DEPARTMENT OF COMMERCE AND LABOR

CIRCULAR
OF THE
BUREAU OF STANDARDS

S. W. STRATTON, DIRECTOR

No. 26

ANALYZED IRON AND MANGANESE ORES—METHODS OF ANALYSIS

[1st Edition]
Issued June 25, 1910

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CONTENTS

I. INTRODUCTION

General information regarding standard samples, including a description of the methods used in their preparation, is published in Circular No. 25. The information and methods given in this circular have special reference to samples Nos. 25, 26, 27, and 28. When other ores are issued, involving the use of new methods, this circular will be revised and copies sent to all those who have ordered samples within the year preceding.

1. MIXING

So far as possible the materials have been thoroughly mixed, as shown by concordant analyses on different samples. Since, however, some small metallic particles (derived from the grinding apparatus) are known to be present in these ores, thorough mixing of each sample is necessary to insure uniformity of composition.

2. DRYING

The analyses of these ores are all based on material dried at 100–105° C (120° C for the manganese ore). While these ores contain but a small amount of moisture as sent from here, experiments have shown that this moisture content fluctuates with the humidity of the surrounding atmosphere, even when the samples are only occasionally opened. In the determination of constituents present in amounts less than 5 per cent, the effect of these moisture changes is negligible. But in such ores as No. 25 and No. 27, differences of a few tenths of 1 per cent in the moisture content will cause appreciable errors in the determination of the manganese or iron.

For this preliminary drying the following procedure is recommended:

An approximate weight of each sample for analysis should be dried in a weighing bottle for one hour at the temperature specified. The bottle should then be stoppered and left to cool in a desiccator. The stopper is removed for an instant, the bottle weighed, and the contents of the bottle are poured into a convenient vessel. By reweighing the bottle the weight of ore used is determined. Numerous experiments have shown that in the usual method of drying on watch glasses and cooling in a desiccator, an appreciable amount of moisture may be taken up from the moist air which entered the desiccator during the introduction of the sample. Similarly, if a large amount of material be dried and preserved in a weighing bottle, the occasional opening of the latter may permit considerable moisture to be reabsorbed. Numerous experiments have shown that only by some such procedure as above recommended can correct results be assured.

3. REAGENTS

No doubt many of the discordant results obtained in commercial analyses are due to impurities in reagents, even though the quality of the latter has been greatly improved in recent years. For accurate work it is necessary to test these reagents for such impurities as might affect the determinations under consideration, and either purify them or make the appropriate corrections. This is necessary even in the use of chemicals with attached analyses, which have sometimes been found to be in error. All the ammonia used at the Bureau was redistilled, and preserved in bottles lined with ceresin, and all reagents were tested by suitable means.

4. APPARATUS

While Jena glass is highly resistant to acid or neutral solutions, alkaline solutions attack it appreciably. Such solutions should not be allowed to stand in glass for any length of time, and especially should not be evaporated in glass. For such purposes either porcelain or platinum should be used. Attention is called to the possible occurrence of iron in platinum ware, especially when new, which may cause appreciable errors if used in the solutions of ores in which iron is to be determined. While it is recognized that the technical chemist, from lack of time and apparatus, may not be able to take all such precautions, he should at least have some idea of the nature and magnitude of the errors involved in his methods, such as can be gained by comparative analyses of standard samples whose composition has been accurately determined.

II. METHODS OF ANALYSIS USED AT THE BUREAU OF STANDARDS

In the following description a brief outline of the methods will be given, with references to more detailed accounts, except in those cases where special methods or modifications were used.

1. SILICA[1]

The ore was dissolved in hydrochloric acid in a porcelain or platinum dish, and evaporated to dryness (twice if there was any apparent gelatinous silica). After taking up in acid and filtering, the insoluble residue was ignited and fused with sodium carbonate. The fusion was dissolved in hydrochloric acid and evaporated to dryness twice (three times for large amounts), with intervening filtration. After filtration and thorough washing, the silica was ignited, finally for twenty minutes over a blast, and weighed. By treatment with hydrofluoric and sulphuric acids the silica was determined by loss in weight.

2. PHOSPHORUS

In the analysis of the Sibley ore (No. 27) three methods were used, in each case including the phosphorus in the insoluble residue—(*a*) Direct weighing of the phospho-molybdate; (*b*) titration with permanganate; and (*c*) precipitation with magnesia mixture from the citrate solution of the phospho-molybdate, and ignition to the pyro-phosphate. In the Crescent ore, containing titanium, the phosphorus was determined by a double fusion with sodium carbonate and precipitation by a small amount of ferric salt, followed by the molybdate precipitation and permanganate titration. In general in these determinations the methods in Blair's Chemical Analysis of Iron (7th edition) were employed. The concordance of the results on phosphorus by different methods, both at the Bureau of Standards and elsewhere, is very satisfactory.

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[1] W. F. Hillebrand: Bull. 305 or 422, U. S. Geol. Survey.

3. ALUMINA

(*a*) **Phosphate (Peters) Method.**—Two grams of the ore was dissolved in hydrochloric acid. The residue was treated with hydrofluoric acid, fused with sodium carbonate, dissolved and added to the main solution, which was evaporated nearly to dryness. It was taken up in 5 cc of hydrochloric acid, diluted to 400 cc, and 3 grams of microcosmic salt (in solution) was added. The solution was just neutralized with ammonia, 2 cc of concentrated hydrochloric acid added, and the solution stirred until clear. After adding 15 grams of sodium thiosulphate the solution was heated to boiling, when 8 cc of 90 per cent acetic acid and 5 grams of ammonium acetate were added. The solution was boiled for thirty minutes (ten minutes was found to be insufficient) allowed to settle, and filtered. The precipitate, which always contained some iron, even after thorough washing, was dissolved in hydrochloric acid and reprecipitated as above. It was finally ignited and weighed as $AlPO_4 + Ti_3(PO_4)_4$. After subtracting the titanium (0.07 per cent) calculated to phosphate, the Al_2O_3 was calculated by the factor 0.4185. (Since the factor for $Ti_3(PO_4)_4 \rightarrow TiO_2$ is approximately the same, i. e., 0.458, for small amounts of titanium the per cent of TiO_2 may be subtracted directly from the per cent of Al_2O_3 calculated from the total weight of the precipitate.)

(*b*) **Ether Separation.**—The solution of the ore (5 grams) was evaporated to dryness and taken up in 35 cc of hydrochloric acid (sp. gr. 1.13) and extracted with 100 cc of ether, followed by 50 cc of ether saturated with hydrochloric acid. The acid layer was evaporated to expel ether, oxidized with a little nitric acid, and precipitated by the basic acetate method; an ammonia precipitation followed. The precipitate, as finally ignited and weighed, consisted of Al_2O_3, TiO_2, about 70 per cent of the P_2O_5,[2] and a small amount of Fe_2O_3. The latter was determined by fusion of the ignited residue with potassium bisulphate, reduction with sulphur dioxide, and titration with permanganate.

(*c*) **Phenylhydrazine Precipitation.**[3]—The chloride solution of the ore (5 g) was diluted to 250 cc, nearly neutralized, and reduced by heating with ammonium bisulphite. A few drops of hydrochloric acid were added, followed by about 3 cc of redistilled phenylhydrazine. After stirring and settling the precipitate was filtered and washed with hot water. It always contained a little iron, which was in some cases removed by a second precipitation, and in others determined in the weighed precipitates. By this method the sum of $Al_2O_3 + TiO_2 + P_2O_5$ was obtained.

(*d*) **Electrolytic Separation.**[4]—The solution of the ore (5 g) was evaporated to the fuming point with a slight excess of sulphuric acid, diluted to 200 cc and nearly neutralized with ammonia. It was then electrolyzed in a beaker containing about 300 grams of mercury as the cathode. A current of

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[2] R. J. Wysor: Jour. Ind. & Eng. Chem., **2**, p. 45.

[3] Hess and Campbell: Jour. Am. Chem. Soc., **21**, p. 776.
E. T. Allen: Jour. Am. Chem. Soc., **25**, p. 421, and Bull. 305 or 422, U. S. Geol. Survey.

[4] Drown and McKenna: Trans. Am. Inst. Min. Eng., **20**, p. 242.
E. F. Smith: Electro-analysis (4th ed), p. 257.

3 ampères was passed through over night, and the iron thus completely deposited. (By the use of a rotating anode and a current of 5 ampères over a gram of iron was similarly deposited in one hour.) The alumina, etc., were obtained by double precipitation with ammonia, and finally weighed as $Al_2O_3 + TiO_2 + P_2O_5$. This separation of the iron proved to be very complete and satisfactory.

4. TITANIUM

(*a*) **Gravimetric.**[5]—The solution of the ore was reduced with ammonium bisulphite, the excess of sulphur dioxide expelled by carbon dioxide, and a a small portion of the iron was reoxidized by bromine water. By the acetate separation this ferric iron, together with all the titanium and phosphorus, was precipitated. This precipitate was dried and fused twice with sodium carbonate, the titanium being left in the portion insoluble in water. This residue was fused with potassium bisulphate, dissolved, reduced with sulphurous acid, and nearly neutralized, after which the titanium was precipitated by boiling with acetic acid and sodium acetate, and finally ignited and weighed as TiO_2.

(*b*) **Colorimetric.**—The titanium present in the ignited precipitates of alumina, etc. (cf. preceding section), was determined colorimetrically,[6] after fusion with potassium bisulphate, of which the same amount was added to the standard titanium solution.

5. STANDARDIZATION OF PERMANGANATE SOLUTIONS

Probably the greatest single source of error in the determinations of iron in iron ores and available oxygen and manganese in manganese ores, is the use of unsatisfactory materials for standardizing the permanganate solutions. The materials most often used for this purpose are iron wire, electrolytic iron, ferrous ammonium sulphate, oxalic acid, iron ores, and sodium oxalate, of which the last was adopted by this Bureau after extensive investigation. The objections to the use of the other materials may briefly be summed up as follows:

Iron wire may contain a variable amount of iron, the assumption of 99.8 per cent iron being frequently unwarranted. Even when the true iron content is known, accurate results can only be obtained by complete oxidation and subsequent reduction. Experiments here and elsewhere have shown that by simply dissolving in acid, the wire may have a working value as high as 100.6 per cent iron, due to incomplete expulsion of hydrocarbons. The magnitude of this error will vary, depending upon the size and shape of the vessel, the volume of acid employed, and the time and method of boiling the solution.

Electrolytic iron is difficult to prepare, and may contain carbon and occluded hydrogen.

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[5] Blair: Chemical Analysis of Iron (7th ed.), pp. 85, 184.

[6] Bulletin 422, U. S. Geol. Survey, p. 128.

Ferrous ammonium sulphate may vary in composition, due to loss of water, oxidation, or the presence of foreign elements such as manganese.

Oxalic acid may vary, due to difficulty in effecting complete drying without loss of the water of hydration.

An *iron ore* is an ideal substance for standardizing permanganate to be used for iron determinations, provided its composition has been accurately determined by independent methods. The Sibley ore is offered by this Bureau to meet just such a purpose.

Sodium oxalate, Sörensen,[7] is of very definite composition, anhydrous and non-hygroscopic, and can be dried at 230° C without decomposition. Owing, however, to the difficulty of purchasing sodium oxalate of requisite purity, all such material used here was purified, either by recrystallization from water, or precipitation by alcohol. Besides insoluble matter, the chief impurity is likely to be sodium carbonate, which may be detected readily by means of phenolphthalein, and estimated by titration, using precautions against the presence of carbon dioxide in the water used. Even when the sodium oxalate has been dried at 230° C, in very accurate work the portions used for analysis should be dried at 130° C as an added precaution, since all powders tend to absorb some moisture from the air, even on occasional exposure. By cooperation with the manufacturing chemists this Bureau hopes in the future to furnish pure sodium oxalate as a standard sample.

6. IRON

(*a*) **Gravimetric.**—This method was used solely as a check on the Sibley ore, and is not recommended except for such purposes. All the operations, except the solution of the ore, were carried out in platinum in order to avoid contamination due to the action of ammonia upon glass, which is very appreciable, especially in the case of relatively small samples. The ore was dissolved in hydrochloric acid in a porcelain casserole and the silica separated and expelled with hydrofluoric acid. The residue was fused with sodium carbonate and added to the main solution, which was then precipitated with ammonia and filtered. A second precipitation was made in the presence of macerated filter paper (in order to make the precipitate porous for the subsequent ignition). After thorough washing this precipitate was carefully ignited and weighed as $Fe_2O_3 + Al_2O_3 + P_2O_5 +$ a trace SiO_2. It was tested with a magnet and found to be free from Fe_3O_4. The constituents other than iron were then determined as in the methods previously given, the iron being separated by electrolysis with a mercury cathode. As titanium, vanadium, manganese, and other interfering elements were proved to be absent the values thus obtained are believed to represent the true content and are independent of any errors due to standardizing materials, etc.

(*b*) **Jones Reductor.**—The ore was dissolved in hydrochloric acid (in porcelain) and the insoluble matter separated, treated with hydrofluoric acid, fused with bisulphate and added to the main solution. While in this Sibley ore the silica may sometimes be obtained practically free from iron,

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[7] Sörensen: Zeit. Anal. Chem., **36,** p. 639; **42,** p. 333; **42,** p. 512, and **44,** p. 156.

in other cases it has been found to contain as much as 0.20 per cent Fe, so this treatment should not be neglected. The solution was evaporated with sulphuric acid until it fumed strongly, diluted to 150 cc and sufficient sulphuric acid added to make about 5 per cent by volume. It was then passed through a Jones reductor, using precautions to exclude air, and finally titrated with permanganate which had been recently standardized with pure sodium oxalate. Corrections were determined and applied for (1) reducing substances derived from the reductor (which proved to be very slight in amount) and (2) the volume of permanganate required to produce a tinge in a solution of ferric sulphate of the concentration employed. In one series volume burettes were employed and in the other weight burettes.

(*c*) **Stannous Chloride Method.**—The ore was dissolved in a slight excess of hydrochloric acid, stannous chloride being added at intervals till the solution was complete. The residue was filtered out and treated as in the preceding to recover any iron contained in it. The solution (25 cc) was then reduced while boiling, by the cautious addition of a dilute stannous chloride solution[8] until just colorless. It was then diluted to 100 cc, cooled, and 10 cc of saturated mercuric chloride solution added. After three minutes it was poured into 300 cc of cold water, to which was added 25 cc of titrating mixture [50 gr. $MnSO_4$, 100 cc H_2SO_4 (1.84), 100 cc H_3PO_4 (1.75) and 600 cc H_2O]. The solution was then titrated with permanganate to the first pink tinge. Tests at this Bureau showed that if the sodium oxalate titer of the permanganate was employed, high results were obtained. If, however, an iron ore of known composition was used as a standard, uniform and accurate results could be obtained. For this purpose we employed the United States Steel Corporation Sibley ore in which we had previously found 68.77 per cent Fe. (United States Steel Corporation value 68.70 per cent Fe.) By the use of such a standard, the influence of blank corrections, etc., is eliminated.

7. AVAILABLE OXYGEN

Available oxygen in the manganese ore was determined by the following methods:

(*a*) **Ferrous Sulphate.**—The ore was dissolved in a measured excess of a standard acidified ferrous sulphate solution, by boiling in an atmosphere of carbon dioxide. The excess of ferrous iron was titrated with permanganate solution, which had been standardized with sodium oxalate.

(*b*) **Oxalic Acid.**—The process was similar to the preceding, a solution of oxalic and sulphuric acids being substituted for the ferrous sulphate, and the solution heated on a steam bath.

(*c*) **Sodium Oxalate.**—The ore was dissolved by means of sodium oxalate and sulphuric acid in a suitable apparatus, through which dry air was finally aspirated. The loss in weight is due to the evolution of two molecules of carbon dioxide for each molecule of manganese dioxide. Correction was made for the small amount of carbonate present in the ore.

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[8] Jones and Jeffrey: Analyst, **34**, p. 306.

(*d*) **Distillation.**—The ore was distilled with hydrochloric acid, the liberated chlorine being absorbed in potassium iodide solution. The free iodine was titrated with sodium thiosulphate, which had been standardized against (1) permanganate, (2) metallic copper, and (3) resublimed iodine.

8. MANGANESE

In the Bureau of Standards, the following methods were employed in determining manganese:

(*a*) **Ford.**—The regular Ford method was used, except that after dissolving the precipitated MnO_2 in sulphurous acid, etc., the iron was removed by a basic acetate separation, as it was always found to contain manganese if precipitated with ammonia. After removal of the nickel, etc., by hydrogen sulphide in the acetic acid solution, the manganese was finally determined as pyrophosphate by the method of Gooch and Austin;[9] in which, in the presence of a large excess of ammonium chloride and microcosmic salt, the manganese is precipitated by the addition of a slight excess of ammonia, heated till crystalline, cooled, filtered (on a paper filter), washed with dilute ammonia, and finally ignited to $Mn_2P_2O_7$. The factor used for $Mn_2P_2O_7$ was 0.38702. Manganese was determined colorimetrically in the filtrates, the maximum found in the nitric acid filtrate being 0.3 mg, and in the phosphate filtrate 0.2 mg.

(*b*) **Ford, Modified.**—The Ford method was employed, with acetate precipitation of the iron. The manganese was then precipitated with bromine and ammonia, the precipitate ignited, and then evaporated with sulphuric acid and weighed as $MnSO_4$,[10] the factor for which is 0.36378.

(*c*) **Acetate.**—The ore was dissolved in hydrochloric acid, the iron and alumina removed by two basic acetate precipitations, and the nickel and copper by hydrogen sulphide (in acetic acid solution). The filtrate was evaporated with sulphuric acid until it fumed, and after dilution the barium sulphate was filtered out. The manganese was then precipitated with ammonium persulphate in acid solution, and the precipitate ignited and converted to $MnSO_4$ as in the preceding. A maximum of 0.7 mg of manganese was found in the persulphate filtrates.

(*d*) **Volhard.**—The ore was dissolved in hydrochloric acid, evaporated to dryness, and taken up in hydrochloric acid and water. A slight excess of zinc oxide emulsion was added, the solution diluted to 300 cc, heated to boiling, and titrated with permanganate to a permanent pink. The permanganate for this and succeeding volumetric methods was standardized by titrating known amounts of manganese under the same conditions. For this purpose two solutions were employed, (*a*) the permanganate used for titration, which had been standardized with sodium oxalate and (*b*) manganous sulphate standardized gravimetrically. In the former operation a measured amount of the permanganate was reduced, either by evaporation with hydrochloric acid or by means of sulphur dioxide, of which the excess

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[9] Gooch and Austin: Am. J. Sci., **6**, p. 243 (1898).

[10] Gooch and Austin: Am. J. Sci., **5**, p. 209 (1898).

was expelled. The resulting solutions were treated with zinc oxide and titrated exactly as was the solution of the ore. Theoretically the titration should consume just two-thirds of the original volume of permanganate, but under the conditions used about 1 per cent less was required, e. g., 33.0 cc, instead of 33.33 cc for 50 cc of the original. The factor thus obtained, which was corroborated by titration of the manganous sulphate solution, was 0.2984 times the iron value, instead of the theoretical factor 0.2951. No doubt this factor will vary with the conditions of operation.

(*e*) The **Ford-Williams** method was carried out in the usual way,[11] i. e., by precipitation with chlorate and nitric acid, the precipitate being dissolved in ferrous sulphate, of which the excess was titrated. The factor, determined empirically was 0.4959 times the iron value instead of the theoretical factor 0.4918. For example, 100 cc of the permanganate after reduction and treatment by the Ford-Williams method was equivalent to 39.67 cc instead of the theoretical 40 cc of permanganate.

(*f*) In the **von Knorre**[12] method the manganese was precipitated with ammonium persulphate in a solution containing not over four per cent of free sulphuric acid. The precipitate was then dissolved in excess of ferrous sulphate solution as in the preceding method. The empirical factor was found to be 0.5058 times the iron value, instead of the theoretical 0.4918.

(*g*) The **Bismuthate** method, carried out according to Blair,[11] was found to require the theoretical factor 0.1967 times the iron value. That is, a given volume of permanganate, after reduction and reoxidation by the bismuthate method, was equivalent to the original volume of permanganate.

(*h*) The **Persulphate Colorimetric** method was used for the determination of small amounts of manganese, e. g., in the Norrie ore. The latter was obtained in a sulphate solution by evaporation with sulphuric acid, and then diluted to a measured volume. To an aliquot portion was added 10 cc of nitric acid (1.2 sp. gr.), and 3 cc of $\frac{N}{10}$ silver nitrate, and one gram of ammonium persulphate. After diluting to 50 cc, the solution was heated to boiling and then cooled and compared in a Wolff colorimeter with the standard. The latter was prepared from the same volume of the ore solution, to which were added nitric acid and silver nitrate, but *no* persulphate. Instead there was added a measured volume of a dilute permanganate solution of known manganese content. In this way the influence of the ferric salts, etc., is entirely eliminated.

Although numerous methods for manganese were used, both at the Bureau and elsewhere, the number of determinations is scarcely sufficient to justify any conclusive comparisons. In the gravimetric methods both positive and negative errors are possible, according as foreign elements may be occluded in the precipitates or as manganese may be carried into filtrates and not determined. The volumetric methods (with the exception of the bismuthate) tend to give low results unless empirical factors are used. In

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[11] Blair: Chemical Analysis of Iron (7th ed.).

[12] von Knorre: Z. Ang. Chem., **1901**, p. 1149.

low manganese ores, however, the Volhard method gives uniformly high results, due probably to uncertainty in the end point. Further investigations of these methods will, it is hoped, remove some of the discrepancies found in these analyses.

9. LIME[13]

In the determination of lime the iron, etc., were removed by two basic acetate precipitations, and the filtrates evaporated to dryness and most of the ammonium salts expelled. The residue was taken up in water and a little hydrochloric acid, and the manganese (and traces of iron) removed by precipitation with bromine and ammonia. The calcium was precipitated from the hot solution by ammonium oxalate, allowed to settle, and filtered. It was dissolved and reprecipitated, and finally ignited to CaO. This weight was corrected for traces of iron oxide and silica contained in it, and also for the lime found in the magnesia precipitate (cf. following paragraph). All operations were carried out in platinum, which is essential for accurate work, as appreciable quantities of lime and silica are derived from the glass by ammoniacal solutions.

10. MAGNESIA[13]

Magnesia was precipitated from the filtrate from calcium by the addition of microcosmic salt and ammonia in excess. This precipitate was dissolved in a slight excess of hydrochloric acid, a little microcosmic salt added, and then a slight excess of ammonia. After stirring until the crystalline precipitate was formed, more ammonia was added and the precipitate filtered out after standing a few hours, and ignited, finally over a blast, to $Mg_2P_2O_7$. After weighing, the precipitate was tested for lime by solution in dilute sulphuric acid and addition of absolute alcohol. The lime thus separated was calculated to tricalcium phosphate, and deducted from the weight of the magnesium pyrophosphate. Consideration of the cooperative results for magnesia on the Crescent ore (cf. certificate No. 27) shows that high and discordant results are usually obtained, due to contamination from the reagents or containing vessels, or the incomplete removal of the preceding elements.

III. METHODS USED BY OTHER ANALYSTS

1. COMMERCIAL CHEMISTS

Booth, Garrett, and Blair used the oxalic acid method for available oxygen, the permanganate being standardized against electrolytic iron, which had been fully oxidized by hydrochloric acid and chlorate, then reduced by zinc and titrated in the presence of titrating mixture. For manganese they employed the bismuthate method, manganous sulphate being used as the primary standard.

Crowell and Murray determined silica after sodium carbonate fusion; iron by stannous chloride reduction and titration with permanganate; phosphorus by the Emmerton method; alumina as the phosphate; and lime and magnesia by the methods of the United States Steel Corporation.

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[13] W. F. Hillebrand: Bull. 305 or 422, U. S. Geol. Survey.

Dickman and Mackenzie determined iron by permanganate; phosphorus by both the acetate and molybdate methods (according to Blair); silica by sodium carbonate fusion; alumina by Peters method; manganese as the pyrophosphate; lime by titration with permanganate; and magnesia as $Mg_2P_2O_7$.

Emmerton employed the stannous chloride and permanganate method for iron; both the alkalimetric titration and gravimetric magnesia method for phosphorus; direct hydrofluoric acid treatment for silica; the Ford method for manganese; Peters method for alumina; and the gravimetric methods for lime and magnesia.

Ledoux and Company used the Ford method for manganese, making corrections for manganese in the filtrates and the impurities in the weighed precipitates; and also the Pattinson method with an empirical factor, derived from the titration of a known amount of manganese. In the determination of available oxygen, using the oxalic acid method, the permanganate was standardized against (*a*) oxalic acid, (*b*) electrolytic iron, and (*c*) ferrous ammonium sulphate.

A. S. McCreath and Son standardized the permanganate for the available oxygen by means of ferrous ammonium sulphate. For manganese, the iron was removed by two basic acetate separations, the manganese precipitated with ammonium sulphide, dissolved and determined as the pyrophosphate.

Rattle and Sons employed the stannous chloride and permanganate method for iron; the Emmerton method for phosphorus; sodium carbonate fusion for silica; the phosphate method for alumina; the Volhard method for manganese; the volumetric method for lime; and the gravimetric method for magnesia.

Ricketts and Banks determined manganese as $Mn_2P_2O_7$ after the acetate separation and bromine precipitation. For available oxygen, the permanganate was standardized by iron wire, which was oxidized, reduced by stannous chloride and titrated by permanganate after the addition of titrating mixture.

P. W. Shimer determined manganese as pyrophosphate after two basic acetate separations and precipitation of the manganese by bromine. For the available oxygen he used a solution of iron wire (99.85 per cent Fe), dissolving the iron and the ore in an atmosphere of carbon dioxide.

O. Textor employed the Volhard method for manganese; the sodium carbonate fusion for silica; the gravimetric molybdate for phosphorus; the stannous chloride and permanganate methods for iron; the phosphate method for alumina; and gravimetric methods for lime and magnesia.

2. WORKS CHEMISTS

J. M. Camp determined the constituents as follows: Silica by double evaporation; iron by bichromate titration; phosphorus by weighing the phosphomolybdate; alumina by both the phosphate and ether methods; manganese by the Ford method for the Norrie ore, and by both Ford and acetate methods for the manganese ore; and lime and magnesia gravimetrically.

R. F. Clanfield made the following determinations, all according to the Steel Corporation's directions: Silica on one and five gram portions; iron by permanganate and bichromate; phosphorus by alkali titration and by weighing as pyrophosphate; lime both volumetrically and gravimetrically; magnesia as pyrophosphate; and manganese by both sodium arsenite titration and peroxide reduction.

W. B. N. Hawk determined silica after sodium carbonate fusion; iron by permanganate; phosphorus by weighing both the phosphomolybdate and the pyrophosphate; alumina by the phosphate method; manganese by weighing Mn_3O_4; and lime and magnesia gravimetrically.

C. A. Little determined manganese as the pyrophosphate, after separating iron by the basic acetate method, and precipitating the manganese, first by bromine and ammonia, and afterwards by ammonium sulphide. For available oxygen, he standardized the permanganate by means of iron wire with an assumed purity of 99.8 per cent Fe.

C. H. Rich employed double evaporation for silica; the bichromate method for iron; the weighing of the yellow precipitate for phosphorus; the phosphate method for alumina; the Ford and also the Mn_3O_4 methods for manganese; and gravimetric methods for lime and magnesia.

3. MINE CHEMISTS

In general, the mine chemists used the methods of the United States Steel Corporation[14] for these ores, the particular methods being indicated in part upon the certificates. Owing to uncertainty as to the methods used for alumina and hence as to the composition of the precipitates weighed, the true alumina can not be calculated in all cases. Since most of these chemists used the phosphate method, their average for apparent alumina is somewhat higher than the most probable value. In general, the agreement of the mine chemists, both among themselves and with the other chemists, is very satisfactory, being due in part, no doubt, to the beneficial influence of the use of uniform methods of analysis as recommended by the United States Steel Corporation.

S. W. STRATTON,
Director.

Approved:
BENJ. S. CABLE,
Acting Secretary.

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[14] Jour. Ind. & Eng. Chem., **1**, pp. 107–115. Electrochem. Met. Ind. **7**, pp. 65–72.

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