ART. XXII.—*An Iodometric Method for the Determination of Phosphorus in Iron*; by CHARLOTTE FAIRBANKS.

[Contributions from the Kent Chemical Laboratory of Yale University, LIV.]

A RECENT paper from this laboratory* showed that molybdic acid was reduced by hydriodic acid to the condition of oxidation represented by the symbol Mo_2O_5 in acid solution, while in an alkaline solution the reduced product was reoxidized by standard iodine.

In acid solution, $2MoO_3 + 2HI = Mo_2O_5 + I_2 + H_2O$
In alkaline solution $Mo_2O_5 + I_2 + H_2O = 2MoO_3 + 2HI$

These reactions obviously present the possibility of developing a method for the determination of phosphorus in the phospho-molybdates.

The very careful work of Messrs. Blair and Whitfield† shows conclusively that the ammonium phospho-molybdate, precipitated under the conditions ordinarily prescribed for the determination of phosphorus in iron or iron ores, is of definite constitution. They find that $24MoO_3$, P_2O_5, $3(NH_4)_2O$, $2H_2O$ expresses the composition of this phospho-molybdate, which therefore contains 1·794 parts of phosphorus to every 100 parts of molybdic anhydride.

This being the case, it is plain that if advantage can be taken of the fact that the amount of iodine necessary to reoxidize reduced molybdic acid is large, as well as of the fact that the amount of molybdic acid compared to the phosphorus contained in the phospho-molybdate is also large, a method of great theoretical accuracy should result.

I have experimented with a process which consists essentially in treating the ammonium phospho-molybdate, produced by the accepted methods of iron analysis, with potassium iodide in the presence of strong hydrochloric acid and under carefully regulated conditions; in neutralizing the residue thus obtained by acid sodium carbonate; and in reoxidizing the reduced molybdenum compound to the condition of molybdic acid by titration with iodine.

The directions prescribed by Messrs. Blair and Whitfield for making the ammonium molybdate solution were followed: 100 grams of molybdic anhydride are intimately mixed with 400^{cc} of distilled water and 80^{cc} of strong ammonia, and after filtering, this liquid is poured into a mixture of 300^{cc} of nitric acid

---

* Gooch and Fairbanks, this Journal, vol. ii, p. 156.
† Jour. Am. Chem. Soc., vol. xvii (1895).

(1·42 sp. gr.) and 700^{cc} of water. This solution, it is said, practically remains unaltered for months; but it is much safer to filter each day the portion to be used.

In order to obtain a standard solution of phosphorus, 1·2 grams of microcosmic salt were dissolved in one litre of water and 50^{cc} of this solution were evaporated, and the residue ignited and weighed as sodium metaphosphate.

Iron free from phosphorus, for admixture with known amounts of phosphorus in the test experiments, was prepared by igniting ferrous oxalate. The oxalate was precipitated by oxalic acid from ferrous sulphate dissolved in warm water. The precipitate was then thoroughly washed with cold water, dried and ignited.

The ferric oxide thus obtained was dissolved in hydrochloric acid, evaporated to dryness, and dried on a hot plate. The ferric chloride was treated with nitric acid and the solution evaporated twice. In this way all but a trace of the chloride was destroyed,

Since in the ordinary determination of phosphorus in iron, potassium permanganate is added, as Dr. Drown says,* to insure the complete oxidation of the phosphorus to the orthophosphoric acid, it seemed best to make sure that this treatment was not detrimental in the process to follow. Enough permanganate was therefore added in my experiments to distinctly color the already boiling solution of ferric nitrate, and then a little tartaric acid was used to clear the solution.

As too much free acid prevents the full precipitation of the ammonium phospho-molybdate, the ferric nitrate solution was treated with ammonia until a precipitate or the ruby wine color appeared. Then dilute nitric acid was added until the color of the solution was a clear amber. Generally four or five grams of ferric oxide were used in each determination.

The ferric nitrate and phosphorus solutions, in volume not less than 150^{cc} nor more than 300^{cc}, were drawn into an ordinary 500^{cc} flask. The flask was heated on the steam bath to just 85° C.—very carefully, since at higher temperatures there is danger of precipitating molybdic acid—and immediately 40^{cc} of the filtered ammonium molybdate solution were so added as to wash down the thermometer and the sides of the flask. The flask was corked, wrapped in a towel, and shaken for five minutes. The contents were filtered at once on an asbestus felt, and the precipitate washed three or four times, first with a 10 per cent solution of nitric acid, and then with a 1 per cent solution of potassium nitrate.

If the nitric acid and potassium nitrate solutions wash the

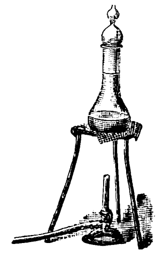
---

* Trans. Am. Inst. of Min. Eng., vol. xviii, p. 93.

flask and cork each time, it will do no harm if some of the precipitate still adheres to the sides of the flask; for the flask, cork and crucible are all finally washed with ammonia. The asbestus felt was transferred to a 100^{cc} flask or narrow based Erlenmeyer. The precipitation flask and cork were thoroughly washed with a mixture of 5^{cc} of ammonia and 10^{cc} of water, and the washings were allowed to rinse the sides of the perforated crucible—standing on a small funnel—and so to run into the 100^{cc} flask. Twenty-five cubic centimeters of strong hydrochloric acid were added and, where the phosphorus does not exceed ·0060 grm., 0·5 grm. of potassium iodide; but, where more than ·0060 grm. of phosphorus is present, a little more potassium iodide is theoretically and practically needed. Experience has shown that the iodide present should not exceed the amount theoretically necessary by more than a half gram.

The liquid was boiled down from a total volume of 40^{cc} to just 25^{cc}, a volume easily marked by two strips of paper pasted on opposite sides of the flask. If the solution is boiled farther, the molybdic acid is likely to be reduced beyond the degree of oxidation indicated by the symbol Mo_2O_5. The residue was neutralized with acid sodium carbonate, according to one or the other of the methods described below, and treated with an excess of standard iodine.

For a trap to prevent loss during boiling, a two-bulbed drying tube was cut off an inch and a half below the largest bulb and this end fitted loosely into the neck of the flask, as shown in the accompanying figure. The addition of two or three little pieces of pumice stone, previously boiled in hydrochloric acid, insures quiet boiling.



While still acid the reduced solution is not appreciably reoxidized in the air, but when once made alkaline it is very easily changed. Therefore great care must be taken either to have the iodine present before the solution is made alkaline; or else to stir up the solution as little as possible while adding the alkalies and to draw in the iodine solution immediately.

The safer method is to put the reduced solution, with one gram of tartaric acid, to prevent the precipitation of the molybdenum, and an excess of the iodine solution, amounting to at least 8^{cc}, into a liter flask. This flask was fitted with a paraffined rubber stopper, carrying a funnel with a stop-cock for admitting slowly the acid sodium carbonate to effect neutralization, and a Will and Varrentrapp trap, filled with a solution of potassium iodide, to catch the iodine thrown off during the effervescence.

The more convenient way, and after a little practice a serviceable method for rapid work, is to put the solution and the tartaric acid in a bottle, to add enough sodium hydroxide to nearly neutralize the free acid, and then to make the solution distinctly alkaline with an excess of acid sodium carbonate, tipping the flask to one side to prevent loss during the effervescence. The iodine solution must be drawn in immediately or atmospheric oxidation will take place and the error of the process be great.

After either method of neutralization the iodine color in the solution should perceptibly fade within fifteen minutes; but for complete oxidation the corked bottle should be set aside, out of sunlight, for an hour and a half, and then the excess of the iodine titrated with a standard solution of arsenious acid.

Since there is a slight tendency on the part of the iodine, especially when the sodium hydroxide and the acid sodium carbonate are used for neutralization, to form a little iodate, it is wise to acidulate the solution in each case slightly with dilute hydrochloric acid after the titration with the arsenic solution, and then to determine by sodium thiosulphate the trace of iodine which has taken the form of iodate.

In the following table the absolute errors in terms of phosphorus are given; and the percentage errors, between the phosphorus taken and the phosphorus found, referred to 10 grams of material—the maximum amount of high grade iron or steel usually taken for analysis—are also added.

	Am't of P taken.	Am't of P found.	Error on P.	% Error of P.	Neutralized by
I	0·002727	0·002778	0·000051+	0·0005 %+	$NaHCO_3$
II	0·001812	0·001743	0·000069−	0·0007 %−	$NaOH+NaHCO_3$
III	0·000909	0·000914	0·000005+	0·00005%+	$NaOH+NaHCO_3$
IV	0·003508	0·003262	0·000246−	0·002 %−	$NaOH+NaHCO_3$
V	0·005454	0·005417	0·000037−	0·0003 %−	$NaHCO_3$
VI	0·001818	0·001861	0·000043+	0·0004 %+	$NaOH+NaHCO_3$
VII	0·003636	0·003716	0·000080+	0·0008 %+	$NaHCO_3$
VIII	0·000909	0·000988	0·000079+	0·0007 %+	$NaHCO_3$
IX	0·000363	0·000289	0·000074−	0·0007 %−	$NaOH+NaHCO_3$
X	0·008180	0·008179	0·000001−	0·00001%−	$NaHCO_3$

The error in IV is obviously high, and, in view of the results obtained in the former paper to which reference has been made, undoubtedly accidental; but the result is inserted in the series because no reason was apparent for excluding it.

In all of the experiments, with one exception, from four to five grams of pure iron oxide were introduced; in experiment IX the amount was 2·5 grm.

In the first nine experiments, 0·5 grm. of potassium iodide was used; in experiment X more was theoretically necessary and 0·75 grm. was added.

The foregoing table shows that satisfactory results in the determination of phosphorus in iron can be obtained by precipitating the ammonium phospho-molybdate according to the usual methods of iron analysis; then reducing the phospho-molybdate thus obtained with potassium iodide and hydrochloric acid; neutralizing the residue with acid sodium carbonate, and reoxidizing with standard iodine.

In conclusion, I wish to express my thanks to Professor Gooch for his help and friendly interest.