METHODS OF CHEMICAL ANALYSIS

AND

FOUNDRY CHEMISTRY

BY

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PART I.

PREFACE.

Because of frequent requests from beginners in iron analysis for methods applicable to the several departments of such work and of late a desire on the part of foundrymen for data relative to cupola mixtures, the following pages have been arranged.

The chemical methods described in detail are those which, after a critical study of texts and papers to which I have had access, seem best adapted to rapid work without sacrifice of accuracy.

Beginners are usually confronted by an inability to select methods which will serve them in time and accuracy to meet commercial demands. They cannot often find in texts how closely their results must agree with those of other chemists operating upon the same samples, hence figures are given.

I shall style the works by Blair, Lord and Troilius, *Common References,* making no further attempt to assign credit for ideas used except in such instances as a study of the reference seems necessary to an understanding of the methods as I use them.

A volume containing methods for the analysis of ore, pig iron and steel, printed by the Chemical Publishing Company, of Easton Pa., contains a description of methods used in the laboratories in and about Pittsburg. To the above work and to the *Journal of Analytical and Applied Chemistry,* which is now merged into the *Journal of the American Chemical Society,* I would refer the reader for the less important methods, to which I make no allusion.

Believing it necessary, when considering any part of a method, to study it in all details, I have refrained from indexing this book, giving only the headings as a table of contents.

Part I is devoted to Analytical Methods and Suggestions.

Part II treats of the application of Chemistry to Foundry Practice.

F. L. C.

Cleveland, August, 1901.

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METHODS OF CHEMICAL ANALYSIS.

INTRODUCTION.

Standard Potassium Permanganate.

The first five methods for the determination of iron, phosphorus, manganese, calcium and sulphur all depend upon the use of a standard solution of potassium permanganate, for which reason I call them a *Family* of methods.

In my experience the solution of permanganate is more easily standardized than any other solution employed in this class of work. It is the basis of a large number of volumetric methods. The permanence of a standard solution of potassium permanganate is made evident by the following data:

An aged solution titrated,

Sept. 2, 1898, 39.7 c. c. on 1.4 gm. ammonio-ferrous sulphate.

Sept. 15, 1898, 39.7+ "
Oct: 3, 1898, 39.7— "
Oct. 19, 1898, 39.7 "
Nov. 3, 1898, 39.7 "
Dec., 1898, 39.8 "

when it was nearly consumed.

The last portions of a standard solution are more subject to variation. To attain such results the solution may be prepared and standardized as follows: A solution containing 2½ grammes of potassium permanganate per litre is of convenient strength for the five methods. Place *n* grammes of the salt in a measured volume of water, by shaking or by aid of blast of air, hasten its solution. When complete allow the solution to age several weeks. The salt may be the commercial article—the water any ordinary tap water. At the end of this aging the clear supernatant liquid should be syphoned from any residual matter, and is ready for use. Were it desired to make a solution for almost immediate use, distilled water and chemically pure salt should be employed. This solution should be brought to boiling for several minutes. It will be ready for use the next day. Its value will not remain as constant as that of the former.

The containers of the permanganate solution, as well as the tubes leading from the same, should be well painted to avoid decomposition of the solution by light. Statements that permanganate solution can not be conveyed unchanged through rubber connections are not well founded, as in obtaining the list of titrations given, a side-filling burette was used, incident to which were two short rubber connections. Such connections become coated almost immediately with oxide of manganese, which prevents further action upon the rubber. Before using apparatus of this kind, connections should stand filled with solution over night, which, when drawn, leaves the train ready for use.

Method of Standardizing.

Oxalic acid, ferrous sulphate, iron wire and ammonio-ferrous sulphate (if of proper quality) may all be used to standardize a permanganate solution. Of these ammonio-ferrous sulphate is most available. Correct ammonio-ferrous sulphate may often be procured in the market under label "Chemically Pure Ammonio-ferrous sulphate for Standardizing." It may as frequently be obtained of perfect quality under label "Dry Commercial Ammonio-ferrous sulphate." It should be kept in rubber stoppered bottles in a dark place. Such samples show no trace of ferric iron and may be either fine or coarse crystals. I have at this time seven varieties of it, varying in age from one to five years, all of which titrate the same with potassium permanganate. When so many varieties of the salt, made under different conditions and at different times, check with one another, it is evident that the salt is permanent and that each is the theoretical article.

To obviate any doubt as to this point, we may compare them by aid of a solution of potassium permanganate with ferrous iron obtained by solution of any good iron wire sold for the purpose which may be called 99.9 per cent iron. For the method of dissolving and treating this iron see Fresinus' *Quantitative Analysis,* Second American Edition, page 268.

To prepare a correct ammonio-ferrous sulphate, dissolve the imperfect salt by agitation in a minimum quantity of distilled water containing not to exceed .5

per cent by volume of sulphuric acid sp. gr. 1.84, evaporate slightly under cover of watch glass, filter, cool to low temperature, when by constant stirring a mass of minutely small crystals will form, quite convenient to weigh. Decant the mother liquor from the mass of crystals, pour the crystals into a large funnel containing a platinum cone, when by pressure upon the mass or brief suction, most of the liquor will be eliminated, wash once with cold distilled water, apply suction and pressure as before. Throw the mass on to filter paper several sheets in thickness, distribute evenly over surface of same, cover with several sheets of filter paper, press the crystals. Repeat this operation several times, often using new paper, expose the mass between filter paper in a warm, dry atmosphere, not to exceed 90 degrees F., away from the light for 48 hours, changing the position of the crystals on the paper and pressing down any aggregations of the same occasionally during the period, when they will be ready to bottle. Compare them with iron wire. I have often re-crystallized two portions of an original sample, after which they showed no change.

There is no objection to desiccating crystals for a brief time over sulphuric acid. A prolonged desiccation will shatter the stability of the crystals and in a longer time abstract a part of the crystal water.

To standardize a permanganate solution, weigh 1.4 grammes of ammonium ferrous sulphate into a beaker of convenient size, add 150 c. c. cold water and 20 c. c. of a cold mixture (one volume sulphuric acid sp. gr.

1.84+3 vols. water) hasten solution by stirring, when it is complete titrate at once. The end reaction is very delicate. Its approach may be noted by a faint darkening of the contents of the beaker, prior to adding cautiously the last .2 to .3 c. c. Duplicates should agree either to the exact tenth or to the fractional part of a tenth. More than one variety of the salt should be used in standardizing a solution. Since 1.4 grammes of ammonio-ferrous sulphate contains .2 of a gramme of iron, multiply the reading of the burette by five and divide this product into one, which will give the value in grammes of iron to which one c. c. of the permanganate solution is equivalent; thus is obtained a permanganate solution standardized in terms of iron, which is the basis of the *Family* of five methods. Since 1.4 grammes of ammonio-ferrous sulphate is always to be used in standardizing a permanganate solution, we may, for convenience, let R=the reading of the burette, then the iron value$=\frac{1}{5R}$.

Sampling Iron Ore, Etc.

The greater part of the iron ore consumed in the United States is shipped from the Lake Superior region in boats. Two very good opportunities are presented for sampling the cargoes; first, when the boat is loading; second, when the cargo is being discharged. The latter time is conceded the better. The usual method of unloading a boat is to make openings in the ore under all or a part of its hatches. When about one-third of the ore has been removed, and the bottom of the boat is exposed, is considered the most suitable time to begin sampling. There are presented at this time new surfaces varying in depth with the capacity of the boat. By a study of these surfaces one may judge of the several varieties of lump and fine ore and estimate their proportion in the cargo, which proportion should be maintained in the sample. Lumps taken should usually be broken from larger ones—should not exceed a cubic inch in size and should present at least half new surfaces. Care should be taken not to break lumps at all times in the planes of easy cleavage, since such surfaces often differ widely from the body of the lump.

Not less than 100 pounds of ore should be taken from the surfaces, proportionately at the several hatches; at least every three square feet of newly exposed surface being represented. Lump ore is then broken finer and the mass intimately mixed, and 30 pounds sampled from the mixture, all or a part of it being protected from loss of moisture by inclosure in a tin can. Much care must be taken to avoid dissipation of moisture in the sample. The ore must not be sampled in bags unless they be previously moistened. In mixing the ore do so rapidly, avoiding exposure to the sun. When a sample arrives at the laboratory it should be weighed at once for moisture. At upper lake ports the ore is sampled at intervals during the loading.

The principles employed in sampling a cargo of ore may be applied when sampling in the mine, on stockpiles, and cars, where the opportunity for judging the kind, character and amount of fine ore is not so good. Remember that in a stockpile much lump will roll to the outskirts of the pile, and that shipment in cars will tend to bring all lump to the surface. The foregoing principles may be used in sampling limestone, coal and coke.

Preparation of Samples.

For iron ore, limestone and coke, crushers run by power are serviceable, but the work may be nicely executed by aid of a chrome steel mortar and rubbing plate. This metal is very hard and strong, yielding no elements to even the hardest iron ore. I prefer to proceed as follows:

Crush the entire sample in the mortar until it will pass a four mesh sieve. Commingle the crushed mass very intimately on oil cloth, by gently rolling it over and over, which may be done by lifting successively alternate corners of the cloth. Spread the ore evenly on the cloth by aid of a trowel, fill a quart cup from the mixture by sampling it systematically. Take special care to dip the trowel entirely through the mass each time. This quart of ore is then crushed in the mortar until it will pass an eight mesh sieve. Mix as before, sampling this time a pint from the mixture, which throw portion-wise upon the rubbing plate, where grind it to pass a 40-mesh sieve. The mass is again mixed and 100 grammes sampled from it. Rub this portion upon the plate until fine enough for analysis, when it will usually pass a 100-mesh sieve. Mix this portion intimately and dry at 212 degrees Fahr. (for most material). When cold it will be ready for analysis and is of sufficient quantity to leave a reserve powder.

Metal Sampling.

To sample iron and steel intelligently necessitates a knowledge of the method of production. For example —iron highest in sulphur and lowest in silicon will be found in beds farthest from the blast furnace, while the more open grades will be found nearer the furnace; hence a sample to represent the entire cast should be composed of mixed drillings judiciously taken. In practice, however, several different analyses are made of such a mixed cast. In similar manner cast ingots are rarely homogeneous, hence mixed drillings from several parts should constitute a sample. While alloys are still molten the lighter metals rise and then solidify, which facts should be considered when sampling them.

METHODS OF CHEMICAL ANALYSIS.

Moisture.

Until recently the sale of ore was based upon its analysis, when dried at 212°F. Of late a careful estimation of moisture is required because the sale is now based, especially in wet ores, upon the percentage of iron in the natural state, figured from the analysis of the ore dried at 212° F. and the percentage of moisture. Not less important is the moisture determination as an index of furnace yields and fuel consumption. A convenient method for making the determination is to weigh the ore into a counter poised pan, distribute evenly over the bottom of the pan, dry from 2 to 6 hours at 212° F., when cold, replace pan and counterpoise, and the weight necessary to add to the pan to make up the loss of moisture when divided by the weight taken will be the percentage of moisture in the sample.

Iron.

Since the percentage of this element regulates the selling price of ore more largely than any element save phosphorus, a correct estimation of it is indispensable. There are only two methods for the determination of iron which have won universal favor among chemists. One depends upon the titration of ferrous iron with a standard solution of potassium bichromate, the end reaction being ascertained by aid of a solution of potassium ferri-cyanide, used as an indicator.

The other method, and the one which I prefer after cautious comparison with the foregoing, depends upon the titration of ferrous iron with a standard solution of potassium permanganate, which of itself acts as an indicator. In standardizing either of these solutions it has become the usual practice to do so by aid of standard ores assigned, a definite percentage of iron, which is the average of closely concordant results. Since the determination of iron involves the titration of a complex mixture, I have usually found the iron value obtained by standardizing on ammonio-ferrous sulphate slightly greater than the value obtained by use of standard ores. The commercially recognized standards, when used to establish the value of a permanganate solution, involve the conditions found in the actual determinations. If one desire to employ ammonio-ferrous sulphate for this purpose he must carry a correction factor. I do not recommend the latter course of procedure. Many reducing agents have been suggested for use with either method. It is generally conceded that stannous chloride is the most rapid and easy of application. In preference to using any salt found on the market, I dissolve pure tin in hydrochloric acid, sp. gr. 1.20, leaving an excess of acid. It is well to make up a large quantity of this solution, keeping it in sealed bottles. It is necessary to ascertain approximately the reducing power of this solution. My solutions are usually of such strength that about

3.5 c. c. will reduce one-half gramme of the average ore. It has been found that if to ore plus the amount of hydrochloric acid necessary to dissolve it, there be added stannous chloride, that solution is very much more rapid and complete than without this addition. I have adopted this plan. It often saves three-fourths of the time otherwise required to dissolve the ore. In dissolving an ore only so much stannous chloride solution should be added as will nearly reduce the iron. When the solution of the ore is complete, add to it, while yet hot, stannous chloride solution from a burette until completely reduced, leaving an excess not to exceed .1 c. c. of the stannous chloride solution In case a larger amount has been added, add permanganate solution until a tinge of ferric iron is produced. Destroy this as above. In both volumetric methods the above conditions must be attained before further procedure. In *Notes on Metallurgical Analysis,* by Lord, page 15, the bichromate method is best described. When operating the bichromate method I prefer to use a mercuric chloride solution of strength described under the permanganate method. I also prefer to conduct all operations, including titration, in a beaker of capacity there described. I think it better to make duplicate weighings for this determination than to take aliquot portions of the same weighing. I prefer the permanganate method as follows:

Weigh one-half gramme of ore into a beaker without lip, 2¾ inches top diameter by 4¼ inches altitude. Treat with 10 c. c. hydrochloric acid sp. gr. 1.10, plus stannous chloride. Effect solution by heat, avoiding vigorous boiling. Proceed while the contents of the beaker is still very hot, to a condition of complete reduction with a limited excess of stannous chloride. The contents of the beaker must now be rendered cold, when add 50 c. c. of mercuric chloride solution (10 grammes per litre), stir vigorously, then add 10 c. c. of titrating mixture, and stir vigorously again. Wash the contents of the beaker into a large white bowl, dilute to 400 c.c. with water. After thorough stirring titrate at once with a standard solution of potassium permanganate.

The approach of the end reaction may be noted by a faint darkening of the solution. The end reaction is a feeble pink. Titration should be rapid. The end reaction is of short duration and must be ascertained without delay. The titrating mixture is made by dissolving 160 grammes of manganous sulphate in water, diluting to 1,750 c. c. and adding 330 c c. of 85 per cent phosphoric acid and 320 c. c. of sulphuric acid sp. gr. 1.84. The manganese sulphate is converted into manganese chloride, thus avoiding possible decomposition of the permanganate solution by hydrochloric acid. The phosphoric acid unites with the ferric iron produced, thereby rendering the titrated solution white and making more evident the end reaction. A beaker of the dimensions named is convenient because it enables one to submerge the ore in a minimum quantity of hydrochloric acid and because it is of sufficient height to condense any chloride of iron that may volatilize. I prefer to titrate in a white bowl because it renders the end reaction more easily detectable. Certain ores contain organic matter which if left unchanged in the solution to be titrated, might be acted upon by the standard permanganate solution. My habit is to dissolve such ores in a minimum quantity of hydrochloride acid sp. gr. 1.20; when solution is complete add at intervals several crystals of potassium chlorate. Evaporate until the chlorine is expelled, when a very small quantity of the acid remains. Proceed with the reduction. If this organic matter be not destroyed, it renders the slight excess of stannous chloride difficult to adjust because it imparts to the solution a color resembling ferric chloride. Results of the permanganate method agree with those of the bichromate method. Time required for a determination by the permanganate method will not exceed 30 minutes; by the bichromate method 35 minutes. An experienced operator can usually make 100 determinations per day, using the permanganate method. When standardizing a permanganate solution by use of ore, divide the percentage of iron which the ore contains by the number of c. c. which it titrated, and the quotient will be the percentage value of one c. c. of the solution. Different chemists working on the same sample should agree within .1 per cent.

Phosphorus.

Of all methods used in the analysis of iron and steel there are no others so extremely accurate as several methods for the determination of phosphorus. In the hands of a careful operator, any one of four methods will give results identical to .001 per cent when operating upon the same sample. There is no reason why phosphorus results upon the same sample should disagree by more than .002 per cent. In the better grades of iron ore, pig iron and steel, a difference greater than the above will cause unfavorable comment. The above statements are rigidly true, no matter what character of material is operated upon, but in case the same contains a considerable quantity of titanium or arsenic the methods must be somewhat elaborated, and there is a tendency to greater difference. It is furthermore true that where the amount of phosphorus exceeds .3 per cent the nice results thus far described are not obtainable, although even in high phosphorus foundry iron the amount sometimes reaching 3 per cent, duplicates by the same method may agree exactly, but by different methods a difference of .02 per cent is often observed. Bessemer iron not exceeding .1 per cent phosphorus contains the most of this element of any stock rigidly guaranteed.

In the treatment of this subject there are only two methods that from personal experience I can especially recommend. One is the Molybdate-Magnesia method (see Handbook by Cremer & Bicknell); the other is the volumetric method, depending upon the titration of molybdic acid after reduction. Phosphorus may be precipitated in form of definite composition, involving molybdic acid in its structure, to the same extent at all times when the conditions are nicely regulated.

The method which I prefer, after almost innumerable comparisons with itself and with the magnesia method, is that depending upon the titration of reduced molybdic acid with a standard solution of potassium permanganate. The method may be operated in such a manner as to make it rank with the most rapid methods, yielding results in harmony with the long-established magnesia method. Results by it may be obtained in about one-third the time that would be required in the most rapid execution of the magnesia method.

My experience with the same had its foundation in the original Emmerton method. (See Blair, first ed.) This experience was soon supplemented in the case of metal by the principles announced in a paper by Dr. Drown (see Transactions American Institute Mining Engineers, Colorado meeting, 1889). The principles he announced eliminated all the unpleasant and laborious part of the Emmerton method. Particularly is this volumetric process applicable to low phosphorus material, where the weight of magnesium pyro-phosphate would be small. I prefer the method for steel as follows:

For metal containing .1 per cent, three grammes is all that should be taken for analysis; for metal containing .01 per cent five grammes is the least amount that should be employed. For routine work, such as the regulation of open-hearth furnaces, a less amount may be taken. Weigh three grammes of steel into a 16-ounce flask (Joliet), treat with 80 c. c. of a mixture—one volume nitric acid sp. gr. 1.42, plus 2 vols. water. Effect solution rapidly by aid of heat, which continue until visible oxides of nitrogen are expelled. Now add, portion-wise, a strong solution (say 30 grammes per litre) of potassium permanganate. Continue these additions and vigorous boiling until brown oxides of manganese persist, say for two minutes, which, unless the steel be very high in combined carbon, is quite sufficient to prove that the combined carbon has all been destroyed and that the phosphoric acid has been oxidized completely to the ortho condition, in which condition alone it is completely precipitated by molybdic acid solution. In case of steels of the ordinary carbon content, if the solution on two minutes boiling is quite opaque, due to the oxide of manganese, nothing further can be desired. As the carbon increases the boiling should be prolonged with some concentration of volume and the oxides of manganese should be kept in greater abundance. Various reducing agents have been suggested with which to destroy the oxides of manganese in excess, thereby clarifying the solution. I prefer tartaric acid.

To the boiling flask add a crystal of tartaric acid, not exceeding one or two pin heads in size. A minute after the first addition there will be noticed a marked diminution in the amount of the oxides of manganese or they may disappear entirely, which is the point that must be attained. Make therefore the additions of tartaric acid portion-wise at intervals of about one-half minute until the oxides of manganese are destroyed with the least quantity of acid, after which boil vigorously for not less than one minute. This will enable the nitric acid to oxidize any slight excess of tartaric acid. The solution is now ready to be precipitated with molybdic acid solution. The temperature of precipitation in my practice is 80 degrees C., but if the steel contain arsenic, as is pointed out in *Common References*, the temperature must be reduced to 35 degrees C When using this low temperature there is great danger, especially in low phosphorus material, that precipitation will not be complete. I prefer to use a molybdic acid solution made as follows:

Weigh 100 grammes of good quality molybdic acid into a 16-ounce flask, form an emulsion with same by adding 100 c. c. of water, add now portion-wise with constant agitation of the flask, 300 c. c. of ammonia, sp. gr. .90, agitate until all molybdic acid is dissolved. In a large porcelain container place 500 c. c. of water, then 100 c. c. ammonia, sp. gr. .90, then 600 c. c. of nitric acid, sp. gr. 1.42, stir and allow to become absolutely cold. When both parts of the solution are cold, add the ammonia solution from a large beaker at once, as with a dash, to the nitric acid solution. Do not disturb or agitate this mixture until cold, at which time it will be observed that certain impurities entangled with a slight amount of molybdic acid have separated. Unless the separated material, as an emulsion with the liquid, exceed 10 c. c. it is of no consequence, and the make-up is good. If it exceeds this amount the molybdic acid is either too impure or the solutions were not sufficiently cold when mixed. The colder the solution the less the separations of molybdic acid. Molybdic acid should be made up at least 48 hours before needed and must be filtered to perfect clearness before being used. Of this solution 80 c. c. is always used for a determination. It differs from most solutions recommended in containing more ammonium nitrate, which fact avoids the necessity of adding ammonia before precipitation, thus eliminating the most perplexing feature of the volumetric method as usually practiced. Add the molybdic acid solution at once to the nitric acid solution in the flask, rinsing off the thermometer by the addition. Immediately give the flask a whirling motion, continue thus to agitate the liquid through a period of five minutes, when precipitation will be complete, as made evident by the rapid settling of the yellow precipitate.

The method of whirling is superior to that of shaking in a stoppered flask, yielding a precipitate coarser and more easily filtered. Filter on a Munktell's No. 2 9 c. m. paper, washing the flask, and yellow with a mixture of one litre of water + 20 c. c. of sulphuric acid, sp. gr. 1.84. All traces of iron, as well as yellow precipitate must be removed from the flask. Washing of the yellow precipitate must be very thorough, beating with a jet especially about the top edges of the paper. With care six washings will always suffice.

Place within the flask about 15 grammes of zinc containing no oxidizable matter. Wash the funnel stem, containing the yellow precipitate, free from any spatterings of the filtrate, then place it within the neck of the flask, dissolve the yellow precipitate into the flask by aid of a mixture of one volume of ammonia, sp. gr. .90 + 2 volumes of water. Three washings with ammonia will usually suffice, but should be followed by two with water. The bulb of the flask should now be about one-third full; add to it 90 c. c. of a mixture, one volume sulphuric acid, sp. gr. 1.84, + 3 volumes of water, bring the flask to a gentle boil, which continue for a period of 20 minutes. Reduction in this time is usually complete. The solution has passed through several changes of color, usually beginning with brown, finally becoming green, which increases as complete reduction approaches, and if the phosphorus is high it may toward the end appear jet black. Filter through a large funnel, in the apex of which has been placed a small piece of absorbent cotton. This may be held in position with a stirring-rod. The cotton will retain all undissolved zinc. After the contents of the flask has run through the filter add one liberal washing of the flask with water to the funnel. When this has completely run through wash the funnel and plug once liberally with water. The total filtrate will now be ready for immediate titration with the standard solution of potassium permanganate. The filtration should be conducted as rapidly as possible.

The phosphorus value of one c. c. of permanganate solution is best ascertained by use of the following equation:

Let P equal phos. value.

Let Fe equal the iron value.

Then P equals Fe × .015816442$2$.

Since 1.4 grammes of ammonio-ferrous sulphate contain .2 of a gramme of iron multiply the reading of the burette by 5 and divide this product into 1, which will give the value in grammes of iron to which one c. c. of the permanganate solution is equivalent. Let R equal the reading of the burette; then the iron value$=\frac{1}{5R}$. Substituting in the above equation we have:

$$P=\frac{.00316328844}{R}$$

In certain especially prepared white irons and in malleable iron castings, combined carbon may reach 3 per cent. To this material the method is not well adapted, although by continued boiling with a large excess of permanganate solution, and the further addition of a few drops of strong nitric acid, this percentage of combined carbon may be entirely destroyed and the phosphorus oxidized. It is the usual practice with such metal to evaporate its solution to dryness in porcelain, then to destroy the combined carbon by baking over the naked flame for at least 15 minutes. In order to proceed the dry mass must be taken up in a small quantity of hydrochloric acid, sp. gr. 1.20, the great excess of this acid evaporated, after which add nitric acid sp. gr. 1.42, and boil vigorously for some time, thus expelling the last traces of hydrochloric acid. Filter into the flask. (Phosphorus is not completely precipitated in the presence of hydrochloric acid.)

The method for pig iron involves the above principles, but since it contains larger quantities of graphite, solution and oxidation are best effected in a 12-ounce beaker, after which the solution is filtered into the flask. The S. & S. No. 589 c. m. paper is best for this purpose.

In case of foundry irons high in phosphorus ½ g. may be weighed directly into the flask and precipitated without filtration from the graphite.

In event pig iron contains titanium, the method must be elaborated, as per *Common References.* When the amount of graphite is small it need not be removed.

For ore dissolve five grammes by digestion with 45 c. c. of hydrochloric acid, sp. gr. 1.20, evaporate to dryness, avoiding a temperature so high as to convert the ferric chloride into ferric oxide. Take this well dried mass up in 35 c. c. of nitric acid, sp. gr. 1.42, boiling until visible oxides of nitrogen are expelled. This will involve a reduction in volume of about 10 c. c., dilute with 30 c. c. of water, filter through S. & S. No. 589 paper into the flask. Wash the insoluble residue from the beaker on to the paper, which wash twice with water. Some ores hold a considerable proportion of their phosphorus in this silicious residue. It may be taken up by methods suggested in *Common References* or by a method suggested by the writer (see *Journal of Analytical and Applied Chemistry,* Vol. 6, No. 9, 1892). The writer now prefers to ignite the residue in platinum, brushing it from the crucible into a porcelain dish, grinding it fine in the same, after which treat it with 5 c. c. of a mixture, one volume of nitric acid, sp. gr. 1.42, + 2 vols. water, which bring to a gentle boil for five minutes. Filter through a No. 589 paper into the flask. Wash once. This method of taking up the residue is very rapid and has been successful when applied to such ores as have come to my notice. In event the ore contains titanium, see *Common References.*

The method for coal and coke may be applied in several ways. (See rapid method by the writer, *Journal of Analytical and Applied Chemistry,* Vol. 7, No. 4, April, 1893.)

A very practical method for limestone consists in igniting intensely the weighed portions in a platinum crucible, the contents of the crucible being treated with dilute nitric acid before mentioned.

For a thorough understanding of the foregoing methods I recommend a cautious study of *Common References.* Extreme care must be used in selection of zinc for this method. After dissolving 15 grammes of the same in dilute sulphuric acid, it should require only a drop or two of permanganate solution to produce the end reaction. I have always found that difficultly soluble zinc is the purest and otherwise most satisfactory for this use. The so-called "mossy" form should be used. (See paper by the writer, *Journal of Analytical and Applied Chemistry,* Vol. 6, No. 7, July, 1892.)

In event an ore contains considerable quantities of organic matter, its nitric acid solution should be oxidized with potassium permanganate, as in the case of steel. Results by different chemists working on the same sample should agree within .001 per cent.

Manganese.

In my opinion there is no method more accurate and direct than Volhard's method for the estimation of manganese. It may be found described in *Common References*. One description differs from another in minor details only. For material varying in manganese from .2 per cent to 8 per cent, one gramme is a suitable quantity for analysis. In case of highly manganiferous material, as ferro manganese or pyrolucite, one-half gramme to one-quarter gramme would be a more suitable amount.

For steel, weigh one gramme into a beaker 5½ inches altitude by 3¾ inches top diameter, without lip, add 30 c. c. of silicon mixture (see under determination of silicon), keep covered and force solution rapidly—best upon a hot iron plate. When it is complete remove the watch glass and evaporate the mass to dryness until fumes of sulphuric acid appear copiously during two minutes. Allow the beaker to cool, add 50 c. c. of water and boil vigorously until the sulphates of manganese and iron are completely dissolved. There may at this time appear flocks of silica, or graphite, or both, which have no effect upon subsequent operations. Fill the beaker with water to within three-fourths of an inch of the top. Bring to boiling, remove from the plate, add zinc oxide portionwise, stirring vigorously between additions, until the supernatant liquid shows that all iron has been precipitated. Add a gramme or two of zinc oxide in excess, stir vigorously and titrate immediately with a standard solution of potassium permanganate, which should be added rapidly, stirring vigorously between successive additions. The precipitated mass settles rapidly and admits of inspection for the faint pink end reaction in supernatant liquid. When a positive pink has been reached, stir again. If it persist the end reaction has been reached. The last stirring and incident delay of about one minute is always indispensable, as the oxidation is not very rapid. Much pains must be taken to titrate as rapidly as possible, thereby preventing cooling of the contents of the beaker, which will always retard the action of the permanganate. Baking the dry mass to the extent named is always sufficient where the combined carbon does not exceed one-half of 1 per cent. In event it is much higher than this the baking should endure through a period of ten minutes, lest some of the combined carbon remain in a condition capable of being oxidized by permanganate.

In event of a very high combined carbon, as in white iron or in malleable iron castings, I would recommend to dissolve the metal in rather strong nitric acid. Evaporate its solution to hard dryness, take up in minimum quantity of hydrochloric acid, sp. gr. 1.20, add silicon mixture, and proceed as in the first instance. It is always necessary that a considerable quantity of sulphuric acid be left in the seemingly dry mass, for experience has taught that a little sulphuric acid to form zinc sulphate is quite indispensable to a nice end reaction. If baking be too long continued some oxide of the iron will be formed and will not dissolve when treated with water. This oxide of iron might entangle some manganese.

Procedure in case of pig iron should be identical with that for steel. The flotent graphite will be entangled with the precipitated iron and will nowise interfere. In case of iron ore complete solution must be effected in hydrochloric acid, sp. gr. 120, then the mixture added, with further procedure as above. In case of bog ore or rocks containing organic matter the baking must be severe, or in event of very much organic matter in the ore add strong nitric acid to its hydrochloric acid solution, evaporate to hard dryness, take up in hydrochloric acid, add the mixture, when proceed as above.

Practically, combined carbon and organic matter are not hindrances to routine work with this method. In my experience no cases have arisen where high results have been due to them. The above precautions are safeguards. This method differs from those ordinarily described in complete neutralization with dry zinc oxide, which is superior to using an emulsion of the same in water, because in a beaker of the size indicated the volume must be limited, and again, the cold emulsion would lower the temperature. Under no circumstances, after the addition of zinc oxide, should the liquid be brought quite to boiling, as, under these conditions, it is said, some manganese may be precipitated. (Dr. Mabery.)

In operating upon highly manganiferous materials, after solution of the sulphates in a little water, they may be transferred to a larger beaker and diluted with 500 c. c. of boiling water. In this case the addition of the large quantity of permanganate solution required, will not have too great cooling effect. Time allowed for the end reaction must be greater when the percentage of manganese is large. In certain cases, if the operation has been retarded, a second heating nearly to boiling, without exposure to bright light, may be necessary. To ascertain the end reaction, care and experience are necessary. An analysis begun and ended in the same container has obviously much in its favor. In this respect I consider the method described superior to the usual method of taking 1.5 grammes of the material, its transfer to a 300 c. c. flask where precipitation is effected, diluted to the mark, agitated, allowed to settle, add 200 c. c. of the supernatant liquid drawn off in a pipette, again heated and titrated.

The precipitated iron and excess of zinc oxide entangles and settles the precipitated oxide of manganese more rapidly than it will settle in the 200 c. c. portion drawn from the flask. A zinc oxide, free from any oxidizable material, is necessary. There are such oxides on the market, but before using them they should be carefully tested. To do this—dilute one c.c. of sulphuric acid, sp. gr. 1.84, to the usual volume, bring nearly to boiling, add zinc oxide in excess and titrate, with permanganate. If the correction be more than 3-10 of a c. c. the oxide is unfit for use because a correction cannot be adjusted with nicety. On iron or steel this method may be carried out within one hour. In case of ore, a longer time is required. The use of silicon mixture has great advantage over consecutive additions of its constituents, since it furnishes just the proper amount of sulphuric acid and may be evaporated with great rapidity and no spattering.

A description of the Acetate and Potassium Chlorate methods for the separation of manganese (see *Common References)* will show them to be more laborious and expensive than the foregoing process, which avoids many errors possibly incident to them. It is the only method which can be called short, where the estimation of manganese does not depend upon some previously standardized material. In verifying its results I prefer the Acetate method completed by weighing as the phosphate.

The Colormetric method is often used where very rapid approximate results are demanded. The value of a permanganate solution may be ascertained by use of the following equations:

Let Fe=Iron value of permanganate solution.

Let Mn=Manganese value of permanganate solution.

Then $\mathrm{Mn} = \mathrm{Fe} \times .2946428571$ or $\mathrm{Mn} = \dfrac{.058928571}{\mathrm{R}}$

The American Foundryman's Association recently placed upon the market a number of carefully standardized samples of cast iron. The work upon these samples was done by Messrs. Cremer & Bicknell; Booth, Garrett & Blair; Mr. McCreath, and Prof. A. W. Smith. The results furnished with the standards are an average of the results obtained by these men. They used dfferent methods. In standard "C" they call manganese .442 per cent. I make the manganese by the above method .460 per cent. In standard "D" they make the manganese .971 per cent, I make it .99 per cent, and in a sample of ore Feb., 1893, Mr. Cremer reported 8.56 per cent manganese by the Acetate method. I obtained 8.42 per cent by the above method.

Calcium.

The determination of this element is frequently demanded in limestone, slag and iron ores. The percentage of the metal found is ordinarily reported as calcium oxide (lime) or as calcium carbonate. From data available I infer that the method depending upon the titration of oxalic acid is more accurate than any other method. It is certainly more rapid. Dec. 29, 1892, I made some comparative experiments. By titration I obtained 55.24 per cent lime in so-called chemically pure calcium carbonate. By weighing the precipitated oxalate of lime I obtained 55.21 per cent. Later experiments have been equally satisfactory. I prefer the volumetric method as follows:

Prepare (as per *Common References*) a suitable weight of material for the precipitation of its calcium, transfer the solution to a graduated flask 500 c. c. capacity, heat to boiling, add from a burette exactly 70 c. c. of a solution of ammonium oxalate (25 grammes per litre), boil for five minutes, cool to ordinary temperature, add water to the mark, agitate and allow to settle. When the supernatant liquid is sufficiently clear, remove an aliquot portion from the flask. Dilute it to 200 c. c. with water, add 10 c. c. of sulphuric acid sp. gr. 1.84, which will aid in bringing the solution to a temperature of 60 degrees centigrade, at which temperature it must be titrated with a standard solution of potassium permanganate. If the temperature exceeds 60 degrees low results may be expected. If it be below this temperature the reaction begins with difficulty. The end reaction is a faint, permanent pink. The ammonium oxalate must be protected as a standard solution. Before using it dilute 10 c. c. with water, add 10 c. c. of sulphuric acid sp. gr. 1.84 and titrate with the standard solution of potassium permanganate. In the determination is titrated the ammonium oxalate not consumed by the calcium. Having ascertained the amount of potassium permanganate solution which the ammonium oxalate used in the determination will consume, and also the amount of permanganate solution which the excess of ammonium oxalate will consume, their difference represents the amount of oxalic acid combined with the calcium.

The following equations yield the lime and calcium carbonate values of any permanganate solution.

Let CaO=the calcium oxide value.

Let $CaCO_3$=the calcium carbonate value.

Then $CaO = \frac{1}{10R}$

and $CaCO_3 = \frac{.178571428}{R}$

The quantity of ammonium oxalate above described is sufficient when working upon limestone. When operating upon other materials the quantity must be varied to suit the occasion.

In event extreme rapidity is demanded, dilution in the flask may be made with hot water, in which the precipitate will subside with great rapidity, or it may be allowed to subside only partially, when sufficient solution to obtain an aliquot portion may be passed through a dry filter into a dry beaker. If these operations are conducted with rapidity the change due to the diminishing temperature will be insignificant.

Sulphur.

The only available method for use at steel works and blast furnaces, where very speedy results are demanded, is based on the fact that all, or a part of the sulphur of such metal, is evolved as hydrogen sulphide when it is dissolved in hydrochloride acid. In some metal it is impossible to obtain the full sulphur content by this method. Some claim this is due to the formation of organic sulphides, probably of the mercaptan series, others to copper and arsenic whose sulphides are precipitated in acid solutions, still others claim that titanium holds back the sulphur as sulphide. While I prefer to use cold hydrochloric acid, sp. gr. 1.10 for the evolution, others claim that it takes acid of 1.20 sp. gr. to evolve the sulphur completely. Williams finds that hot acid evolves more sulphur than cold acid. (See proceedings of *Engineers' Society of Western Pennsylvania,* vol. 8, page 328.)

The hydrogen sulphide evolved may, when taken up in any of several absorbents, be again liberated by hydrochloric acid and titrated with a standard solution of iodine. Caustic soda is often recommended. One c. c. of a 10 per cent solution of this base will absorb .057 per cent sulphur, when operating upon five grammes of metal, which weight is the basis of data in this paper. Any absorbent used must be tried for the amount of iodine solution it will consume. I prefer to use cadmium chloride as an absorbent, for investigation upon which see a paper by the writer, *(Journal of Analytical and Applied Chemistry,* vol. 7, No. 5, May, 1893). The yellow sulphide formed (always in containers of the same size) may tell the chemist about what percentage of sulphur is present. One c. c. of a cadmium chloride solution, 20 grammes per litre, will absorb .069 per cent sulphur. Cadmium chloride solution is best made by dissolving 20 grammes of the salt in 500 c. c. of water and adding 500 c. c. of strong ammonia. I prefer an iodine solution of such strength that 1 c. c. will equal .005 per cent sulphur. Theoretically a solution of iodine, two grammes per litre, will give the above value. Some chemists re-sublime the purest obtainable iodine and take two grammes per litre, calling the value .005 per cent per c. c. Others prefer to call the value .005 plus or minus, to account for the sulphur not evolved from the particular kind of metal upon which they are working, or because, according to certain standards in their possession, it seems higher or lower. Still others prefer to standardize the iodine solution upon drillings, the evolved sulphur of which has been carefully and repeatedly determined by gravimetric methods. Such a course of procedure has much to commend it for commercial work. This has been my habit for many years. Others prefer to get the value by direct titration of theoretical crystals of sodium hypo-sulphite, while yet others prefer to standardize it by aid of a standard solution of potassium bi-chromate. This course of procedure is long and involves comparatively much time and manipulation. The above methods check very well with one another when carefully conducted. For a complete understanding of the methods I recommend a careful study of all references herein mentioned.

I am enabled to bring this volumetric method into the *Family* of methods so far as standardizing the iodine solution is concerned. For this I am indebted to Mr. H. L. Payne, who published a paper in the *Journal of Analytical and Applied Chemistry* (vol. 6, No. 9, September, 1892) and who published some corrections of the same in the *Journal* *of the American Chemical Society*, vol. 16, No. 2, February, 1894. I have recently taken up his paper and am able to suggest some additional details, based upon experiment. The theoretical values obtained by his process are in accordance with the best gravimetric results on iron and steel. The preparation of starch solution is described in *Common References*. While it is not a usual practice, I prefer to add the same amount of starch solution (3 c. c.) to each determination. The solution should always be agitated to render it homogeneous before drawing off a portion of it for the determination. After a starch solution has stood the supernatant liquid will give quite a different tinge in end reaction, from the thicker deposit on the bottom. Some prefer to use the supernatant liquid only. I like better the end reaction due to the homogeneous mass.

According to Mr. Payne's paper, the sulphur equivalent of any standard permanganate solution is $\frac{2}{7}$ of its iron value (see reactions which he furnishes)—that is, any permanganate solution will liberate iodine from potassium iodide equivalent to $\frac{2}{7}$ of the iron value of the permanganate solution, but since the iron value $= \frac{1}{5R}$ the sulphur equivalent will $= \frac{2}{7}$ times $\frac{1}{5R}$ $= \frac{2}{35R}$ I prefer an iodine solution one c. c. of which shall equal .005 per cent sulphur when 5 grammes of metal are taken. This is equivalent to an iodine solution one litre of which will react to completion with .25 grammes of sulphur.

To obtain the number of cubic centimeters of standard permanganate solution which it is necessary to add, according to his method, to potassium iodide, divide .25 grammes by $\frac{2}{35R}$ In other words the number of cubic centimeters of any standard permanganate solution, which must be added to potassium iodide to produce one litre of the above iodine solution =4.375 × R.

To prepare one litre of a standard iodine solution, dissolve six grammes of potassium iodide in 150 c. c. of water, transfer the solution to a litre flask, add the amount of permanganate solution deduced from the formula, then add 20 c. c. of a cold mixture, 1 volume sulphuric acid sp. gr. 1.84, + 3 vol. of water; agitate the mixture. When the oxides of manganese are dissolved, dilute to the mark and again agitate. Each cubic centimeter of this solution equals .005 per cent sulphur when five grammes of sample are operated upon. A calculation will show that sufficient potassium iodide of the six grammes is left unchanged to hold in the solution the iodine liberated (see Blair). The data to follow seems to prove that the value of this iodine solution is correct and that the solution is perhaps less subject to change than iodine solutions prepared in the ordinary way. The time required to make such a standard solution will not exceed five minutes. In March and April, 1899, I made three solutions by the above formula, finding them identical from 30 minutes to 20 days after they were prepared, using the same drillings for comparison. My experiments have been about 30 in number, and were based upon careful gravimetric estimation of evolved sulphur.

In the American Foundryman's Association standards [see note concerning them under manganese determinations] I obtained results very close to those furnished with the standards. In their sample "B" I find .038 per cent sulphur against their .038 per cent. In their sample "D" I find .025 against their .024 per cent sulphur. In a standard prepared by Booth, Garrett & Blair in February, 1892, I make the evolved sulphur .051 per cent; they reported it .052. My experiments with these solutions have covered a wider ground. Further figures here seem unnecessary. I have discovered that as much as one-third of the sulphur capable of being evolved is often held back owing to the decomposition of hydrogen sulphide, if the evolution be conducted in bright sunlight.

The operation is conveniently conducted in a 16-ounce flask provided with a rubber stopper carrying a one bulb thistle tube and a glass tube $\frac{5}{16}$ of an inch in diameter, bent after leaving the stopper at right angles with the neck of the flask and extending therefrom about 6½ inches. (The thistle tube should be of such length that when the stopper is fitted, it should be about ¼-inch from the bottom of the flask. The glass tube should extend just through the stopper.) To the outer end of the glass tube is applied a rubber connection 4½ inches long. The other end ot the rubber tube connects with a straight glass tube 6 inches long, which dips to the bottom of a common glass 5 inches in altitude, with top and bottom diameter 3 inches and 2 inches respectively. When using the apparatus, connection is always made and broken at the upper end of the straight glass tube (which may be used as a stirring rod). To use the apparatus, add to the glass 10 c. c. cadmium chloride solution, 125 c. c. water and 3 c. c. starch solution. Place five grammes of drillings in the flask, insert the stopper and make connection with the straight tube leading to the bottom of the absorbent. Add through the thistle tube 70 c. c. cold hydrochloric acid sp. gr. 1.10.

When the evolution of gas becomes slow, place the lowest possible Bunsen flame beneath the flask, increase the heat cautiously to complete solution of the drillings. This will usually require about 20 minutes. When the line of demarkation between the boiling froth and the darker liquid below is sharp, the drillings are usually dissolved. Just before disconnecting increase the heat for a few seconds to expel the last traces of hydrogen sulphide from the flask. Immediately add to the absorbent an equal volume of cold water. Then, with stirring, add hydrochloric acid, sp. gr. 1.10 from a wash bottle until all traces of the yellow sulphide are dissolved. Titrate at once from a previously filled burette to a distinct blue end reaction. Duplicate results agree nicely.

On a sulphur determination the difference of .003 per cent between two chemists would be admissible. There are certain irons, notably those mentioned later under the silicon determinations which are with difficulty soluble, to which this method cannot be well applied. Irons with high combined carbon dissolve more readily than others. At some blast furnaces it is the custom to correctly estimate the evolved sulphur, adding to its percentage such an amount as is usually found in the residue of the particular class of iron produced.

SULPHUR IN IRON ORES, ETC.

For the determination of sulphur in iron ores the fusion method as given in *Common References* is the recognized standard. For a more rapid method use the following:

Weigh 3 grammes of ore into an 8 oz. beaker; add 10 c c. nitric acid sp. gr. 1.42. Heat gently until most of the acid is expelled, thus tending to oxidize any sulphides present. Now add 25 c. c. of hydrochloric acid sp. gr. 1.20, bring to a gentle boil, adding crystals of potassium chlorate from time to time during solution. Remove the glass and evaporate to hard dryness. Take up in 15 c. c. of hydrochloric sp. gr. 1.20, dilute, filter and wash well with water, then add 20 c. c. barium chloride solution (100 g. per litre) evaporate until barium chloride begins to crystallize, dilute, bring to boiling, filter on double No. 589 paper, wash thoroughly with water and weigh as barium sulphate. Weight × .0458 = per cent sulphur in sample. While this method in rare cases will not yield all the sulphur, it is in most ores very satisfactory.

Graphite.

The estimation of this form of carbon in pig iron and castings is demanded more frequently than it was some years ago; it being now known that the softness of gray iron castings depends upon the percentage of graphite. In the *Journal of the American Chemical Society,* Vol. 16, No. 2, Feb. 1894, the writer published a paper entitled *Experiments on the Estimation of Graphite in Pig Metal.* From that time to the present he has used the principles there published. His results have been compared favorably with those of other chemists using different methods.

Weigh 2 grammes of metal into a 12-ounce beaker, treat with 100 c. c. of nitric acid, sp. gr. 1.135, force solution by application of heat, keep volume constant by addition of water. When solution is nearly completed, or only a few particles of undissolved iron can be seen darting through the liquid, add 3 c. c. B. & A. 40 per cent hydrofluoric acid, being careful not to allow it to touch the glass. Immediately give the beaker an oscillatory motion, after which solution will usually be complete. Filter at once, by aid of suction, through counter-poised papers folded together. By aid of a jet of water free the beaker from all graphite and continue to wash the paper with the same, four times, then twice with hydrochloric acid, sp. gr. 1.10. This washing may show yellow ferric chloride, in which case wash again with water, then twice with ammonia (one vol. sp. gr. .90 + 2 vol. of water), then twice with hydrochloric acid, then finally several times with water to remove the last traces of reagents from the paper. Take the papers from the funnel, straighten them as they were previous to being folded, revolve the inner paper so that its lines of folding will no longer coincide with those of the outer paper. Dry them in this position at about 100 degrees centigrade. If all reagents are not thoroughly washed from the papers they will be dark and brittle when dry. The difference in weight between the two papers will be the weight of graphite in the metal, which divided by two will give the percentage. It is my habit, when operating upon irons that do not dissolve readily to burn the paper containing the graphite. Traces of silica remaining, if any, should be deducted from the weight of graphite. If extreme accuracy is required, the weight of silica should be multiplied by 1.0526, and the product deducted from the weight of graphite. There are two classes of iron to which this method is not so easily adapted as to the usual varieties. First, the softeners alluded to under determination of silicon. In this event more hydrofluoric acid must be used and at an earlier stage in the process, since such iron is with difficulty soluble in nitric acid alone. Irons in which the combined carbon is very high should be digested somewhat longer in nitric acid. The quantity of hydrofluoric acid should be greater, the washings with ammonia should be more numerous and it is advisable to warm the ammonia to a temperature not exceeding 50 degrees centigrade. Irons that resist solution in dilute nitric acid also resist it in solutions of the double chlorides. In these exceptional grades of iron the determination of graphite is not often required. A cautious study of my original paper will lead to a more thorough understanding of the method as described. I find best suited for this method E. H. Sargeant & Co.'s No. 500, 9 c. m. papers. With reasonable experience, good suction and drying facilities, the estimation of graphite in ordinary irons may be conducted in one and one-half hours. With special hot draught ovens results may easily be had in 40 minutes. Duplicates agree nicely. I cite the following:

April 12, 1899, casting—2.35% 2.37%
April 8, 1899, pig iron—3.10% 3.13%

I am unable to add to the carbon determination any ideas not found in *Common References.* I am pleased with the combustion process as described by S. M. Rodgers, *Iron Trade Review,* Vol. 34, No. 19, May 9, 1901, page 20.

Silicon.

The determination of this element is universally demanded at steel works and blast furnaces. Of the several methods proposed those in which dehydration is effected by sulphuric acid at a high temperature are most effective, and leave the silica in a flocculent condition, from which the carbonaceous matter is more readily burned than when obtained by evaporation in any other acid. The following mixture of acids gives the most satisfactory results; bumping is very rare. I have never lost a determination by its use. It consists of

1450 c. c. water,
250 c. c. sulphuric acid, sp. gr. 1.84,
100 c. c. hydrochloric acid, sp. gr. 1.20,
650 c. c. nitric acid, sp. gr. 1.42,

added in order named to a common acid bottle, which the mixture will fill to a convenient point. This mixture has very rapid solvent effect because of its mixed acids in state of proper dilution. When used to the extent of 30 c. c. for one gramme of metal it leaves sufficient free sulphuric acid to dehydrate silica. In case of the manganese determination a suitable amount to form the zinc sulphate required.

For pig iron weigh .47 grammes (the factor weight) into a 3½ R. B. Dish, add 15 c. c. of mixture, cover with a watch glass, place on a hot iron plate. Evaporation should be gentle at first, so that drillings may be dissolved before the acid is too far expelled. Later the plate may be brought to redness if desirable. When the mass becomes dry and assumes a yellow tinge, and at the same time gives off sulphuric acid for a period of two minutes, dehydration is complete. Remove the dish from the plate after allowing it to cool, take up in 20 c. c. of hydrochloric acid sp. gr. 1.10 by aid of heat, boil until the sulphate of iron is completely dissolved, with an occasional oscillation of the dish to make sure all particles come to solution.

When ready for filtration the body of the liquid will be perfectly clear; no hard particles can be felt with the rod. Gelatinous silica flocks of graphite, and occasional masses of combined carbon may be seen floating in it or adhering tenaciously to the sides of the dish. Too long boiling in taking up must be avoided. The total act should not require over two minutes. Filtration must follow immediately, since it has been discovered that prolonged boiling or exposure may dissolve some silica. The filtration may be performed without the aid of the pump in case sufficiently open papers are used. Filtration proceeds much more rapidly if dehydration has been severe. Bearing this fact in mind will enable one to filter as rapidly as he can pour; pig iron and steel through S. & S. No. 589. After beating all material possible from the dish with a jet of water it should be wiped with a bit of filter paper and again beaten with a jet of water. Five or six washings of the mass in the paper with water, between which have been given two washings with hydrochloric acid, sp. gr. 1.10 is quite sufficient. Allow the paper to drain for a moment, place it in a platinum crucible, burn off paper and carbon at the highest temperature of the blast lamp. The combustion may be hastened by aid of a jet of oxygen.

Some irons will not dissolve in this mixture or any single acid (save hydrofluoric acid) without prolonged digestion. Such irons are characterized by a silicon content of from 6 to 14 per cent, and are used in foundry practice as softeners. My habit with these irons is to dissolve them by repeated additions of hydrochloric acid and prolonged digestion, then after evaporating nearly to dryness, add 15 c. c. of mixture and proceed as above.

In case of steels at least twice the factor weight should be taken, and where very low in silicon five times the factor weight is required. Steels require more severe dehydration and more thorough washing than does cast iron. The method as described, when applied to ordinary material, may be easily completed within one hour, or if a jet of oxygen be available the time may be reduced 15 minutes.

Perhaps the most rapid method consists in dissolving the metal in a platinum dish by aid of hydrochloric acid over the direct flame, taking up in hydrochloric acid while the mass is still hot, filtering at the pump through a previously fitted paper, and burning in a jet of oxygen. Some results recently obtained are as follows:

Open-hearth steel, duplicates give . .	.16 and .17
Another sample of same, duplicates give	.23 and .23
Pig iron, duplicates gave	3.40 and 3.45
Pig iron, duplicates gave	2.80 and 2.81
Pig iron, duplicates gave	9.10 and 9.16

The results indicated also show the agreement customary between chemists operating upon the same sample, and are commercially all that can be desired.

SILICA IN IRON ORES, ETC.

Weigh 1 gramme of ore into platinum crucible and mix with it 8-10 grammes dry powdered sodium carbonate and heat over the blast until fusion is liquid, cool and dissolve by placing crucible directly into a 12 ounce beaker containing 50 c. c. hydrochloric acid 1.10 sp. gr., warm gently until fused mass is free from crucible, remove crucible, rinsing with water, and evaporate the solution to dryness. Take up in 20 c. c. hydrochloric acid 1.20 sp. gr., and evaporate very hard dry again, now take up in 15 c. c. hydrochloric acid 1.20 sp. gr., dilute to 100 c. c. with water, heat nearly to boiling and filter on ashless paper (preserving filtrate in a 20 oz. griffin lip beaker if to be used for alumina determination). Wash 10 or 12 times with water and with hydrochloric acid 1.10 sp. gr. after the fourth and eighth washings, let drain and ignite over the blast in platinum crucible, cool and weigh as silica.

This method is less tedious than obtaining the silicious residue and then fusing it with sodium carbonate, and is applicable to all ores.

Aluminum in Iron and Steel.

After some experience with methods for the determination of aluminum in iron and steel, I prefer the following:

Weigh one gramme into an 8-oz. beaker and add a mixture of 15 c. c. nitric acid sp. gr. 1.20, and 10 c. c. of hydrochloric acid sp. gr. 1.10. Cover and boil until solution is effected. Remove the cover and evaporate to hard dryness. Take up in 15 c. c. of hydrochloric acid sp. gr. 1.20, dilute, filter on ashless paper, and wash well with water. Make the volume of the filtrate up to 200 c. c. Neutralize with ammonia water to a mahogany color (no precipitate should exist), add 7 c. c. of hydrochloric acid sp. gr. 1.10. Now add 10 c. c. of a solution of microcosmic salt, 200 grammes per litre. Stir until any precipitate formed is dissolved, following this add, with vigorous stirring, 15 grammes of sodium hyposulphite dissolved in 75 c. c. of water and immediately 15 c. c. of acetic acid sp. gr. 1.04 (about 1 pt. glacial and 2 pt. water). Bring rapidly to boiling which maintain under cover of watch glass for 15 minutes. Filter rapidly at pump, keeping paper full. Wash rapidly with hot water. Ignite in porcelain and weigh as aluminum phosphate which × .22181=per cent. of aluminum.

By introducing known amounts of aluminum with pig iron and steel I have in many experiments recovered them within .05%. I have worked on quantities from .2% to 2.5%.

The purest available material and highly ashless papers must be employed at all stages of the method. Washing must be very thorough which is also necessary with the method for copper to follow.

ALUMINA IN IRON ORES.

Dilute the filtrate from the silica determination to 200 c. c., neutralize and proceed as in the aluminum determination. The weight of aluminum phosphate × .41846 = per cent. of alumina.

Copper in Iron, Steel, and Iron Ores.

Having had occasion to determine copper in iron and steel, in amounts varying from a trace to 1%, I have found the following method rapid, accurate, and best adapted to this line of work.

Weigh 1 gramme of iron or steel into an 8-oz. beaker, add 15 c. c. nitric acid 1.20 sp. gr. and 10 c. c. hydrochloric 1.10. sp. gr. Cover and heat to solution. Remove cover and evaporate to hard dryness. Take up in 15 c. c. hydrochloric acid 1.20 sp. gr., dilute to 50–75 c. c. with water and filter on ashless paper into 12-oz. beaker, wash well with water, and dilute filterate to 150 c. c., heat nearly to boiling and add crystals of sodium hyposulphite with constant stirring until the contents of beaker is perfectly white, showing complete reduction of iron. Now pass a rapid current of hydrogen sulphide for five minutes and filter at once at pump through ashless paper and wash very thorougly with hot water. Burn off paper and free sulphur in a weighed porcelain crucible, cool and moisten residue with two or three drops nitric acid 1.42 sp. gr. Dry, and ignite over bunsen burner, cool in desiccator and weigh as $CuO + Cu_2S$, which multiplied by .79818 = per cent. copper, since both CuO or Cu_2S contain same per cent. of copper. For iron ores dissolve 1 gramme in 20 c. c. hydrochloric acid 1.20 sp. gr. and 5 c.c. nitric 1.42 sp. gr, evaporate to hard dryness, take up and proceed as in metal.

I find this method will give very accurate results and duplicates will often agree identically, as proven by having introduced known amounts of copper. Details must be rigidly observed.

General Remarks.

Apart from the selection of good methods for use in the Iron Laboratory there are many details in its arrangement which add much to the rapidity and accuracy of results. In building a laboratory so arrange it, when possible, that working surfaces shall be in front of north and west windows. The hood should be large and provided with means to effect strong draught. Good water pressure and porcelain sinks with tile outlets are desirable. Iron sinks and outlets are too frequently destroyed. A balance-room opening into the laboratory is also best provided with north and west windows. It should be of sufficient size to accommodate balances and also shelves on which may be placed metal-mounted apparatus not in use. It should also be provided with cupboards divided into apartments sufficient to hold a year's samples

It would be impossible to describe many conveniences in arrangement of a laboratory which would best adapt it to all iron plants and iron mines. With few exceptions chemicals and apparatus should be of the best quality. I prefer Troemner's short-armed balances. They are rapid, accurate and serviceable. Work may be greatly expedited if provision is made for strong suction and blast appliances. Indeed these are wholly indispensable at blast furnaces and steel works. Oxygen, with which to hasten the burning of several precipitates is very advantageous. Carboys may well be employed to hold standard solutions, being properly connected with side-filling burettes (100 c. c. capacity). Containers for much used liquid reagents are more convenient when provided with glass stopcocks. Automatic filtering, stirring and shaking apparatus are often desirable. Particularly indispensable is a strong gas pressure with many available connections. (Recently modified gasoline appliances may be used in lieu of gas.) Nothing can be of greater advantage in any laboratory than some steam plates under the hood, on which evaporations may be safely conducted during the night.

A record book, ruled in harmony with the several varieties of report forms, is a great convenience. No results should be reported until the final record is made, simultaneously with which the report form should be filled in with like data. After this the package containing the remainder of the sample should be filed in the balance room, and should not be destroyed until the chemist is assured that the stock it represents is undisputed.

A beginner in the work should form as many friends in similar work as is convenient. An interchange of ideas is very essential to progress.

He should provide himself with several standard works upon his chosen branch, and should also have at hand several works on general chemistry. Especially at isolated mines and works are some peculiar demands made upon the chemist. Questions involving a knowledge of chemistry apart from his routine work are often asked. Preliminary care of injured workmen often devolves upon him. By making preparation for such emergencies he may often win advancement. From my experience, after establishing a laboratory, it requires about two years for one to become thoroughly familiar with the requirements and with all those things that are best suited to advance his work. An occasional chemical periodical should very much interest him.

By aid of emery paper one can roughen a small spot upon beakers and other containers on which record of contents may be made in lead pencil, or he may buy beakers with such spots already on them. The marks are easily removed. This method is superior to the use of paper labels. Operations in any method should always be conducted in containers of the same size. All determinations in a sample should be finished at as nearly the same time as possible.

The experienced chemist will, when recording his results, recall all details of the work. Duplicate determinations are the safe-guard of every chemist.

PART II.

PREFACE, PART II

It has been my effort to place before foundrymen in the following pages, such ideas as I have demonstrated to be of value, together with information carefully selected and condensed from the papers and books of eminent authorities. In this I have aimed, even at the expense of repetition, to instil into the minds of foundrymen the necessity of setting aside all prejudices based upon the appearance of metal, for a selection depending upon ideas other than its percentage composition is both unsatisfactory and unscientific. A study of Part I. by the foundryman will make evident the vast amount of work that has been done in bringing chemical methods to their present state of perfection. These methods in skilled hands, when applied to foundry materials, will bring forth figures, the proper interpretation of which can advance the economies and certainties in casting iron as they have advanced the steel industry. Some foundrymen have learned by experience the inherent variations in the same brands and grades of pig iron. Since the composition of pig iron is not revealed in name or grade, it is a growing custom to buy iron of guaranteed analysis, best suited to the work in hand. Careful consumers have for a long time verified the analyses furnished by the seller and mixed their irons according to constituents present, or have rejected the irons as unfit for their use, or have required an adjustment with the seller.

Since it is impossible to take two or more samples from any material not quite homogeneous, that shall be absolutely identical; since also different operators on the same sample will often report slightly different figures, it is admissible to allow slight deviations from a guarantee, so long as such deviations are not constantly in one direction.

F. L. C.

Cleveland, August, 1901.

FOUNDRY CHEMISTRY.

Variations in Pig Iron.

There is a lingering belief among foundrymen that pig iron produced at the same furnace, or upon the same ore mixture, must of course produce the same quality of castings. The blast furnace chemist soon recognizes the absurdity of such ideas. Some years ago I was sent four samples of drillings in which the variations in silicon were nearly one per cent, and in sulphur from .01 per cent to .10 per cent. The founder for whom these results were obtained stated that I had furnished evidence of their correctness in that three of the samples were drillings from three different pigs of the same car-lot, while the fourth was a careful mixture of equal weights of the other three; the analysis of the fourth showing almost the exact numerical average of the first three samples. He desired an explanation of this proven variation. To understand these variations one must know that a blast furnace on the same burden may, because of leaking tuyeres, hanging, differences in blast pressure, etc., produce perfectly white iron with sulphur as high as .50 per cent, and may produce in the same cast with it an open foundry iron with only a trace of sulphur and much higher in silicon than the former; hence, for foundry purposes a car of iron is frequently selected from the more or less open portions of several casts, with variations as extreme as those first mentioned. The means of overcoming variations in castings when using such a car of iron will be made evident in the context. Further causes that lead to differences in the product of a furnace are—different ore mixtures, varying amounts of fuel employed, its quality, the humidity of the atmosphere, together with many causes beyond the manager's control which are always incident to complicated processes. It thus appears that the selection of foundry metal by analysis is the only safe means. By investigating each car-lot of iron the foundryman will avoid failures due to variations in different consignments.

Sampling Pig Iron.

Increased rapidity of chemical methods has enabled consumers to hold iron in cars while it is being analyzed, so that if not suited to their use, it may be rejected without further cost. A good method of sampling consists in selecting two pigs from the surface of the car-lot equidistant from each side or end of the car, and two more from the bottom at the same or different distances from each side or end of the car, depending upon no other ideas for the selection. These pigs should be broken to expose new sections and drilled about one inch from the middle, which drillings will represent the pig as well as any sample can represent the car-lot. Equal quantities of the fine sand-free, oil-free drillings should be intimately mixed by rolling on paper. One ounce of this mixture is sufficient for complete analysis. If several cars of the same lot of iron are to be sampled, one pig from the top and one from the bottom of each car is sufficient, they being selected by some mechanical means as above, and drillings from all cars mixed as before.

If several cars of the same iron are to be placed in one pile in order to equalize the differences in the car-lots, the first car unloaded should be distributed horizontally and evenly throughout the length of the proposed pile, the second car-lot similarly on top of this and so on. Then by using vertically from one end of the pile, iron will be obtained which will conform very closely to the analysis of the mixed drillings from the cars.

Scrap and Shot Iron.

Scrap from the previous day, including shot iron, will need no analytical attention. It will generally be found .25% lower in silicon than the mixture. It will have lost about one-fifth of its manganese, provided that was not very high, in which case it will have lost somewhat more. Its sulphur will be higher to an extent indicated under "figuring mixtures" to follow.

Foreign scrap should be piled according to its kind. A fit sample for analysis would be mixed drillings from several representative pieces. The prejudices existing in relation to the return of the shot iron to the cupola are quite unfounded, since this material is identical in silicon, sulphur, phosphorus and manganese, with the castings from the same heat. It will usually differ from the castings in containing somewhat less graphitic carbon and more combined carbon (due to greater chilling), but on remelting this equality will be restored under the influence of the silicon in the mixture. Every economical foundryman will employ some means of recovering it.

Coke and Coal.

Coke is the usual foundry fuel, the better grades of it consist chiefly of large, bright pieces, clean and strong, with but few very dark ends. Visible moisture, lumps coated with fine material, and any considerable quantity from the size of hickory nuts to sawdust, are deleterious. Coke as well as coal may be sampled by taking many pieces not to exceed a cubic inch in size, from different parts of the lot. Most of the pieces should be broken from larger ones and display at least one-half new surfaces. If there is a considerable quantity of fine material, and is to be used, a due proportion of it should be added to the sample. It is important to carefully note the relative amounts of the lump and fine coke in the lot to be sampled, and see that these as well as the proportion of dark ends, be maintained in the sample. This sample should be broken to the size of sawdust and intimately mixed. One ounce of the mixture is sufficient for complete analysis. Since the sulphur in castings is largely dependent upon the amount of sulphur in the fuel, a knowledge of the latter is important. The amount of coke needed to melt the charge also influences the sulphur in the castings as well as the expense of melting. Therefore, coke high in fixed carbon and low in ash should be sought. In good practice about 4% of the sulphur in the coke is taken up by the iron, as illustrated by example to follow. Rapid melting tends to lessen the sulphur taken up by the iron. Good foundry coke should not contain to exceed .8% sulphur, which will yield about .032% to the casting. Hard bituminous coal as well as anthracite is sometimes used as a foundry fuel, but both are devoid of many advantages possessed by coke. From the best statistics available, I find that in the average cupola one pound of coke will melt nine pounds of iron; one pound of anthracite will melt six pounds of iron; one pound of bituminous will melt five pounds of iron.

Thus it appears, when freight, the higher sulphur of the usual coals, and the working of the cupola are considered, coke is the more economical fuel.

Figuring Mixtures.

To illustrate, take the following formula for light gray iron castings, which has been repeatedly tried and is known to produce soft castings with low shrinkage and ample strength.

Silicon	in mixture about	3.60%
Sulphur	" not to exceed	.04 "
Manganese	" " " "	.50 "
Phosphorus,	between .6 and	1.00 "

A mixture conforming to the above is most readily obtained by tabulating the quantities of pig and scrap according to their analyses, as is shown in the following examples, and will yield a casting about 3.35% in silicon, .080 in sulphur and .40 in manganese, with phosphorus slightly increased according to coke content.

Since the quality of a casting is most easily regulated by adjusting the silicon content of the mixture, this is the first element to be taken into account when figuring a mixture. Other elements of a mixture thus temporarily established should next be calculated, and if not within prescribed limits, must be brought in by some rearrangement or substitution of irons or scrap, which will not affect the silicon content, yet eliminate the objection of the preliminary mixture.

Silicon.

Kind of Iron.	Pounds Used.	Silicon Content.	Total Points Silicon.
Home Scrap............	800	3.35	2680.00
Foreign Scrap..........	100	2.00	200.00
Pig Iron A.............	200	1.45	290.00
Pig Iron B.............	550	2.40	1320.00
Pig Iron C.............	350	7.80	2730.00
	2,000	=	7220.00

Therefore, 7220 ÷ 2000 = 3.61% silicon in mixture = about 3.35% silicon in the casting.

Sulphur.

Kind of Iron.	Pounds Used.	Sulphur Content.	Total Points Sulphur.
Home Scrap............	800	.080	64.000
Foreign Scrap..........	100	.100	10.000
Pig Iron A.............	200	.025	5.000
Pig Iron B.............	550	.021	11.550
Pig Iron C.............	350	.010	3.500
	2,000	=	94.050

Then, 94.05 ÷ 2000 = .042 sulphur due to iron and adding .032 sulphur due to coke gives .074 sulphur in casting.

It may be readily seen from the above examples that they are simply the result of a relative adjustment of the different irons, tabulated in such a manner as to admit of a ready change in the irons used and of the kind of castings produced. Thus, in case it were desired to drop pig A, and substitute all pig B, it would be effected by increasing pig B somewhat more than the weight of pig A used, and decreasing the weight of pig C, keeping 2,000 pounds in the mixture. Other constituents of the mixture should be figured in analogous manner.

From an analysis of the casting any necessary adjustment of the mixture may be made.

The method called alligation alternate employed by some, in figuring mixtures, besides being extremely difficult of application, seems to possess other disadvantages.

When it is desired to produce castings of definite composition it is best to mix irons of composition as nearly like the casting sought as conditions will permit, because irons differing materially in their percentage of silicon and other elements are of different specific gravity, hence when molten are liable to be imperfectly mixed as they are drawn from the cupola, thus yielding castings that are not uniform in composition.

Formulae for Other Castings.

The safest method of obtaining mixtures that will produce other varieties of castings is to analyze mixed drillings judiciously taken from several castings that have proven satisfactory. The drillings should be taken before the castings have been annealed. The carbon in annealed malleable castings varies with the area of the cross sections, therefore drillings should be taken by planer from cross sections.

With such information and a knowledge of the method of melting, one may select irons of suitable analysis to duplicate the castings in question.

In such selection all pre-formed prejudices, whether based on fracture, analysis or previous use, must be put aside, for it is to be remembered that no matter how inferior an iron may be when considered alone, it may be so blended in mixture with others as to produce superior effects, and it may constitute an economical part of the mixture. When this method is followed, the consumer will be the only testing machine necessary. It is a growing custom among consumers to demand castings conforming to rigid specifications, which can only be made by scientific methods of procedure.

It is impossible in the abstract, to prescribe the composition of a casting which shall conform exactly to all specifications involving its physical properties. These may, however, be approximated and by the use of the above principles actually accomplished.

Annealing.

The stresses which exist in castings are greatly lessened by annealing, which also softens the castings to a marked degree. It has become quite universal to anneal small castings to save tools and time in the machine shop. The process is quite inexpensive and is sure to soften the castings. A good method is to pack small castings in cast iron pots with wood shavings or the light charcoal from previous annealing. The iron is then gradually heated to bright redness, which should require from 10 to 12 hours, when it is allowed to cool through a like period. The castings are sometimes placed in the open furnace where the flame and gases are allowed to pass over and between them, or they are packed in cast or wrought iron boxes. The former method produces more scale and the latter requires a longer time, but no other differences result. In the annealing process a part or all of the combined carbon present is changed to the graphitic or a related condition, which renders the castings more easily machined, but this change is influenced largely by the silicon and manganese present. Very low silicon and manganese castings while being softened by the process are rendered less tenacious and often break under the tool. Silicon promotes a satisfactory carbon change to a greater degree than manganese. Where the castings are packed in charcoal some carbon is taken up by the iron and during the process is converted into the graphitic or a related form of carbon.

The process of annealing malleable castings is somewhat the reverse of the above, and consists in heating them in closed boxes filled with finely-powdered hematite. The surface of the casting is decarburized at the expense of the oxygen in the hematite with the production of a malleable coating. Before annealing, all sand and scale should be most thoroughly removed from the casting, otherwise ruffened spots will be produced on them during the annealing process. For a like reason the hematite or analogous material used should be as free as possible from lime, magnesia and manganese.

Influence of Elements on Cast Iron.

Silicon promotes fusibility and fluidity.

Decreases shrinkage and strength.

Diminishes the power of iron to combine with carbon

Lessens blow-holes and reduces chilling capacity.

Strongest castings are made from iron that will produce sound castings with the least silicon.

Other conditions being right, about 3.35 per cent silicon will produce maximum graphite in a casting. Hence in heavy castings, or when great density, strength or chilling capacity is required, silicon is often reduced to one per cent or below.

Sulphur increases fusibility, but makes iron sluggish when molten, thus giving rise to blow-holes.

It weakens iron and increases shrinkage, hardness, and chilling capacity.

For means tending to its removal from cast iron see General Remarks and Manganese to follow.

Phosphorus, when very high, say 3 per cent, seems to diminish the power of iron to combine with carbon.

It tends to render metal very limpid when molten, adapting it to ornamental patterns.

The above conditions are usually described by saying that it promotes fluidity and reduces shrinkage.

It renders iron cold-short, and often easily broken by shock-like or vibratory stresses.

When considerable strength of casting is required high phosphorus and high silicon must not co-exist.

Manganese.—Considerable quantities of this element tend, during melting to the removal of sulphur, hence assist in the prevention of blow-holes and red-shortness.

It increases the power of iron to combine with carbon, hence increases chilling capacity and shrinkage.

It increases strength and hardness.

Soft castings with low shrinkage cannot exist with high manganese.

Carbon.—The usual grades of pig iron contain 3.65 per cent total carbon or less.

On melting in the cupola this percentage is usually somewhat diminished. I have never known a case in which it was increased, hence when high carbon castings are required pig metal containing this element in suitable quantity must be selected. Graphite opens the grain of metal and renders heavy castings porous when excessive. In most castings of whatever character the total carbon is not less than 3.15 per cent.

Carbon affects the color, strength, hardness and fusibility of cast iron.

Combined carbon increases the hardness, brittleness and shrinkage of iron, while graphite softens and toughens it.

White iron may result from chilling, high sulphur, low silicon, or high manganese.

So little is known of the influence of copper, aluminum and titanium upon cast iron that a discussion seems unprofitable. In the case of the former it may be said that its percentage is not perceptibly diminished by melting in the cupola and that it seems to affect the casting as does sulphur.

General Remarks.

Iron for stove plate and other light work, as well as for malleable work, should be poured hot, while by good authority it is asserted that chilled rolls and car wheels should be poured dull. Under these conditions the product is less liable to crack.

The depth of chill called for varies from ⅝ inch to ⅞ inch.

Bessemer iron can be melted hot enough for stove plate. For steam cylinders and hydraulic work as well as for machine castings, it is excellent because of the greater strength due to low phosphorus.

Notwithstanding opinions to the contrary, charcoal iron is no better than coke iron of like analysis. It is furthermore not difficult to secure coke iron, the analysis of which is practically identical with the usual brands of charcoal metal.

Both charcoal and coke metal quite low in sulphur, when melted in the air furnace, produce excellent castings (other conditions being right) because of the small amount of sulphur taken up. The air furnace process is more expensive than cupola melting but possesses an advantage, in that greater bodies of metal are available at one time, and that heavy scrap may be more easily handled. It is especially safe for hydraulic work, in which freedom from blow-holes is indispensable. Melting iron at a high temperature with a little lime flux will assist very materially in producing castings low in sulphur, because at high temperature sulphur has a greater affinity for calcium than for iron.

Limestone low in sulphur, especially as sulphides, is perhaps the cheapest and best flux, though some prefer fluorspar. Fifty pounds of limestone or thirty pounds of fluorspar is the usual amount employed per ton of iron melted.

From available data it would seem that the loss in melting pig iron alone due to its superficial sand, etc., should not exceed four and one-half per cent, a part of which loss is due to the oxidation and fluxing off of some silicon, manganese and iron. Some carbon is also frequently burned out of the metal. The higher the temperature and the greater the volume of blast the greater the amount of oxidation.

A ton of sand pig is sold at 2,268 pounds, while a ton of machine or chill cast pig is sold at 2,240 pounds. The difference represents roughly the weight of sand on the former. It is more economical to buy sand pig that has stood in the yard for some time, or suffered a rehandling after exposure.

High silicon irons are called *softeners* for the reason that when they are mixed in suitable proportion with low silicon foundry irons, the resulting casting will be softer than if produced by either iron alone.

Not infrequently do I meet foundrymen who though using such irons (8-15%) really believe them to be soft, when in reality they can only be drilled with the extremest difficulty.

The Relation of Chemist to Foundryman.

Some foundrymen still fail to understand the scope of assistance which the chemist can give them They regard the establishment of a laboratory as a somewhat useless expenditure, perhaps more as a fad than as a benefit. The unparalleled advances in the manufacture of steel are largely the results of a chemical interpretation of the several processes of manufacture. The advancement of the foundry business must in like measure depend upon the application of scientific principles, experiments and intelligent inquiry. The sources of production of pig iron have increased so greatly in number within the last decade as to make an absolute means for its selection more necessary than formerly. The chemist should inquire into the qualities of nickel anodes, babbitts, brasses, etc., which are usually sold of guaranteed composition and perhaps under fancy names at advanced prices. The quality of oils for cores and lubricants may be investigated, and knowing their nature, the same materials may often be purchased under an original name at greatly diminished prices.

The chemist insures his employer of securing materials, of whatever kind, fully up to the specifications, and best adapted to the work in hand. He may after a study of the water supply, suggest some cheap material for the prevention of boiler scale. Of several sources of water supply, his judgment should be accepted in selecting the better one for boiler or drinking purposes. It often happens that the acids used by the foundry are not of standard strength, which fact he can make known. Under his guidance broken castings due to faulty mixtures are eliminated or those too hard to drill or filled with blow-holes, are avoided. In addition to the duties enumerated, he should see that all iron is piled according to its analysis convenient for use. He should figure the mixtures to be placed in the hands of the cupola manager and make such physical tests as may be deemed necessary. The furnace manager and chemist should hold conferences from time to time tc take up ways and means of improving the product or maintaining its excellency. These discussions should be based upon carefully tabulated data comprising chemical analyses and physical tests if any. It is not good business policy to return material to the producer's laboratory for analysis. Smaller concerns need not of course employ a chemist regularly, but may avail themselves of the services of such men as have established to do this line of work. By the proper application of chemistry to foundry practice a uniform output of any desired character may be obtained at the least cost.

In buying and mixing irons by analysis foundrymen may use less expensive irons because the advantage of a wider market is afforded by abandoning the use of a certain few expensive brands that formerly proved satisfactory.

The thoughtful foundryman will recall a period when a special grade or brand of iron has yielded entirely different results than on former occasions. He will remember cupola linings of short life, and paints that blistered or became totally obliterated by a short exposure to the elements. A chemist could have pointed out the objections previous to the use of the materials. With increasing competition and demands for more perfect castings the services of a chemist are becoming more and more indispensable in progressive foundries.