ride with sodium sulphate after neutralizing, and also from the calcium chloride when the liquor does not receive sufficient sodium sulphate for complete decomposition

When special prepared phosphate bone is used in the manufacture of syrup and sugar, phosphates are found in the ash. I have found as high as nineteen per cent. of phosphorus pentoxide present.

Iron is present in every ash. It is introduced into the process at the outset and is taken out and as often replaced up to the finish. Batches of glucose made from thin liquor first boiled in a vacuum pan after boiling out with muriatic acid, contain an abnormal amount of iron.

WAVERLY FARM, TOPEKA, KAN.,
January 20, 1895.

THE ZIMMERMANN-REINHARDT METHOD FOR THE DETERMINATION OF IRON IN IRON ORES.[1]

BY C. T. MIXER AND H. W. DUBOIS.

Received March 6, 1895.

THE methods chiefly employed in this country for the determination of iron in ores, are the permanganate and Kessler's modification of the old bichromate method (Penny's).

Recently a method has been proposed by R. W. Mahon in the *American Chemical Journal*, **15**, 360. The chief feature of this method consists in the proposed use of an indicator solution, for titration with stannous chloride. The indicator solution consists of platinic and mercuric chlorides, the end reaction being indicated by the darkening of the mercurous chloride (formed by the slight excess of stannous chloride), which is caused by the formation of mercurous platinochloride.

As regards this method, it would seem that the frequent standardizations of the stannous chloride that must be made, is a serious objection, and further, the indicator which is used, cannot compare in distinctness with that produced by potassium permanganate.

The objections to the first two methods are mainly those of time consumed in their operation, which specially concerns those who have to make large numbers of determinations. Their general accuracy can hardly be questioned.

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[1] This article includes the modifications of the method, as practiced in the Lake Superior iron region.

A preliminary note of the method to be described, appeared in the *Engineering and Mining Journal*, April 14, *1894*.

It has been used with most excellent results during the past few years in some of the laboratories on the Lake Superior iron ranges.

The standard works on chemical analysis contain no reference to this method. Furman in his Manual of Practical Assaying, page 173, refers rather indifferently to the use of manganous sulphate for titrating in a hydrochloric acid solution with potassium permanganate, but does not seem to be aware of the rapid and accurate method which can be formulated by its use.

Methods have been proposed for titrating directly in a hydrochloric acid solution, but have never proved to be practicable for technical analysis.[1]

The chlorine liberated under such circumstances, seriously affects the results, and it is by the use of manganous sulphate that this is prevented. The use of the above salt for this purpose was first proposed by C. Zimmermann.[2] In this article there is simply outlined the efficacy of manganous sulphate for titrating in hydrochloric acid solutions. Zinc was employed for reduction. A large number of analyses are given, showing the agreement between results obtained from sulphuric acid solutions and hydrochloric acid solutions treated in this manner.

Reinhardt[3] suggested the improvements of reducing with stannous chloride and taking up the excess of the latter, with mercuric chloride, which was then, as now, used in connection with the bichromate method. Later[4] he gives a comprehensive review of the method and suggests a very valuable improvement in the addition of sulphuric and phosphoric acids to the manganous sulphate solution. The addition of the phosphoric acid allows the formation of iron phosphate, which being nearly colorless, renders the end reaction more distinct. Otherwise, the presence of the yellow iron chloride will greatly obscure the end reaction.

The solutions required are as follows :

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[1] Löwenthal and Lenssen, *Ztschr. anal. Chem.*, 1, 329, and David H. Browne, *J. Anal. Appl. Chem.*, 5, 362.

[2] *Ber. d. chem. Ges.*, *1884* Jahrgang, 15, 779.

[3] Stahl und Eisen. Jahrgang, 4, 704.

[4] *Chem. Ztg.*, Jahrgang, 13, 323. The Journal of the Iron and Steel Institute, *1889*, 1, 400, gives a synopsis of this article and an incorrect reference to it.

Solution A. Stannous Chloride.—One pound of stannous chloride is dissolved in one pound of hydrochloric acid 1.2 sp. gr., to which water has been added and, when dissolved, is diluted to two liters.

Solution B. Hydrochloric Acid 1.1 sp. gr.—Made by mixing equal volumes of acid 1.2 sp. gr. and water.

Solution C. Mercuric Chloride.—A saturated solution is made by dissolving in hot water, allowing to cool and crystallize, and then filtering.

Solution D.—One hundred and sixty grams of manganous sulphate are dissolved in water and diluted to 1750 cc. with water. To this are added 330 cc.[1] of phosphoric acid (syrup), 1.7 sp. gr., and 320 cc. of sulphuric acid, sp. gr. 1.84.

This solution permits the titration to be made in a hydrochloric acid solution and thus obviates the deleterious action of the chlorine that is liberated by the action of the hydrochloric acid on the potassium permanganate.

Solution E. Potassium Permanganate.—Two hundred and fifty grams of potassium permanganate are dissolved in water and diluted to fill an ordinary carboy (about 44 liters). For more accurate determinations, a solution just one-half this strength is used. For the weight we employ, the main solution has the strength, such that one cc. equals two per cent. This solution is standardized by means of an iron ore, the exact value of which has been ascertained in a number of different ways.

The Standardization.—For ordinary commercial work, less than one-half gram of the standard ore is taken, the precise weight being so adjusted that one cc. of the potassium permanganate solution is equivalent to two per cent. of iron. Thus, if the standard ore contain 61.20 per cent. of iron, the weight would be so taken, that the reading of the burette would be 30.6 cc. If, however, it should be 30.7 cc., then either the weight would be diminished in the proportion of 30.6 : 30.7, or one-tenth cc. would be subtracted on all subsequent readings of the burette. The latter is the method generally employed when the discrepancy is so slight as this. For the obtaining of the percentage,

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[1] Reinhardt recommends a solution more than twice this strength of phosphoric acid, but we have found the above quantity sufficient.

the burette reading is doubled, after making the correction, if such be necessary.

It will be found conducive to accuracy, and require very little extra work, to accompany each series of determinations by a standard ore, which, being under precisely the same conditions, any error in weight or solutions will immediately be detected.

The Method.—About one-half gram of ore (exact weight depending, as shown above, upon the standard ore) is placed in a No. 0 lipless beaker, and two and five-tenths cc. of stannous chloride (*Solution A*) added, this being a sufficient amount for ores analyzing between fifty-five and sixty-five per cent. of iron. It is advisable to use a little less for leaner ores. Then ten to fifteen cc. of hydrochloric acid is added (*Solution B*), and, placing a watch-glass on the beaker, the contents are allowed to boil gently on an iron plate until the ore is completely dissolved.

This will generally require only a few minutes, depending mainly on the character of the ore.

When the ore is dissolved, and while the solution is still hot, additional drops of stannous chloride are added from a burette, until all the iron is just reduced to the ferrous state, which is indicated by the disappearance of the greenish-yellow color.

In case a number of ores are being analyzed, it will be found more convenient to bring several of the solutions up to this point and then slightly oxidize them by the addition of a few drops of the potassium permanganate solution.

In case an excess of stannous chloride has been added originally, the solution is also oxidized as above.

The solution, in its slightly oxidized condition, should be kept warm, and the final reduction be made by a drop or two of stannous chloride. It is desirable to have the least possible excess of stannous chloride, after complete reduction has taken place.

During this operation of reduction and oxidation, the solution is constantly agitated by giving the beaker a rotating motion, which alternates in opposite directions.

The final reduction having been made, the sides of the beaker are washed down and five cc. of mercuric chloride (*Solution C*) added to take up the excess of stannous chloride, which forms a white silky precipitate of mercurous chloride.

After the addition of mercuric chloride, the contents of the beaker are washed immediately into a 500 cc. beaker, in which has been placed six to eight cc. of *Solution D* and about 400 cc. of water. The solution is now ready for titration.

Ores containing organic matter, some magnetites, and pyritous ores, require the usual precautions. With ores containing very large amounts of organic matter, it is generally most advantageous to burn off directly and follow with the regular method. Ores containing small amounts of organic matter, and pyritous ores, are dissolved in hydrochloric acid and oxidized with potassium chlorate, after which the regular method is pursued.

The use of stannous chloride to hasten the solution of an ore, is particularly convenient in laboratories located in the mining regions. Reinhardt does not mention the use of it. We are not able to state who first proposed its use, but it is not improbable that it may have been accidentally devised independently, by several chemists.

The action of the stannous chloride is doubtless that of converting the iron sesquioxide into the more basic protoxide, towards which the hydrochloric acid asserts a more powerful solvent action.

A tabulation of some results is here given showing the relative rates of dissolving with hydrochloric acid alone, and hydrochloric acid and stannous chloride.

Ore.	No.	Solvent.	Time required for solution.	Iron in Residue.
Soft hematite,	1A	$HCl + SnCl_2$	2 min.	0.11
	B	HCl	26 "	0.22
Soft hematite,	2A	$HCl + SnCl_2$	4 "	0.09
	B	HCl	35 "	0.12
Specular hematite,	3A	$HCl + SnCl_2$	6 "	0.09
	B	HCl	24 "	0.10
Blue granular ore,	4A	$HCl + SnCl_2$	6 "	0.18
(Hematite)	B	HCl	30 "	0.21

In order to compare the results afforded by this method with other methods, the following tabulation of analyses has been prepared.

No.	Chemist.	Location.	Ore.	Method.	Per-cent.	Mixer and DuBois Zimmermann-Reinhardt Method.
1	B. E. LaLonde,	Pittsburg and Lake Angeline Iron Co.	Lake Angeline Hematite.	Bichromate.	63.40	63.40
2	A. G. McKenna,	Edgar Thompson Steel Works.	Pewabic.	"	64.75	64.80
3	A. G. McKenna,	Edgar Thompson Steel Works.	Toledo.	"	41.30	41.20
4	E. P. Jennings,	Ironwood, Mich.		"	61.95	62.05
5	E. E. Brewster,	Iron Mountain, Mich.	Pewabic.	"	63.32	63.38
6	Lerch Bros.	Virginia, Minn.	Mesabi.	Permanganate.	67.44	67.26
7	Porter W. Shimer,	Easton, Pa.	Alabama "fossil ore."	"	48.36	48.25
8	W. E. Hotson,	Iron Mountain, Mich.	Chapin.	Bichromate.	61.87	61.90
9	E. T. Griese,	Mountain Iron, Minn.	Mesabi.	Zimmermann-Reinhardt.	62.19	62.15
9	R. B. Green,	Minnesota Iron Co., Two Harbors, Minn.	"	"	62.12	62.15
9	C. B. Murray,	Edgar Thompson Steel Works.	"	Bichromate.	62.20	62.15
9	E. P. Jennings,	Ironwood, Mich.	"	"	62.12	62.15
9	Lerch Bros.,	Virginia, Minn.	"	Zimmermann-Reinhardt.	62.12	62.15
9	C. A. Buck,	Bethlehem Iron Co.	"	Permanganate, Jones'Reductor.	62.19	62.15
10	Average of seven chemists,		Lake Superior Hematite.	All methods.	67.03	67.02
	Illinois Steel Co.	South Chicago, Ill.	Salisbury Hematite.	Bichromate.	62.65	62.70
	" " "	" " "	"	"	61.74	61.80
	" " "	" " "	"	"	61.32	61.30
	" " "	" " "	"	"	61.85	61.80
	" " "	" " "	"	"	59.27	59.30
	" " "	" " "	"	"	61.95	62.00
	" " "	" " "	"	"	62.32	62.40
	" " "	" " "	"	"	61.62	61.70
	" " "	" " "	"	"	62.22	62.30
	" " "	" " "	"	"	62.11	62.10
	" " "	" " "	"	"	62.15	62.20
	" " "	" " "	"	"	62.85	62.80
	" " "	" " "	"	"	61.44	61.50

In numbers 1 to 6, inclusive, our figures were based upon the same standard used by the respective chemist, so that the comparison between the methods is rendered independent of any difference due to the standard employed. All the rest of the analyses were based upon our own standard ore, which represents the mean of a large number of determinations, both by ourselves and other chemists, involving a variety of modes of standardization.

The merits of the Zimmermann-Reinhardt method may be summed up as follows: (*a*) That the liquid resulting from the solution can be treated directly and without the use of special apparatus. (*b*) The operation of titration is not tedious as in the bichromate method. (*c*) That the simplicity of operation permits determinations to be made with rapidity[1] and without sacrifice of accuracy.

The authors desire to express their obligations to Dr. Harry F. Keller, of Philadelphia, Pa., for valuable suggestions made during the preparation of this paper.

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ON THE MANUFACTURE OF SOLUBLE NITROCELLULOSE FOR NITROGELATINE AND PLASTIC DYNAMITES.[2]

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Received March 16, 1895.

THE discovery that a nitrocellulose could be prepared, which was soluble in a mixture of ether and alcohol, other light hydrocarbons, and in nitroglycerol, gave a start to several industries, of which not the least important was that of the manufacture of nitrogelatine, discovered by the Swede, Alfred Nobel. The use of this substance in the production of celluloid, etc., is ot great importance to the industries of this country, but falls outside of the scope of this article.

In order that nitrocellulose should be easily soluble in nitroglycerol it ought to be, as nearly as possible, a pure trinitrocellulose. Higher nitration degrees are insoluble in nitroglycerol, a lower one is fully as unsatisfactory in its action and, therefore, the preparation of this substance is considered one of the most difficult problems encountered in the explosive industry. It is, in fact, considered so difficult to produce, that its manufacture is avoided by explosive companies, they preferring to buy the collodion-cotton made for celluloid manufacturing, at a high

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[1] In ordinary practice in our laboratory, determinations can be made in five to ten minutes after the ore is weighed out.

[2] Read before the Washington Section, March 14, 1895.