,
Chemist to the Carnegie Steel Company, Duquesne, Pa.

It is the object of this paper to deal exclusively with the cinder made in furnaces making Bessemer iron, for the reason that this iron is almost exclusively the product of the furnaces of this region, the largest producers and consumers of the world being found here; and also for the reason that the writer's experience has been particularly confined to that field. On account of the easy solubility of cinders, and the simplicity of the analysis in general, this paper is dedicated to those who know nothing of the subject. In it they will find much that is old and, possibly, some few things that are new.

In the analysis of cinder, like many others, it is of prime importance that the results, to be of service to the furnace manager, be obtained quickly. Consequently, the methods used are those yielding the quickest results with the maximum accuracy, the trifling errors, due to the rapid manipulation, being offset by variations in each cinder flush, and variations from flush to flush. This difference is due to several causes, chief among which are the following:

1st. Changes in the burden, due to variations in the weights of ore or flux. 2d. Variations, more or less great, in the ore, flux, or fuel, which the method or time of sampling will not show. 3d. Most important, and ever varying changes, due to the reduction of more or less silica to silicon in the hearth, and its consequent absorption by the iron and loss to the cinder. This latter change is due to the variation in the temperature of the hearth, and may be caused by (1) a reduction of the bur-

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[1] Additional methods which have been contributed by chemists of the Pittsburg region to the transactions of the Chemical Section of the Engineers' Society of Western Pennsylvania.

[2] Read before the Chemical Section of the Engineers' Society of Western Pennsylvania, January 21, 1897.

den, (2) extra coke, or, as is commonly called, a black charge, (3) to a higher or lower temperature of blast, (4) a slip in the furnace with the resulting introduction of cold stock into the hearth, (5) to a reduction in the volume of air forced into the furnace, with its resulting concentration of heat at the hearth, and (6) changes in the moisture content of the air. As a consequence of the above changes, sometimes working in unison, and again at variance with each other, the production of cinder within certain close limits, is an unsolved problem. The writer has known one or two instances, when the cinder of two consecutive days showed exactly the same silica, but the laboratory was credited with this fine piece of metallurgical work. In the selection of samples, individual flushes are sometimes analyzed to represent the day's work, but the practice is bad, for the reasons given above, and it is preferable to sample each flush during the day of twenty-four hours. This is usually done by one of the furnace employees, by breaking equal-sized pieces from the test-mold samples taken during the day. These samples, properly labeled, are delivered at the laboratory early in the morning, and are there crushed in an iron or steel mortar by the boy to whom this task is allotted, and the entire sample passed through a forty-mesh sieve. In case the sample contains iron in the form of shot, these are thrown aside as not being part of the cinder. Only such iron should be shown in the analysis as is present in the form of oxide. Part of the samples, sufficient for the analysis, are then placed in the agate mortar grinding machines, and are there ground till, in the judgment of the analyst, they are sufficiently fine, and the samples, after passing a magnet through them to separate any fine shot iron, are ready for the analysis.

SILICA.

In the determination of silica, or as it is commonly called, insoluble residue, on account of the method of analysis, 1 gram of the sample is weighed off into an 11-cm. porcelain dish, with watch-glass cover; 10 cc. water are added and the powder stirred up until it is all moistened. 10 cc. of strong hydrochloric acid are now added, and if the sample contains much iron, a few drops of nitric acid, and the solution, still covered, evaporated to dryness over an Argand burner and thoroughly dried. When dry the dish is allowed to cool, and the residue is moistened with about 3 cc. of strong hydrochloric acid, and again evaporated to hard dryness. This is an essential point for rapid filtration, as a single evaporation, no matter how well done, does not dehydrate the silica, and a serious loss of time may result in filtering. The dish is again allowed to cool, and the residue taken up with a mixture of 20 cc. strong hydrochloric acid and 40 cc. water, the large amount of hydrochloric acid being added to form ammonium chloride in the subsequent part of the operation. The dish and its contents are heated to near the boiling-point for a few minutes, and filtered through a 9-cm. filter, washed with hot water till free from chlorine, burned and weighed. The native Bessemer ores used at present are practically free from barium, consequently volatilization of the silica with hydrofluoric acid is not needed.

The following are some comparative results by the above method, and those obtained by carbonate fusion, solution in water, acidifying with hydrochloric acid, evaporating to dryness and treating as usual:

No.	Insoluble residue by solution. Per cent.	Silica by fusion. Per cent.
1	31.09	31.29
2	31.67	31.65
3	31.55	31.50
4	30.47	30.50
5	31.75	31.96
6	29.38	29.50
7	30.26	30.37
8	30.37	30.50
9	30.74	30.75
10	31.40	31.34

IRON OXIDE AND ALUMINA.

Alumina.—The filtrate from the silica, in a No. 3 beaker, with a watch-glass cover, is heated to boiling, and a slight excess of strong ammonia added, and the solution boiled for a few minutes. The beaker is then removed from the heat and placed in a cold water-bath to cool and for the precipitate to settle. When the precipitate has settled completely, filter and wash by decantation through an 11-cm. filter, keeping the paper full until the precipitate is reached. Then let the funnel drain and pour the precipitate on the filter with a steady stream until the beaker is drained. Wash with hot water until free from chlorine, burn, and weigh as iron and aluminum sesquioxides.

Iron.—Into a No. 2 beaker, without lip and with a watch-glass cover, there had been previously weighed off 1 gram of the original sample; to this was added 30 cc. of water and 20 cc. of strong hydrochloric acid, and set on the steam-bath to dissolve. This solution is now boiled for a few minutes till all is dissolved, and the hydrogen sulphide all driven off. To this, while still hot, a slight excess of stannous chloride is added (about three drops), as the iron is all present in the ferrous form, and the solution diluted with cold water to about 300 cc. 10 cc. of the mercuric chloride solution are now added, the solution is stirred, and after waiting one minute it is titrated with potassium bichromate solution, as previously described before this society.[1] The iron is reported as iron, but subtracted as sesquioxide from the iron oxide + alumina obtained before.

LIME.

The filtrate from the alumina in a No. 4 beaker is heated to boiling and 25 cc. of a saturated solution of ammonium oxalate added, and 10 cc. of strong ammonia. This is boiled for a few minutes, removed from the heat and the precipitate allowed to settle. It is then filtered through an 11-cm. filter, washed with hot water till free from chlorine, and burned in a muffle furnace, allowed to cool in a desiccator, and weighed as lime. The heat of a muffle furnace, at an ordinary red heat, will thoroughly decompose calcium oxalate, for in no other case after treating as above, and then heating at the highest temperature of the blast-lamp, was there found a greater difference than 1.2 per cent. In case the cinder is high in magnesia, due to the use of all or part dolomite as a flux, a double precipitation is made of the lime as oxalate.

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[1] *Transactions Engineers' Society Western Penna., Vol. XI.*

MAGNESIA.

The filtrate from the lime, which need not exceed 400 or 500 cc., in a No. 5 beaker, is cooled by placing it in a cold water-bath, and slightly acidulated with hydrochloric acid, about 5 cc. For a cinder containing not over 8 per cent. of magnesia, 10 cc. of a 10 per cent. solution of sodium phosphate are added, and gradually from a measure, with constant stirring, 50 cc. of strong ammonia. Stir thoroughly and at intervals for two or three hours, then filter, wash with dilute ammonia (1 : 3) till free from chlorine, burn, and weigh.

MANGANESE.

The behavior of manganese in the furnace is similar to that of silicon. The higher the heat the more of the oxides are reduced and alloy with the iron, and *per contra*, the lower the heat, the less are reduced, and remain in the cinder. In the method detailed above no attention has been paid to this element, part of the manganese being weighed with the oxide of iron and alumina, and part with the lime. The amount in the cinder is, as a rule, low, and the trifling error introduced does not affect the metallurgical value of the results. Many determinations have been made, by the writer, of manganese in the iron and alumina and lime precipitates, as determined above, and in separate samples of the cinder, with the object of finding a rule whereby a certain amount of the total could be deducted from each, but without avail. And in case an accurate, complete analysis is desired, instead of an ammonia precipitation of the iron and alumina, a double basic acetate precipitation must be made, and the manganese precipitated in the united filtrates with bromine, before precipitating the lime. For some time past the writer has been using the colorimetric method on cinders, exactly as it is used for the determination of manganese in pig iron and steel, with very satisfactory results.

Herewith are given some comparative results, using the colorimetric method and those obtained by the potassium chlorate method :

No.	Colorimetric. Per cent.	Potassium chlorate. Per cent.
1	0.40	0.42
2	0.41	0.40
3	0.31	0.29
4	0.35	0.33
5	0.47	0.48
6	0.23	0.22
7	0.27	0.26
8	0.30	0.31
9	0.33	0.32
10	0.36	0.36

SULPHUR.

A blast-furnace cinder will contain practically all the sulphur of the ore, flux and fuel, less the amount contained in the iron, which amount is dependent on the temperature of the hearth. The higher the temperature the lower the sulphur, and *vice versa*. Cinders will vary in sulphur under normal conditions of ore and fuel, from 1 to 2 per cent., depending on the proportion of cinder produced to the ton of iron. The determination is effected as follows: Into a dry half-liter flask, introduce about ½ inch, equal to about 5 grams of chemically pure stick zinc, and then 0.25 gram of the cinder. The flask is provided with a doubly perforated rubber stopper. Through one opening a funnel-tube is placed, reaching to the bottom of the flask, and through the other a short piece of glass tubing, bent at right angles, and connected by a short piece of rubber tubing to the delivery-tube, also bent at right angles, reaching to the bottom of a 1-inch by 10-inch test-tube, into which about 10 cc. of the ammoniacal solution of cadmium chloride are introduced, and the test-tube filled about three-fourths full of cold water. 10 cc. of water are now added to the flask, and gently shaken till the cinder is moistened, to prevent caking on the bottom. The apparatus is connected, and 50 cc. of dilute hydrochloric acid added, one of acid to two of water. The cinder is dissolved almost instantly, liberating a large volume of hydrogen sulphide.

The compact zinc dissolves more slowly, liberating hydrogen, which gradually displaces the hydrogen sulphide, and carries it over to the absorbent. A gentle heat is applied, which is gradually increased until the zinc is dissolved, and nothing but steam escapes from the delivery-tube. The apparatus is then disconnected, and the solution titrated with iodine, using the same solution as is used for the determination of sulphur in iron or steel.

The following are some results obtained as described above and those obtained by fusion with the mixed carbonates and niter solution, evaporation to dryness, solution, filtering, and precipitating with barium chloride :

No.	Titrating with iodine. The evolved hydrogen sulphide. Per cent.	Weighing as barium sulphate. Per cent.
1	1.55	1.56
2	1.65	1.63
3	1.57	1.59
4	1.67	1.69
5	1.58	1.59
6	1.93	1.96
7	1.64	1.62
8	1.80	1.79
9	1.82	1.83
10	1.80	1.82

PHOSPHORUS.

Phosphorus, under normal conditions of temperature, is practically all reduced in the hearth of the furnace, and there combines with the iron, the amount remaining in the cinder varying from a trace up to 0.02 per cent., the average being much nearer the former than the latter figure. The determination is as follows :

10 grams of the cinder are weighed off into a 12-cm. porcelain dish with a watch-glass cover, and stirred up into a paste with water. 50 cc. of strong hydrochloric acid are now added and 2 cc. of nitric acid, and the solution evaporated to hard dryness. The dish is allowed to cool and then moistened with about 25 cc. strong hydrochloric acid, and again evaporated to hard dryness. When cool, from 15 to 20 cc. strong hydrochloric acid are added, sufficient to moisten the residue, and the dish and its contents warmed for a few minutes, and diluted with warm water to about 100 cc. This is filtered through an 11-cm. filter into a half-liter flask, and slightly washed with hot water. To the fil-

trate a slight excess of strong ammonia is added, about 25 cc., and then a slight excess of strong nitric acid, and the solution heated to 85° C. and 75 cc. of ammonium molybdate solution blown in by aid of a pipette. The flask is shaken for about five minutes, and the yellow precipitate collected and weighed the same as in ores, pig iron, or steel.

This analysis, like the determination of alkalies which are ever present in cinders, has no known metallurgical significance, for they are beyond control, and are rarely if ever determined, except for the gratification of idle curiosity, and in a furnace and steel works laboratory so much is wanted that is essential to the proper metallurgical operation of the plant, that scant time is left for work which is not essential.

BARIUM HYDROXIDE AS AN ABSORBENT IN CARBON DETERMINATIONS.[1]

By A. G. McKenna,

Chemist to the Sterling Steel Company, Demmler, Pa.

In the determination of carbon in iron or steel, potassium hydroxide has been commonly used as an absorbent for the carbon dioxide formed by combustion of the carbonaceous residue left after treatment of the metal by an appropriate solvent. In the somewhat similar determination of carbon dioxide existing in the atmosphere, barium hydroxide has been almost universally employed as the absorbent. As the use of the latter absorbent offers some striking advantages over potassium hydroxide, the society may be interested in a number of experiments showing what precautions are necessary if barium hydroxide is used in the combustion method.

The apparatus employed in all the experiments consisted of a platinum combustion-tube containing copper oxide and platinum gauze arranged as usual to insure complete oxidation of the carbon to carbon dioxide with the customary means for purifying the current of oxygen and air from carbon dioxide before entering the tube. The barium hydroxide, to absorb the products of the combustion, was contained in an absorption-tube consisting of a series of ten bulbs as shown in the sketch.

In the first experiments the fixed carbon from a coke was used as a material for combustion. A known amount was weighed into a platinum boat which was then inserted into the tube. The absorption-tube containing 100 cc. of a solution of barium hydroxide of known strength was next attached directly to the combustion-tube through which a slow current of oxygen was forced. The burners were now lighted in the usual order and the combustion continued for fifteen minutes, at the end of which time the burners were extinguished, but the current of oxygen was continued for another fifteen minutes in order to carry all carbon dioxide into the absorption-tube. The tube was now

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[1] Read before the Chemical Section of the Engineers' Society of Western Pennsylvania, March 15, 1895.

disconnected and its contents filtered into a flask, using a gentle suction so as to bring as little air as possible in contact with the solution. In washing it was found necessary to free the wash water from carbon dioxide by boiling just previous to use. The filtrate in the flask was now titrated with standard sulphuric acid, using phenol-phthalein as an indicator. The end-point is remarkably sharp and distinct. The sulphuric acid used was $\frac{1}{20}$ normal, in which 1 cc. = 0.0003 gram carbon. If the barium hydroxide solution is also made $\frac{1}{20}$ normal, the difference between 100 cc. and the number of cubic centimeters of sulphuric acid used in the titration multiplied by 0.3 will give the milligrams of carbon in the sample.

If the barium hydroxide is stronger or weaker it is simply necessary to substitute in the calculation for 100 cc. the equivalent amount of barium hydroxide used. The following results were obtained by the coke combustion:

Amount taken. Gram.	Amount found by titration. Gram.
0.0007	0.0075
0.0256	0.0250
0.0298	0.0290

Two grams of a steel containing 1.07 per cent. carbon were now dissolved in 150 cc. of a 50 per cent. solution of copper potassium chloride containing 5 per cent. of concentrated hydrochloric acid. The solution was kept agitated for one hour at a gentle heat by means of a stirring apparatus. It was then allowed to remain quiet for several hours and filtered on asbestos in a platinum boat, washing with dilute hydrochloric acid, and then with hot water. The carbonaceous residue was burned without drying, exactly as the coke had been. The results were 1.11 and 1.12. As these results are decidedly high (the results using potassium hydroxide as an absorbent being 1.072 per cent., 1.068 per cent., 1.066 per cent., 1.070 per cent.), several combustions were made on sugar with the following results:

Amount taken. Gram.	Amount found by titration. Gram.
0.0168	0.0164
0.0162	0.0160
0.0188	0.0185
0.0170	0.0166

Another series of combustions on standard steels gave the following results, the barium carbonate precipitate being weighed after ignition as well as the solution titrated :

Found by potassium hydroxide. Per cent.	Found by titration. Per cent.	Found by weighing barium carbonate. Per cent.
0.477	0.489	0.484
0.477	0.477	0.471
0.311 0.312 0.314	0.325	0.310
0.195 0.196 0.194	0.205	0.193
0.099 0.097 0.098 0.099 0.102	0.110	0.103

It will be seen that in general the results are just a trifle low on carbon from other sources than steel, while the results on steel are distinctly higher by titration, and a trifle high by weight.

The cause of the errors in steel was traced to the formation of sulphurous and sulphuric acid from the carbonaceous residue. To obviate this error a solution of potassium permanganate in sulphuric acid was interposed between the combustion-tube and the barium hydroxide. With this form of apparatus the following results were obtained, the combustion being made as before, but thirty minutes being used to aspirate :

Found by potassium hydroxide. Per cent.	Found by titration. Per cent.	Found by weighing barium carbonate. Per cent.
0.603 0.599 0.594	0.60 0.599	0.595 0.594
0.477	0.473 0.470	0.470 0.465

In order to test decisively this theory of the causes of errors, four more determinations were made using ten grams in each of a soft steel containing 0.075 per cent. carbon. Two of these combustions were made without interposing any permanganate. The results were :

Found by titration. Per cent. carbon.	Found by weighing barium carbonate. Per cent. carbon.
0.084	0.080
0.084	0.079

The precipitates of barium carbonate were now dissolved in hydrochloric acid and filtered. The barium sulphate found in the first case weighed 0.0095 gram, and in the second case 0.0075 gram. The results of the combustion corrected by these amounts give respectively 0.075 per cent. and 0.074 per cent.

The other combustions, interposing permanganate, gave the following results:

Found by titration. Per cent. carbon.	Found by weighing barium carbonate. Per cent. carbon.
0.081	0.075
0.080	0.075

The barium carbonate obtained from these combustions contained nothing insoluble in hydrochloric acid.

In conclusion I would say that it will be found much simpler to burn and weigh the barium carbonate rather than to titrate. The high combining weight of barium renders it possible to weigh extremely small amounts of carbon when present as barium carbonate.

AN IMPROVEMENT IN THE ZINC REDUCTOR FOR THE DETERMINATION OF IRON OR PHOSPHORUS.[1]

By A. G. McKenna,

Chemist to the Sterling Steel Co., Demmler, Pa.

In using the ordinary form of reductor, for reducing solutions of iron or molybdic acid by passing through a column of finely granulated zinc, an enormous amount of zinc is consumed in the useless reaction between the free acids necessarily present and the zinc, while a comparatively small amount takes part in the reaction by which the iron or molybdic acid is reduced.

The reactions spoken of are

$$Fe_2(SO_4)_3 + Zn = 2FeSO_4 + ZnSO_4$$

$$\text{and } H_2SO_4 + 2Zn = ZnSO_4 + H_2.$$

The great volume of hydrogen set free by the second reaction proves very annoying during the operation of reduction, and unless an extremely powerful suction is used, the liquid can scarcely be drawn through the zinc.

As it is known that zinc which has been amalgamated is scarcely attacked by weak acid, it occurs to the writer to try the effect of amalgamating the granulated zinc before using it in the reductor.

The results were most satisfactory. The reaction between the zinc and the free acid was almost entirely suppressed, there being scarcely any evolution of hydrogen during the passing of the solution through the zinc, while the speed of the reduction was not in the least diminished.

The form of apparatus used is shown in the accompanying sketch. In preparing it for use a small plug of asbestos is placed in the bottom of the tube just above the stop-cock. A very thin layer of asbestos will be found sufficient. It should be packed loosely so that a steady stream of water will run through without suction. On this plug about 200 grams of granulated

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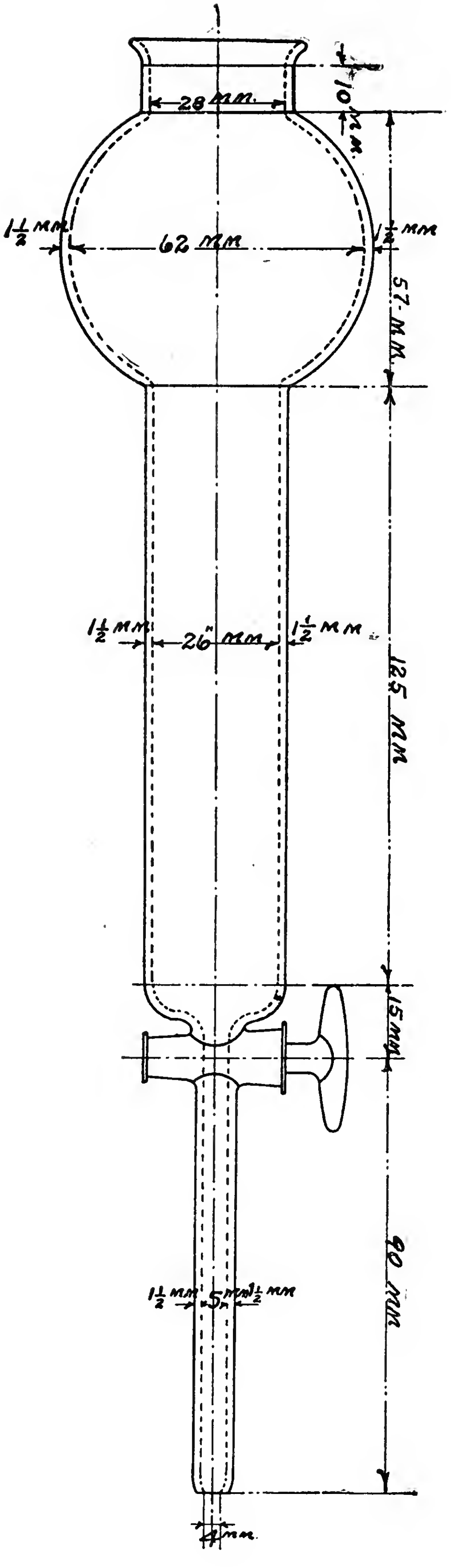
[1] Read before the Chemical Section of the Engineer's Society of Western Pennsylvania, September 29, 1895.


28 MM.
10 MM.
1½ MM
62 MM
1½ MM
57 MM.
1½ MM
26 MM
1½ MM
125 MM
15 MM
90 MM
1½ MM
5 MM
1½ MM
4 mm.

zinc are placed. The zinc should be of such fineness that it will pass through a 20-mesh sieve but not through a 30-mesh. Before placing it in the reductor it is thoroughly amalgamated by stirring up with it, in a small beaker, about 5 grams of mercury and 25 cc. of a 5 per cent. solution of sulphuric acid. The zinc fills the straight part of the tube about two-thirds full, leaving a sufficient space to allow the addition of the solution which is to be reduced. After the zinc is in position the tube is inserted in a filtration flask by means of a rubber stopper and the flask connected with the suction. The zinc is washed several times with a 5 per cent. solution of sulphuric acid and is then ready for use.

For the determination of iron in ores, the solution of the ore after the excess of free hydrochloric acid has been driven off, is diluted and filtered into a 500-cc. graduated flask and diluted to the mark with water after cooling. By means of a 100-cc. pipette, 100 cc. are transferred to a small beaker; 5 cc. of a 50 per cent. solution of sulphuric acid are added and the contents of the beaker are poured into the reduction-tube, the glass stopcock being opened sufficiently to allow the solution to be drawn through by a gentle suction. There will be scarcely any evolution of gas, and the reduction will be complete even though the solution runs through in a steady stream. The tube is now washed four times with a 5 per cent. solution of sulphuric acid, using in each washing about 50 cc. of solution. It is important during the washing to avoid drawing successive amounts of air through the zinc, as, for reasons stated below, this will lead to low results. The reduced solution is now titrated by standardized permanganate and a duplicate determination is made on another 100 cc. taken from the graduated flask. These duplicates should agree within 0.1 per cent.

In some of the first experiments it was found that a blank made by washing five successive portions of 5 per cent. sulphuric acid through the tube, allowing a current of air to be drawn through for a half minute between the washings, required an amount of permanganate equivalent to 0.003 gram of iron, although no iron could be found in the solution. Blanks made in a similar way, except that no air was drawn through the tube, were colored by the first drop of permanganate. Duplicate determinations of iron, allowing in one case air to be drawn through and in the other not, invariably gave results from 0.2 to 0.3 per cent. low, in the cases in which air was drawn through alternately with the sulphuric acid. The facts evidently point to the formation of some compound which oxidized iron and was itself oxidized by permanganate. A test for hydrogen peroxide was made in one of the blanks by adding a few crystals of potassium iodide; on standing a few minutes the solution began to show the characteristic color of free iodine. On titration with hyposulphite it was found that 0.0009 gram hydrogen peroxide was present in the blank. This amount of hydrogen peroxide would be sufficient to oxidize about 3 mgms. of iron. In regard to the amount of zinc consumed in the reduction of a gram of 63 per cent. ore, it may be said that a determination of the zinc in the solution after complete reduction, gave 0.6 gram of zinc.

ON SOME EVOLUTION METHODS FOR SULPHUR IN IRON AND STEEL.

BY W. E. GARRIGUES.

By utilizing the property of caustic alkali to effectually check a current of hydrogen sulphide, followed by oxidation after washing out the single test-tube necessary for absorbing the gas, a clean and inoffensive solution is rapidly prepared for final precipitation.

The evolution is conducted exactly as for the iodine titration except that 10 grams of the drillings are used in place of 5. The absorbing liquid is 10 per cent. caustic soda, and 65 cc. are used for a determination, being contained in a single test-tube, to the bottom of which the delivery-tube dips.

50 cc. of water are poured on the drillings in the flask, followed by 40 cc. strong hydrochloric acid, the heat of the reaction starting a brisk evolution of gas at once. After complete solution of the metal and boiling, the test-tube is rinsed into a beaker, 10 cc. of 5 per cent. potassium permanganate added and heated to boiling; this completes the oxidation. 20 cc. of strong hydrochloric acid are next poured in, followed by 15 cc. saturated oxalic acid, which leaves the liquid clear and colorless. Neutralize the ammonia, just clearing with hydrochloric, and precipitate boiling with barium chloride. The neutralization seems to be necessary.

Bromine was tried before permanganate, but gave indication of low results. The possibility of correcting this error seems assured, but bromine is sufficiently unpleasant to let alone when something else will answer equally as well.

The figures obtained on a sample of steel by the above two methods of oxidation, the evolution being identical, and also by the aqua regia method, follow:

Aqua regia.		Bromine.	Potassium permanganate.
0.048	1	0.042	0.046
0.049		0.042	0.046
	2	0.045	0.047
	3	0.047	0.048
		0.047	0.049

The bromine results need an explanation.

No. 1 was oxidized as follows: Bromine water added to alkaline solution, heated to boiling, acidified, and bromine boiled off.

No. 2 ditto, except alkaline solution boiled one-half hour after addition of bromine.

No. 3 ditto, boiled one hour.

The one objection to alkaline oxidation methods is the practical impossibility of obtaining caustic soda free from sulphur in some form. This necessitates subtracting a "blank." Some attempts to get rid of the sulphur were only partly successful; using a saturated solution as a basis (obtained in exactly the same manner as was described for getting rid of carbonate in the first part of this paper), reduced the blank from 16 to 7.7 mgms. Adding excess of barium chloride and letting stand two days reduced it to only 12.1 mgms. The saturation process is recommended, the clear liquid being diluted to 15° B., at which density it contains about 10 per cent. of sodium hydroxide.

The above-described process should be especially advantageous in the accurate analysis of pig-iron, where the sulphur content of the residue is to be determined. In that case there is certainly no advantage in titrating the evolved sulphur with iodine and then working the residue gravimetrically; instead the two are combined and only one precipitation made.

As to the iodine titration of the evolved sulphur arrested by caustic alkali, some experiments warrant the conclusion that the method is a strictly empirical one, not depending upon complete reactions like the gravimetric results.

In other words the equation,

$$H_2S + I_2 = 2HI + S,$$

in which 253.7 iodine are equivalent to 32 sulphur, cannot be assumed as a basis for calculating the sulphur value of an iodine solution of known strength. The results thus obtained, when caustic alkali is used, are always too low.

A solution standardized empirically, *i. e.*, against a steel of known sulphur content, will contain less iodine than one standardized by calculating from its oxidizing power. As the equation before stated is the simplest which can be assumed to take place between hydrogen sulphide and iodine, the least possible amount of iodine as compared to sulphur entering into it, the choice of two explanations remains to account for the discrepancy: (1) The sulphur is not all evolved from the steel as hydrogen sulphide, and (2) the hydrogen sulphide is partly oxidized to sulphuric acid in the alkaline solution during evolution.

Experiment No. 1 must be dropped for the reason that when cadmium chloride is used the whole of the sulphur evolved precipitates as cadmium sulphide, and again becomes hydrogen sulphide on acidifying, as shown by its requiring the full theoretical quantity of iodine. The suggestion of partial oxidation alone remains then, to account for the shortage, it having been proved by direct experiment that no hydrogen sulphide escapes during titration. The means of doing this was to add at once an excess of iodine and then titrate back with sodium thiosulphate.

Following are results obtained on the same sample of steel mentioned before, and shown to contain about 0.048 per cent. sulphur. The absorption in caustic alkali was carried out in precisely the same manner as were the gravimetric analyses previously recorded:

Caustic soda absorption.		Cadmium chloride.
Direct with iodine.	Back with sodium thiosulphate.	
0.038	0.039	0.047
0.039	0.039	0.047
0.042	8.041	0.049

Similar results were obtained by the sodium hydroxide method on standard samples kindly furnished by Mr. Camp and Mr. Handy, all of which were sufficiently concordant to have been apparently correct had any one of the samples been used for standard titrating solution instead of taking its theoretical value. They did not, however, agree among themselves quite as well as either the gravimetric results or those obtained volumetrically with cadmium chloride as an absorbent, the series above given being rather better than the average. Both absorbents gave a blank titration equivalent to 0.002, which was subtracted. To sum up: An iodine solution cannot be used indiscriminately for titrating sulphur evolved into caustic alkali and cadmium chloride. The former requires a standard steel as a basis of calculating, all evolutions being made as nearly as possible under the same conditions, while the latter can be interpreted from the theoretical value of the iodine solution, the results agreeing more closely among themselves and being obtained with less attention to minute details. Hence the cadmium chloride is recommended.

THE DETERMINATION OF CHROMIUM.[1]

By A. G. McKenna,

Chemist to the Sterling Steel Co., Demmler, Pa.

The following method for the determination of chromium in steel will be found more accurate and rapid than any of the published methods known to the writer. By its use he has made several thousand chromium determinations with uniformly satisfactory results.

The process is based upon the well-known fact that chromic salts can be oxidized completely to chromic acid by the addition of potassium chlorate to a concentrated nitric acid solution, and the fact, not so well known, that the presence of nitric acid does not interfere with the titration of chromic acid in a cold solution by means of ferrous sulphate and permanganate.

In case the steel contains manganese and a determination of the same is wanted in addition to the determination of chromium, the method is as follows: Weigh 3 grams of steel into a 400-cc. flask, add 35 cc. of strong hydrochloric acid and boil for five or ten minutes, which will be found sufficient to dissolve completely even the highest chrome steels. When most of the hydrochloric acid is boiled off, add 150 cc. strong nitric acid, and continue the boiling until no more brown fumes are seen at the mouth of the flask, showing that the hydrochloric acid has all been driven off. Remove the flask from the flame or hot plate, allow to cool for two or three minutes, and then add 10 grams of potassium chlorate in crystals. It is best to allow the solution to cool slightly before adding the chlorate in order to diminish the violence of the effervescence due to the action of the chlorate on the chromic salts. Replace on the hot plate and boil down to about 40 cc. in order to decompose completely the potassium chlorate. It is necessary to decompose the chlorate completely

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[1] Read before the Chemical Section of the Engineers' Society of Western Pennsylvania, June 18, 1896.

or results will be from 0.1 to 0.2 per cent. high, but the amount of nitric acid left in the solution is not important. At this stage the chromium will all be in the solution in the form of chromic acid. The manganese will be precipitated as dioxide and generally some crystals of potassium nitrate arising from the decomposition of the chlorate will have separated out. Filter off the manganese dioxide on an asbestos plug, washing the precipitate three times with cold water. Transfer the asbestos and the manganese dioxide to the flask, in which the original precipitation was made, titrate with ferrous sulphate and permanganate, according to Williams' well-known modification of Ford's method.

Make the filtrate from the manganese dioxide which contains all the chromic acid in a nitric acid solution up to about 500 cc. with cold water, and add standardized ferrous sulphate solution in slight excess indicated by the disappearance of the yellow color of the chromic acid and the appearance of the clear green color of chromic nitrate; then add standardized permanganate to oxidize the excess of ferrous sulphate used, the end-point being the well-known faint pink color.

The standard ferrous sulphate is made by dissolving iron wire of known purity in an excess of dilute sulphuric acid, diluting with water until 1 cc. contains 0.003223 gram of iron in the ferrous condition.

The permanganate solution is made by dissolving 1.818 grams of pure potassium permanganate in a liter of water; 1 cc. of the permanganate solution will then oxidize exactly 1 cc. of the ferrous sulphate solution, and the number of cubic centimeters of ferrous sulphate used to reduce the chromic acid minus the cubic centimeters of permanganate necessary to oxidize the excess of ferrous sulphate, will give the amount of chromium present in milligrams.

For example, to 3 grams of steel treated as above, 35 cc. of the ferrous sulphate are added to reduce the chromic acid and then 5 cc. of permanganate solution are found necessary to produce a permanent pink; hence 3 grams of this steel contain 0.03 gram of chromium or 1 per cent. If these same solutions are used for the titration of the manganese dioxide by the Williams' method, each cubic centimeter of ferrous sulphate used in excess of the cubic centimeters of permanganate used in the back titration equals 0.001418 gram manganese.

In case the determination of manganese is not required and it is desired to avoid the filtration from the manganese dioxide, the method may be modified by diluting the solution after it has been boiled down to 40 cc. by the addition of 100 cc. of water and a few drops of hydrochloric acid, which will at once dissolve the manganese dioxide without action on the chromic acid. The solution then must be boiled for a few minutes to remove the chlorine set free by the reduction of the manganese dioxide, after which it may be cooled and titrated as above.

In very many chrome steels the amount of manganese is so inappreciable in comparison with the chromium that for practical results it is not necessary to remove the manganese dioxide either by filtration or solution in hydrochloric acid but the solution may be diluted after the evaporation to 40 cc. and titrated at once. Of course, in high chrome steels it is not necessary to take more than a gram for the analysis.

For the determination of chromium in ores, slags, and ferro-chromes, beyond a doubt the best method of decomposition is by fusion with sodium peroxide in a nickel crucible, which brings about complete decomposition in two or three minutes, if the sample is at all finely ground.

Duplicate determinations on ores, slags, and ferro-chromes, made by the solution of the sodium peroxide fusions in nitric acid and oxidation by potassium chlorate, gave on titration results equivalent to those obtained by the usual methed of acidifying with sulphuric acid, after decomposing the excess of peroxide by boiling in a water solution. Consequently there would be no advantage in the chlorate method for these over the usual method, except that, by obtaining a clear solution of fusion in the nitric acid preliminary to oxidation with chlorate, all danger from incomplete decomposition leading to the presence of particles of metal, which might reduce some chromic acid on the addition of sulphuric acid, is avoided.

However, in the writer's experience, the decomposition has always been complete.

NOTES ON THE ANALYSIS OF MILL AND PUDDLE CINDERS.

BY JOS. M. WILSON.

Mill cinder is used in our furnace as part of the burden and is almost wholly brought in car-load lots. As the railroad people are constantly pushing us for prompt unloading, methods for rapid determination of the constituent elements of these cinders are important. Formerly we were required to report the iron and insoluble matter at once and later the silica. At present iron and phosphorus are also required and occasionally manganese. Our methods are as follows :

IRON.

Weigh out 0.25 and 0.5 gram into lipless beakers, moisten with 10–15 cc. water, making certain that the mass is well broken up, add quickly 20 cc. concentrated hydrochloric acid, cover, boil gently for twenty minutes (or let digest upon a steam-table one hour, then bring to a good boil), add stannous chloride solution, from a pipette, till the liquid is colorless, boil two minutes, remove to the steam-table and allow to settle. The supernatant liquid must be colorless. The residue will vary from light gray to black according to the amount of powdered coke present.

Wash into a No. 5 or 6 beaker, rinse a small beaker thoroughly with cold water, taking care to remove *all* the insoluble matter. Make the volume 300 cc., stir well, add 30–40 cc. mercuric chloride solution, *all at once*, stir, run in potassium dichromate until 4 drops give no blue coloration with a drop of ferricyanide indicator in one-half minute.

Solutions Used.—Potassium dichromate, 4.9 grams of the salt in 1 liter of water. 1 cc. = 0.005 gram iron. Stannous chloride, 100 grams in 1 liter hydrochloric acid (1 : 1). Mercuric chloride, 50 grams in 1 liter of water. Ferricyanide indicator, 5 cc. of a 5 per cent. solution in 40 cc. water.

INSOLUBLE MATTER AND SILICA.

Weigh 1 gram into a 5-inch Royal Meissen dish, stir up with 20 cc. water, add 20 cc. concentrated nitric acid, stir well, cover, evaporate to dryness, and ignite till all acid smell is gone. Cool, add 10 cc. concentrated hydrochloric acid, evaporate to dryness, ignite, cool, add 25 cc. hydrochloric acid, evaporate to 10 cc., add 30 cc. water, and heat to boiling. Filter through a 9-cm. filter, wash with hot hydrochloric acid (1 : 1) and with cold water twice, ignite, cool, and weigh *insoluble* matter. Fuse "insoluble" with six to eight times its weight of sodium carbonate, dissolve the fusion in water, acidify with hydrochloric acid, evaporate to dryness, ignite, cool, add 10 cc. concentrated hydrochloric acid, dry, and ignite to render silica entirely insoluble and granular. Cool, add 25 cc. hydrochloric acid, evaporate to one-half, add 30 to 40 cc. water, heat to boiling, filter on a 9-cm. filter, wash twice with hot water, filling the filter each time to remove salts, then with hot hydrochloric acid (1 : 1), and with cold water twice, then four to six times with hot water, ignite, cool, and weigh; or moisten insoluble matter with water, add hydrofluoric acid till a clear solution is obtained, then 5 or 6 drops of sulphuric acid (1 : 3), evaporate, dry, ignite on hot plate till no more fumes of sulphur trioxide come off, then heat to redness, cool, and weigh. Loss = SiO_2.

MANGANESE.

This is determined by precipitation with potassium chlorate, purification of the manganese dioxide precipitate, and final weighings as $Mn_2P_2O_7$, by the acetate method or by color.

PHOSPHORUS.

Having found phosphorus in our pig metal and being unable to determine its source we sought it in ore, flux, and fuel, but not finding it in either we were compelled to turn to the mill cinder. Up to this time we, like many others, supposed that *all* the phosphorus was "soluble" inasmuch as mill cinders are easily decomposable silicates, but as we could not locate the trouble elsewhere we turned our attention to the residues which we fused and treated for phosphorus; the results took us completely by surprise, for we found that no matter what the total amount of phosphorus in the cinder the insoluble residue invariably carried between 0.03 per cent. and 0.04 per cent.

As the fusion of the residue and its subsequent treatment took more time and attention than we could give it, we had to devise a method by which we could obtain results rapidly. After some experimenting we settled on the following scheme: Weigh 5 grams substance into a platinum dish, stir up with 30 cc. water, add 30 cc. hydrofluoric acid, and 30 cc. hydrochloric acid. Cover with platinum foil supported by a platinum triangle, evaporate to dryness over an Argand burner turned low, add 20 cc. hydrochloric acid, evaporate again to get rid of hydrofluoric acid, add 30 cc. hydrochloric acid, evaporate one-half, and wash into a No. 3 beaker. Evaporate to a sirup, add 50 cc. nitric acid, evaporate till no more brown fumes come off and liquid is sirupy, add 30 cc. water, and heat to boiling. Filter through a 7-cm. filter into a 16-oz. flask, wash filter twice with cold water, and once with hot nitric acid (sp. gr. 1.20), dropping acid from a pipette on the side of the funnel just above the top of the filter; wash acid out of filter. Filter retains the coke.

Boil filtrate, add potassium permanganate (12½ grams to 1 liter of water) till a brown precipitate of manganese dioxide separates and remains. 20 to 100 cc. will be required, according to the amount of carbonaceous matter dissolved and the completeness with which hydrochloric acid has been driven off by the nitric acid used in the last evaporation. Reduce the manganese dioxide with ferrous sulphate (free from phosphorus). After reduction is complete, boil ten minutes, cool, and add strong ammonia till the ferric hydroxide makes a thick mud. Redissolve in strong nitric acid to clear amber-colored liquid, and insert a thermometer. When temperature is 88° C. pour in 100 cc. molybdate solution. (Wood's 1888 formula), shake five minutes, let settle, filter off yellow precipitate, wash with 2 per cent. nitric acid (or Dudley's acid ammonium sulphate) five times. Remove acid by five washings with potassium nitrate (1 : 1000), and determine phosphorus by any convenient method: (1) weigh yellow precipitate, (2) titrate the reduced molybdic acid with potassium permanganate, (3) titrate back the excess of standard sodium hydroxide, etc., etc. A determination by this method can be made in six hours without hurrying the evaporations with hydrofluoric acid and hydrochloric acid.

The following method has been used when not in a hurry: 5 grams in a 5-inch deep dish are moistened with 20 cc. of water, and 80 cc. concentrated nitric acid. Hydrochloric acid gelatinizes the silica, which encloses particles of undissolved slag and is very troublesome to handle. Evaporate to dryness, ignite till no more acid fumes are perceptible, cool, moisten with 20 cc. hydrochloric acid, take up in 50 cc. water, filter, wash with hot hydrochloric acid (1 : 1), and with cold water till free from iron. Ignite, fuse with five to six times its weight of sodium carbonate, dissolve in hot, dilute nitric acid, evaporate to dryness, ignite till free from acid fumes, cool, moisten with hydrochloric acid, dry, ignite again, cool, moisten with hydrochloric acid, take up with water, filter, and boil filtrate. Add slight excess of ammonium hydroxide, boil two minutes, filter, wash precipitate three times with hot water, then wash into a beaker containing the original acid solution, and boil to a sirupy consistency. Add 40 cc. concentrated nitric acid, boil down to a sirup, add 25 cc. water, heat to boiling, filter through a 7-cm. filter into a 16-oz. flask, wash with nitric acid and water, and precipitate and determine phosphorus as above.

The precipitation of iron and aluminum phosphate from a solution of fusion freed from silica, serves to get rid of the great excess of alkaline salts and leaves the phosphorus in better condition for precipitation.

As stated above, nitric acid is a better solvent for mill cinders than hydrochloric acid, as it does not gelatinize the silica and leaves the insoluble matter more sandy and more easily filtered and washed.

Below are a few results :

			Per cent.
Car. No.	405,	Soluble phosphorus	0.045
“ “	493,	“ “	0.130
“ “	3354,	“ “	0.800
“ “	3354,	phosphorus by solution in nitric acid and fusion of residue	0.830
“ “	4818,	Insoluble phosphorus	0.035
“ “	537,	“ “	0.038
“ “	405,	Phosphorus by method above	0.080
“ “	493,	“ “ “ “	0.165
“ “	3354,	“ “ “ “	0.825
“ “	4818,	Total phosphorus	0.155
“ “	537,	“ “	0.060

THE COMPLETE ANALYSIS OF CHROME ORE.[1]

BY A. G. MCKENNA,
Chemist to the Sterling Steel Co., Demmler, Pa.

A serious objection to most methods of chrome ore analysis has been the difficulty of obtaining complete decomposition of the ore without prolonged and repeated fusions with the reagents generally employed for that purpose.

By fusing the ore with sodium peroxide, which is now coming into general use as an analytical reagent, any chrome ore is completely decomposed in a few minutes. The fusion should not be made in platinum as the peroxide attacks the crucible strongly. A nickel crucible is best to use, although it is also attacked and cannot be used more than twenty or thirty times. On leaching out the fusion with water all the chromium goes into solution as sodium chromate; the oxides of iron, nickel, and magnesium remain in the undissolved residue. The following method for the determination of silica, oxide of iron and chromium, alumina, lime, and magnesia is based on the above-mentioned facts.

DETERMINATION OF OXIDES OF IRON AND CHROMIUM.

0.5 gram of the finely ground sample which has been dried at 100° C. for one hour is weighed into a nickel crucible of about 20 cc. capacity, in which have been placed 3 or 4 grams of sodium peroxide; after thoroughly mixing the contents, the crucible is held over a Bunsen burner by means of a pair of suitably shaped tongs, until fusion begins. The mass is kept in a liquid condition at a low red heat for about one minute, which is sufficient to insure complete decomposition if the ore is at all finely ground. After allowing the crucible to cool it is placed in a 400-cc. beaker with a watch-glass cover and hot water added until the crucible is covered.

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[1] Read before the Chemical Section of the Engineer's Society of Western Pennsylvania, March 18, 1897.

The beaker is placed on a hot plate for a few minutes until the fusion is dissolved; the crucible is then removed by means of a glass rod and the contents of the beaker allowed to settle for a few minutes. When the insoluble matter has subsided it is collected on a 9-cm. filter-paper, the filtrate being received in a half-liter flask. The residue on the paper which contains all the iron is ignited in a platinum crucible, fused with 2 or 3 grams of potassium bisulphate, dissolved in dilute sulphuric acid (1 : 10), reduced by filtration through amalgamated zinc, and titrated in the usual manner with standard permanganate. The result is calculated to ferrous oxide.

The filtrate in the half-liter flask, which contains all the chromium as sodium chromate in an alkaline solution, is boiled for about ten minutes in order to insure the removal of all peroxide which, if allowed to remain until the solution is acidified, would react on the chromate, reducing it to the sesquioxide.

When the removal of the peroxide is complete the solution is allowed to cool and then acidified with a large excess of dilute sulphuric acid (1 : 4).

The solution is transferred to a 1-liter beaker, and diluted to about 800 cc. with cold water. To this solution 70 cc. of a ferrous sulphate solution, containing 10 grams of iron (in the ferrous condition) to the liter, are added; this is sufficient to reduce the chromic acid corresponding to 0.3167 gram of chromic sesquioxide. The excess of ferrous sulphate which has been added, is determined by back titration with standard permanganate solution, of which 1 cc. is equivalent to 1 cc. of the ferrous sulphate solution. Such a permanganate contains 5.643 grams potassium permanganate to the liter. The difference between the cubic centimeters of ferrous sulphate used and the cubic centimeters of permanganate used, multiplied by 0.905, gives the percentage of chromic sesquioxide in the ore.

For the determination of silica, alumina, ferric oxide, chromic sesquioxide, lime, and magnesia, fuse one-half gram of ore in a nickel crucible as before, dissolve in about 50 cc. hot water in a covered 5-inch porcelain dish, remove crucible and acidify with hydrochloric acid, evaporate to dryness, take up in dilute hydrochloric acid (1 : 4), filter, ignite, and weigh as SiO_2. To the filtrate add 10 cc. strong hydrochloric acid, make ammoniacal, pass hydrogen sulphide, allow to settle, filter off the precipitated hydrates of chromium and aluminum and the sulphides of iron and nickel. Dissolve the iron, chromium, and aluminum in dilute hydrochloric acid and reprecipitate as before with hydrogen sulphide and filter. In the combined filtrates determine lime and magnesia in the usual manner.

Redissolve the iron, chromium, and aluminum precipitates from the filter-paper with dilute hydrochloric acid, oxidize with a few drops of nitric acid, precipitate with ammonia, filter, wash free from chlorine, ignite, and weigh as Al_2O_3, Cr_2O_3, Fe_2O_3. From this weight subtract the $Cr_2O_3 + Fe_2O_3$, calculated from the percentage of iron and chromium found in previous analysis, which will give the alumina.

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