XV. AN EXAMINATION OF SOME OF THE METHODS FOR DETERMINING PHOSPHORUS IN IRON ORES.

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The present investigation was undertaken with a view to obtain a more rapid method of determining phosphorus than those at presin use, by utilizing some suggestions which have recently been made.

Two lines of experiment were followed: That sugested by Prof. Classen (*Quantitative Analyse auf Electrolytischem Wege, Aachen* 1882), and that of M. P. Derome (*Comptes Rendus, LXXIX*, 925 translated in *Chem. News*, XL, 292).

For the purpose two limonites were taken, which by ordinary methods of analysis yielded as follows:

	"High"	"Low"
Fe	54.50	52.35
P	1.06	0.08

These had been pulverized and passed through an "80 mesh" sieve.

Electrolytical Separation (Classen).

In this the idea was to separate the iron by the use of the battery, thus incidentally determining the percentage of iron, and then, in the solution thus freed from the disturbing influence of such large quantities of iron (relative to the amount of phosphorus), to determine the phosphorus.

An experiment with an indefinite amount of ferric chloride showed that it took about two hours to deposit a little over 0.5 gm. of iron by the battery. The conditions, as specified by Prof. Classen, are that the solution—nearly neutralized—must receive the addition of a large excess of ammonium or potassium oxalate, and that the electrolysis shall be carried on in the solution heated to about 80° C. Three freshly charged Bunsen cells, of about 3 pints capacity each, were used. Prof. Classen states that enough oxalate must be used to form the double oxalate (of iron and ammonia or potassa) and then 3 or 4 gms. more of the oxalate must be added. The action of the battery converts the oxalate into bi-carbonate, and any deficiency of oxalate is soon perceived from the appearance of flocculent masses of ferric hydrate in the solution. It was found that considerably more oxalate in excess had to be used than the amount specified by Dr. Classen.

As so much oxalate was required it was not deemed possible—even with a platinum dish of over 250 c.c. capacity—to use more than 1 gm. of ore for the determination. The ore was fused with alkaline carbonates, dissolved in dilute HCl, and evaporated down to separate silica, taken up with dilute HCl, filtered, nearly neutralized, and the oxalate added. In the first experiment on the "High" ore only ammonium oxalate was used, and in this case, after a certain time, a flocculent precipitate of ferric hydrate formed, which refused to dissolve on addition of more alkaline oxalate, or to reduce to metallic iron, though the battery was allowed to act upon it all night. The solution, with precipitate, was therefore poured off and examined for phosphoric acid.

The substitution of potassium oxalate in part for ammonium oxalate, a proceeding suggested, though not insisted upon, by Prof. Classen, remedied this difficulty, though the amount of oxalate necessary was so great that the solution, when cold, was nearly solid with the interlocking crystals of the alkaline salts.

The action of the battery, aided by the temperature necessary, (80° to 100° C.) kept the solution in such a lively state of effervesence that some of the solution was inevitably lost mechanically. When the solutions gave no reaction for iron they were poured off, the dishes rinsed with hot water, and finally with alcohol and ether. The deposited iron was not quite smooth, apparently containing granules of what was probably alumina hydrate or phosphate, which tenaciously adhered, and in some cases appeared to be partially covered with a coating of metallic iron. The solutions also were slightly turbid, apparently from the presence of alumina compounds. These solutions were evaporated down twice with concentrated nitric acid, then diluted and filtered into a molybdate solution containing 10 or more gms. of ammonium nitrate; the molybdate precipitate, after heating for some hours, filtered off, washed, dissolved in ammonia and the phosphoric acid separated by magnesia mixture. The results were :

	"High"	"Low"
Fe	56.01	50.45
P (Fe partly separated)	1.04	
P (Fe entirely separated)	0.988	0.089

Prof. Classen remarks (p. 29) : "In presence of alumina the electrolytic method gives but little advantage in the determination of phosphoric acid. In this case a precipitation of that constituent in a separate portion with molybdate solution is to be preferred."

The observation might obviously have been applied to the determination of iron also.

SULPHATE METHOD (DEROME).

M. Derome's method consists in fusing the mixture of ferric oxide, alumina and phosphoric acid,. (precipitated by ammonia or basic acetate), with five to six times its weight of dry sodium sulphate over a blast lamp for 8 to 10 minutes, and then extracting with water. In the solution thus obtained it is asserted that the phosphoric acid can be directly precipitated with magnesia mixture. The ores were fused, &c., as above described, and the amount of filtrate from silica, representing 1 gm. of ore, precipitated with ammonia, washed, dried, ignited and fused as prescribed. To insure the change to sodium phosphate, the fusion was kept up for 15 minutes at the highest attainable heat of the blast lamp.

The water solution was found to contain small amounts of iron and manganese, possibly some other compounds, so that the addition of magnesia mixture gave a precipitate containing much beside pure magnesium ammonium phosphate, and it was found necessary to separate by molybdate solution before using the magnesia mixture. The precipitate taken just as it was, after ignition, appeared to be too coarse to permit of the satisfactory action of the sulphate, so in one experiment it was pulverized finely before fusing. The results for phosphorus were :

	"High."	"Low."
Precipitate fused direct..................	0.669	0.028
" pulverized and fused.........		0.058

Experiments were also made as to the effect of fusing the ore direct with the neutral sulphate. On account of the presence of small amounts of lime (under 1 per cent.), the mass after fusing was extracted with acid. Hot acetic acid took out much of the phosphoric acid which refused to dissolve in water, but interfered perceptibly with the precipitation by molybdate solution. Dilute nitric acid was found to dissolve what would dissolve out satisfactorily, the greater part of the iron oxide remaining undissolved in crystalline scales. The results were :

	High.	Low.
Ore fused with Na_2SO_4	0.356	0.0194

The use of some acid sulphate was then tried; 3 gms. of each ore were fused with 3 gms. $NaHSO_4$ at a low red heat until fumes ceased to come off ; then 3 gms. Na_2SO_4 were added, and the whole fused at the highest heat of the blast lamp for ten minutes. On cooling the mass was extracted with about 200 c.c. of water, to which was added 10 c. c. conc. nitric acid, and after heating for half an hour, at just short of boiling, the solution was filtered into molybdate solution into which some 10—15 gm. of crystals of ammonium nitrate had been thrown, &c., the phosphorus being finally weighed as the magnesium compound. (See result below). The neutral sulphate appeared to give but little advantage, and in this case the proportion of acid sulphate was evidently insufficient to completely disintegrate the ore. The experiment was therefore repeated, using three times as much $Na\ HSO_4$ as ore ; fusing for some time (one hour or a little over) at a low heat until fumes had almost ceased to come off, and then using the blast lamp for full ten minutes, extracting with dilute nitric acid, &c., as before. The results in the two last experiments were :

	High.	Low.
Ore fused with equal weights, $NaHSO_4$ and $Na_2\ SO_4$,	0.98	0.067
Ore fused with three times its weight, $NaH\ SO_4$,	1.05	0.083

This last mode of procedure, then, appears to be satisfactory for a rapid method of determining phosphorus in an iron ore. The amount of iron going into solution in the nitric acid is extremely small, so that that disturbing influence is removed. I propose making further experiments on the application of this method to titaniferous and other ores, and to bar iron and steel.