DEPARTMENT OF COMMERCE

CIRCULAR
OF THE
BUREAU OF STANDARDS

S. W. STRATTON, DIRECTOR

No. 26

ANALYZED IRON AND MANGANESE ORES—METHODS OF ANALYSIS

[3d Edition]
Issued May 26, 1913

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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, 28, and 29. 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 exposed. 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 Nos. 25, 27, and 29, 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 been found sometimes 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

Although 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 solution 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 ammoniacal solution of the phospho-molybdate and ignition to the pyrophosphate. In the Crescent ore (No. 26), 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

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

titration. In the magnetite ore (No. 29) the phosphorus was precipitated with molybdate in the usual way. Upon treating the yellow precipitate with ammonia there was a white residue which was found to contain phosphorus. It was therefore ignited, fused with sodium carbonate, extracted with water, and the filtrate acidified with nitric acid. This solution was precipitated with molybdate, and the precipitate dissolved in ammonia and added to the main solution, which was then precipitated with magnesia mixture. 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.

3. SULPHUR

(*a*) **Carbonate Fusion.**—Five grams of the ore was fused for thirty minutes with 15 g of sodium and potassium carbonate, over an alcohol lamp. The mass was extracted with water, and a few drops of bromine water were added (to oxidize any sulphides or sulphites). The solution was then acidified with hydrochloric acid (1–5), of which an excess of less than 1 cc was present, in a volume of 350 cc. The solution was heated to boiling; precipitated with 5 cc of 0.5 N barium chloride solution, and boiled for some time. It was allowed to stand thirty-six hours, filtered, washed with hot water, ignited and weighed as $BaSO_4$. From this weight was deducted the weight of $BaSO_4$ found in a blank experiment upon the reagents. According to Allen and Johnston [2] the solubility of $BaSO_4$ under the above conditions is about 1.0 mg, which is apparently independent of the amount present. The use of a blank correction, therefore, obviates the necessity for applying a solubility correction.

(*b*) **Carbonate and Nitrate Fusion.**—One gram of potassium nitrate was added to the fusion mixture and the product of the fusion was extracted with water. Since the resulting solution was green, a few drops of alcohol were added to precipitate the manganese. The solution was then acidified and precipitated as in the preceding paragraph.

4. ALUMINUM

(*a*) **Phosphate (Peters') Method.**—Two grams of the ore (No. 26) 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 g 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 g of sodium thiosulphate the solution was heated to boiling, when 8 cc of 90 per cent acetic acid and 5 g 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,

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[2] J. Am. Chem. Soc., **32**, p. 592; 1912.

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.) In ores containing considerable titanium—e. g., the magnetite ore, this method was found to be unsatisfactory, owing to uncertainty as to the composition of the precipitated titanium phosphate. In general the method is not very accurate as at present employed; it was only included because of its frequent technical use. Further investigation is necessary to establish the conditions for accurate operation of this method.

(*b*) **Ether Separation.**—The solution of the ore (5 g) 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,[3] 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.**[4]—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.**[5]—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 g of mercury as the cathode. A current of 3 amperes was passed through over night and the iron thus completely deposited. (By the use of a rotating anode and a current of 5 amperes 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.

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[3] R. J. Wysor: J. Ind. & Eng. Chem., **2**, p. 45; 1910.

[4] Hess and Campbell: J. Am. Chem. Soc., **21**, p. 776; 1899.
E. T. Allen: J. Am. Chem. Soc., **25**, p. 421; 1903, and Bull. 305 or 422, U. S. Geol. Survey.

[5] Drown and McKenna: Trans. Am. Inst. Min. Eng., **20**, p. 242; 1891.
E. F. Smith: Electro-analysis (4th ed.), p. 257.

(*e*) **Separation in the Presence of Vanadium.**—In the magnetite ore, containing about 0.08 per cent V_2O_3, most of the vanadium was found in the ignited precipitates from the phenylhydrazine and electrolytic methods. These precipitates were fused with sodium carbonate and extracted with water, leaving the TiO_2 (and any Fe_2O_3) in the insoluble residue and the Al_2O_3, P_2O_5, and V_2O_5 in the solution. The TiO_2 was then determined in the former as under Titanium (5). The aqueous solution was acidified with hydrochloric acid and then made faintly alkaline with ammonia, precipitating the Al_2O_3, P_2O_5, and part of the V_2O_5. This precipitate was ignited and weighed and then fused with sodium carbonate, dissolved in nitric acid, and the P_2O_5 determined with citrate and magnesia mixture. The Al_2O_3 was determined by difference. Owing to uncertainty as to the exact distribution of the V_2O_5 in this process [6] and the difficulty of determining accurately such small amounts of vanadium the results given for Al_2O_3 are subject to slight errors, unavoidable with our present knowledge

5. TITANIUM

(*a*) **Gravimetric.**[7]—The solution of the ore was reduced with ammonium bisulphite, the excess of sulphur dioxide expelled by carbon dioxide, and 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,[8] after fusion with potassium bisulphate, of which the same amount was added to the standard titanium solution.

6. VANADIUM

To determine the vanadium in such materials as this magnetite ore, the following method was found to be most satisfactory. It is simply an adaptation and combination of previously published methods, and no claim is made for originality.

(*a*) The ore (5 g) was dissolved in hydrochloric acid, the residue collected, and from it the silica was expelled with hydrofluoric acid and the final residue fused and added to the main solution, which was evaporated to expel the excess of hydrochloric acid. This solution was diluted, nearly neutralized

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[6] T. J. Pope: Trans. Amer. Inst. Min. Eng., **29**, p. 379; 1899.
C. H. Ridsdale: J. Soc. Chem. Ind., **7**, p. 77; 1888.

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

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

with sodium carbonate, and reduced with sulphur dioxide, of which the excess was expelled by boiling. Zinc-oxide emulsion was then added in slight excess, and the solution boiled for fifteen minutes and filtered rapidly. The precipitate contained all the vanadium, together with aluminum, titanium, and a little iron. It was ignited, fused with sodium carbonate, extracted with water, and the residue again fused and extracted. The solutions from the two fusions were combined, nearly neutralized with dilute nitric acid,[9] boiled, and the precipitate of alumina, etc., filtered out. To the filtrate was added mercurous nitrate in excess; the solution was heated and filtered. The precipitate was ignited to expel mercury, and the residue fused with sodium carbonate, extracted with water and acidified with sulphuric acid. Platinum was precipitated by hydrogen sulphide, the solution filtered, and the hydrogen sulphide expelled from the filtrate by boiling. The solution was then titrated with 0.01 N permanganate, reduced with sulphur dioxide, and again titrated. The vanadium was calculated to V_2O_3.[10]

(*b*) In this method the iron was removed by electrolysis (cf. 4*d*), after which the vanadium was precipitated by zinc oxide and determined as under (*a*).

7. 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.[11] The objections to the use of the other materials may be summed up briefly 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 be obtained only 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, owing 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.

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

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

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[9] Bulletin 422, U. S. Geol. Survey, p. 150.

[10] Bulletin 422, U. S. Geol. Survey, p. 149.

[11] Consult Circular 40, Bureau of Standards, on "Sodium Oxalate as a Standard in Volumetric Analysis."

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,[12] is of very definite composition, anhydrous and nonhygroscopic, and can be dried at 240° C without decomposition. Owing, however, to the difficulty of purchasing sodium oxalate of requisite purity, all such material formerly used at this Bureau 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.[13] Even when the sodium oxalate has been dried at 240° C, in very accurate work the portions used for analysis should be dried at 105° C as an added precaution, since all powders tend to absorb some moisture from the air, even on occasional exposure. After considerable trouble and delay we have succeeded in obtaining a large amount of sodium oxalate of the requisite purity, manufactured especially for us by the Mallinckrodt Chemical Works, St. Louis, Mo., which is issued as standard sample No. 40, in bottles containing 120 and 200 grams, the fees for which are $2 and $3, respectively. With each sample is sent a certificate stating the composition of the material and brief directions for its use. Recently McBride[14] has investigated at this Bureau the conditions for the standardization of permanganate with sodium oxalate. He found that over a considerable range of conditions the variations were less than one part in a thousand, and recommended the following conditions as leading to satisfactory results:

"In a 400-cc beaker, dissolve 0.25–0.3 g of sodium oxalate in 200 to 250 cc of hot water (80 to 90°) and add 10 cc of (1:1) sulphuric acid. Titrate at once with 0.1 N $KMnO_4$ solution, *stirring the liquid vigorously and continuously*. The permanganate must not be added more rapidly than 10 to 15 cc per minute and the last 0.5 to 1 cc must be added dropwise with particular care to allow each drop to be fully decolorized before the next is introduced. The excess of permanganate used to cause an end-point color must be estimated by matching the color in another beaker containing the same bulk of acid and hot water. The solution should not be below 60° by the time the end point is reached; more rapid cooling may be prevented by allowing the beaker to stand on a small asbestos-covered hot plate during the titration. The use of a small thermometer as stirring rod is most convenient in these titrations, as the variation of temperature is then easily observed." For more dilute $KMnO_4$ solutions (e. g. in the bismuthate

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[12] Sörensen: Zs. Anal. Chem., **36**, p. 639; 1897. **42**, p. 333; 1903. **42**, p. 512, and **44**, p. 156; 1905.

[13] Blum: J. Am. Chem. Soc., **34**, p. 123; 1912.

[14] McBride: J. Am. Chem. Soc., **34**, p. 393; 1912.

method) the titration should be conducted in a proportionately smaller volume, in order to reduce the uncertainty of the end point to a minimum. The factor for the conversion $Na_2C_2O_4$ to Fe is 0.8334, using 1913 atomic weights.

8. IRON (TOTAL)

(*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, in other cases it has been found to contain as much as 0.20 per cent iron, 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 the analysis of the magnetite ore it was also necessary to make corrections for vanadium (0.08 per cent V_2O_3) and titanium (0.99 per cent TiO_2). In the Jones reductor vanadium is reduced quantitatively to V_2O_2 and titanium (in small amounts) to Ti_2O_3,[15] provided

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[15] Experiments at this Bureau have shown that for amounts of titanium up to 0.05 g TiO_2, this procedure gives accurate results, but with larger amounts the reduction is incomplete.

precautions are taken to prevent reoxidation. This was effected by placing in the receiver of the reductor an excess of ferric sulphate solution, which was reduced by the V_2O_2 and Ti_2O_3, forming equivalent amounts of ferrous salt, which was included in the final permanganate titration. In the presence of the excess of ferric salt, it was found desirable to add phosphoric acid to give a sharper end point in the titration.

(*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[16] 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 g $MnSO_4$, 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, results slightly high 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. In the magnetite ore it was found necessary to correct for the vanadium, which is reduced to V_2O_4 by stannous chloride, while titanium is not affected in this method of reduction.

(*d*) **Reduction by Sulphurous Acid.**—This method of reduction was used only for the magnetite ore, which was dissolved in hydrochloric acid, of which the excess was expelled by evaporation and the residue treated with hydrofluoric and sulphuric acids, fused, and added to the main solution. This solution was nearly neutralized with ammonia, heated to boiling, and reduced by a rapid stream of sulphur dioxide. When reduction was complete, the excess of sulphur dioxide was expelled by boiling in a stream of carbon dioxide and the solution cooled. After the addition of 25 cc of titrating mixture (see 8*c*) the solution was diluted to 300 cc and titrated with permanganate. Correction was made for the vanadium (reduced to V_2O_4) and for the blank necessary to produce a pink color in a dilute hydrochloric acid solution similarly treated. This reduction by sulphurous acid was found to be much more rapid and complete in a chloride solution than in the sulphate solution usually employed. If excess of hydrochloric acid is avoided and the titrating mixture is added, the results are accurate, as

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[16] Jones and Jeffrey: Analyst, **34**, p. 306; 1909.

indicated by the concordance of the results on the magnetite ore by this and the two preceding methods.

9. IRON (FERROUS)

Ferrous iron was determined in the magnetite ore by the Pratt method,[17] which was carried out as follows: The ore (0.5 g) was treated in a large platinum crucible with 10 cc of sulphuric acid (1–3) and 40 cc of water (freshly boiled). The crucible was covered, the air expelled by a current of carbon dioxide, and the contents boiled for a short time. Hydrofluoric acid was added (7 cc) and the mixture boiled gently for ten minutes. This was then poured into a large platinum dish containing 100 cc of 5 per cent sulphuric acid and 200 cc of water (both freshly boiled and cooled) and an amount of permanganate slightly less than required (as determined by a preliminary test). The liquid was then titrated quickly to the first pink. Tests with a standard ferrous sulphate solution, similarly treated, showed that the method is accurate. Allowance was made for the vanadium, which was assumed to be present as V_2O_3. Since no organic matter was present, and only 0.025 per cent of S (condition unknown), the value given is believed to represent very closely the true content of ferrous iron.

10. 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.

(*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.

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[17] Bulletin 422, U. S. Geol. Survey, p. 127.

11. 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, since 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,[18] 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 0.3870. 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 $MnSO_4$,[19] the factor for which is 0.3638.

(*c*) **Acetate.**—The ore was dissolved in hydrochloric acid, the iron and alumina were 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 a permanganate to 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 was expelled. The resulting solutions were treated with zinc oxide and titrated exactly as was the solution of the ore. Theoretically the titration

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[18] Gooch and Austin: Am. J. Sci., **6**, p. 243; 1898.

[19] Gooch and Austin: Am. J. Sci., **5**, p. 209; 1898.
Blum: J. Am. Chem. Soc., **34**, p. 1379; 1912.

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,[20] 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**[21] method the manganese was precipitated with ammonium persulphate in a solution containing not over 4 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,[20] 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 and Magnetite ores. These were 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 0.1N silver nitrate and 1 g 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 low

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

[21] von Knorre: Zs. Ang. Chem., **1901**, p. 1149.

manganese ores, however, the Volhard method gives uniformly high results, probably because of uncertainty in the end point. Subsequent to the original analyses of the manganese ore (No. 25) an exhaustive investigation of the bismuthate method was conducted at this Bureau,[22] from which it was concluded that this method, under proper conditions, yields results of high accuracy. Pending similar study of the other methods employed at this Bureau and elsewhere, the value 56.25 per cent Mn, found in this investigation, may be assumed to represent the true content more closely than the certificate average 56.36 per cent.

12. LIME [23]

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.

13. MAGNESIA [23]

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, owing to contamination from the reagents or containing vessels or the incomplete removal of the preceding elements.

14. ALKALIS

Sodium and potassium in the magnetite ore were determined by the J. Lawrence Smith method.[23] One gram of the ore was fused in a cylindrical crucible with 1 g of ammonium chloride and 8 g of calcium carbonate.

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[22] Blum: J. Am. Chem. Soc., **34**, p. 1379; 1912.

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

The mass was extracted with water and most of the calcium removed by double precipitation with ammonia and ammonium carbonate. The filtrates were evaporated to dryness and the ammonium salts carefully expelled. From the solution of the residue the rest of the calcium was precipitated by ammonium oxalate. The filtrate was evaporated with hydrochloric acid, and ignited, giving the combined chlorides. These were separated by means of chlorplatinic acid in the usual way. After the precipitate of K_2PtCl_6 was washed with alcohol, it was dissolved in hot water, and some pure zinc and hydrochloric acid were added. After the platinum was completely precipitated the excess of zinc was dissolved in hydrochloric acid and the platinum filtered out, ignited, and weighed. From its weight was calculated the amount of potassium present. One analyst weighed the potassium as K_2PtCl_6. Correction was made for the amount of alkalis obtained from a blank experiment upon the reagents, similarly treated.

15. WATER (100°+)

The water still present in the ore after drying at 100° (120° for the Manganese ore, No. 25) was determined by heating in a current of dry air to red heat for fifteen minutes. The moisture was collected and weighed in a calcium chloride tube.

16. CARBON DIOXIDE

(*a*) **Evolution Method.**—The ore was treated in a suitable apparatus with dilute hydrochloric acid, the evolved carbon dioxide being expelled by a current of dry air and absorbed and weighed in a tube containing soda lime and calcium chloride.

(*b*) **Ignition Method.**—The ore was strongly ignited in the apparatus used for carbon combustions, the carbon dioxide evolved being absorbed in a weighed soda-lime tube. The agreement of this and the preceding method indicated the absence in the magnetite ore of any organic matter.

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. In the magnetite ore the phosphorus was precipitated by the acetate method,[24] followed in one case by the molybdate reduction and in the other by precipitation with magnesia mixture and conversion to pyrophosphate.

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[24] Blair: Chemical Analysis of Iron (7th ed.), p. 85.

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.

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. He determined phosphorus in the magnetite ore by the molybdate-magnesia method, using precautions to recover the phosphorus in the precipitate left insoluble by treating the yellow precipitate with ammonia. He determined silica both by evaporation with hydrochloric acid and with sulphuric acid. For iron he used both the hydrogen sulphide and zinc reductor methods, correcting for titanium in the latter case, but not for vanadium in either case. For vanadium he fused the ore with sodium carbonate and sulphur; extracted with water and precipitated vanadium sulphide by acidifying with sulphuric acid. This precipitate was dissolved in hydrochloric acid, evaporated first with hydrochloric acid and then with sulphuric, and titrated with permanganate (Campagne's method).

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[25] for these ores, the particular methods being indicated in part upon the certificates. The first results for alumina were discordant, and in general too high. Subsequent determinations, by the phosphate method, in which precautions were taken to purify the first precipitate by a reprecipitation, showed results in very close agreement with those of the

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[25] J. Ind. & Eng. Chem., **1**, pp. 107–115; 1909. Electrochem. Met. Ind., **7**, pp. 65–72; 1909.

other chemists. In general, the agreement of the mine chemists, both among themselves and with the other chemists, is very satisfactory, owing in part, no doubt, to the beneficial influence of the use of uniform methods of analysis as recommended by the United States Steel Corporation.

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Approved:
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