THE EXACT DETERMINATION OF PHOSPHORUS BY THE MOLYBDATE METHOD IN IRON, STEEL, AND ORES, WHICH CONTAIN ARSENIC.[1]

BY JAMES O. HANDY, Chemist of The Pittsburgh Testing Laboratory, L't'd.

CLASSIFICATION OF EXISTING METHODS FOR PHOSPHORUS.

1. The acetate method of Blair and others.
2. The molybdate methods.
   (a) Methods in which the phosphomolybdate is weighed (methods of E. F. Wood and others).
   (b) Methods in which the amount of yellow precipitate is estimated volumetrically.
      (a′) By permanganate (methods of Emmerton, Drown, Jones, and others).
      (b′) By alkali (methods of Manby, Handy, and others).
3. The combination methods.
   (a) The acetate and molybdate methods.
   (b) The molybdate and magnesia methods.

In the "acetate" methods the phosphorus is precipitated as phosphate, after separating by hydrogen sulphide, any arsenic which is present. The methods are long and the manipulation difficult.

In the "molybdate" methods, the phosphorus is precipitated as ammonium phosphomolybdate and weighed or titrated. Arsenic, which is believed to be of rare occurrence, is disregarded. It is, however, a fact, that, when arsenic is present in a solution from which phosphorus is precipitated as phosphomolybdate, a portion of the arsenic accompanies and contaminates the phosphorus precipitate.

The "molybdate" methods are in general, very short and their manipulation simple; they are widely used. With the drawback of arsenic interference removed, the molybdate method takes front rank for simplicity, brevity and accuracy.

---

[1] Read at the Baltimore meeting, December 28, 1893.

TABLE I.
EXTENT OF THE INTERFERENCE OF ARSENIC IN PHOSPHORUS DETERMINATIONS.

Substance analyzed.	Phosphorus per cent. contained.	Arsenic per cent. contained.	Method.	Temperature of precipitation.	Apparent per cent. phosphorus.	Error caused by arsenic.	Remarks.
Steel	0.096	0.050	J. O. Handy	85° C.	0.094	None	Within limit of error
"	0.096	0.050	"	"	0.095	"	
"	0.098	0.100	"	"	0.098	"	"
"	0.098	0.100	"	"	0.099	" to 0.001	"
"	0.096	0.250	"	"	0.099	0.003	
"	0.096	0.350	"	"	0.102	0.006	
"	0.096	0.500	"	"	0.106	0.010	
"	0.096	0.750	"	"	0.111	0.015	
"	0.096	1.870	"	"	0.125	0.029	
"	0.012	0.100	"	"	0.012	"	"
"	0.012	0.500	"	"	0.011	"	"
"	0.012	1.000	"	"	0.011	"	"
Pig iron	0.036	0.100	"	"	0.039	0.003	
" "	0.036	0.150	"	"	0.043	0.007	
" "	0.083	0.100	"	"	0.088	0.005	
" "	0.083	0.150	"	"	0.094	0.011	
" "	0.297	0.500	" and we'h'g	"	0.315	0.018	
Ferro-mang'se	0.292	0.500	evaporat'n neutraliz'n weighing	"	0.313	0.021	
Iron ore	0.096	0.500	"	"	0.135	0.038	
Mang'se ore	0.212	0.500	"	"	0.264	0.052	

EXPERIMENTS PROVING THAT ARSENIC DOES NOT PRECIPITATE WHEN LITTLE OR NO PHOSPHORUS IS PRESENT.

Experiments.—Two grams of magnetic iron ore, (a very pure concentrate), showed 0.002 per cent. phosphorus. A duplicate containing 0.500 per cent. of arsenic, in the fully oxidized form, showed also exactly 0.002 per cent. of phosphorus.

The filtrate, which contained arsenic, was heated for a short time to 60°–70° C. before molybdic acid or arsenomolybdate began to separate. The same result was repeatedly obtained with arsenical filtrates from phosphomolybdate precipitates.

A solution of arsenic acid in nitric acid, properly prepared as for phosphorus determination gives no precipitate at 85° C. with molybdate solution unless the heating is continued.

The experiments described prove very clearly that the precipitation of arsenic with phosphomolybdate is a mechanical one; that the arsenic is only *dragged* down. With little or no phosphorus, no arsenic precipitates.

The case is parallel to the contamination of the first ferric hydroxide precipitate, with lime, or of the first oxalate of lime precipitate, with magnesia.

In these cases, solution and re-precipitation of the contaminated precipitates, effects their purification.

Experiments (Table II) prove that the same treatment, properly applied, is equally efficient in purifying arsenical phosphomolybdate.

The exact method of procedure follows:

TABLE II.

ELIMINATION OF ARSENIC FROM PHOSPHOMOLYBDATE.

Substance analyzed.	Phosphorus contained.	Arsenic contained.	Method.	Temperature of precipitation.		Phosphorus found.	Error.
				First	Second		
Steel	0.096	0.500	J. O. Handy	80° C.	75° C.	0.096	none
"	0.096	0.500	"	"	"	0.096	"
"	0.096	0.500	"	"	"	0.097	0.001
"	0.096	1.000	"	"	"	0.097	0.001
"	0.096	none	"	"	"	0.095	0.001
"	0.096	"	"	"	"	0.095	0.001
"	0.096	"	"	"	"	0.094	0.002
"	0.096	0.500	"	85° C.	85° C.	0.097	0.001
"	0.096	0.500	"	"	80° C.	0.094	0.002
"	0.038	0.500	"	80° C.	75° C.	0.036	0.002
"	0.038	0.500	"	"	"	0.037	0.001
"	0.038	0.500	"	"	"	0.039	0.001
"	0.038	none	"	"	"	0.037	0.001
Pig iron	0.082	0.500	"	"	"	0.081	0.001
" "	0.082	0.500	"	"	"	0.081	0.001
Ferro-mang'se	0.282	0.500	evaporat'g weighing	85° C.	75° C.	0.281	0.001
Pig iron	0.286*	0.500	J. O. H. and "	"	"	0.289	0.003*
Iron ore	0.083	0.500	Evap. " "	"	"	0.085	0.002
Manganese	0.199	0.500	" " "	"	"	0.200	0.001

* NOTE.—A little lost.

THE METHOD OF REDISSOLVING THE PHOSPHOMOLYBDATE AND FREEING IT FROM ARSENIC.

Having separated the phosphorus as phosphomolybdate by any good method and washed it well with one per cent. nitric acid, place a twelve ounce Erlenmeyer flask under the funnel.

Dissolve the yellow precipitate by ammonium hydroxide wash (1 : 6), using about fifteen cc. in all, and wash it into the flask. Dilute the solution to about seventy-five cc. and heat to 75° C. and add a mixture of ten cc. HNO_3 (1.42) and twenty-five cc. of molybdate solution (E. F. Wood's formula), shake well, filter and wash

(a) with one per cent. nitric acid, dry and weigh, or

(b) with one per cent. nitric acid and $\frac{1}{10}$ per cent. potassium nitrate, dissolve and titrate (Handy's method).

The greater part of the analytical work of this paper has been done by my assistant Mr. Geo. O. Loeffler.

METHODS USED.

For Steel and Pig-iron.—The method used in all analyses of steel and pig-iron, was the one published by the author in 1892 (*Trans. Engineer's Society of Western Pennsylvania* March, *1892*, and *J. Anal. Appl. Chem.*, April, *1892*).

For Ferromanganese.—Two grams, dissolved in nitric acid, (1.42), and the solution evaporated to dryness. The residue, having been redissolved in hydrochloric acid, (1.20) the solution was diluted and filtered. The filtrate was treated with ammonium hydroxide till ammoniacal, then acidified with nitric acid, heated to 85° C. and precipitated with fifty cc. of molybdate solution.

For Iron and Manganese Ores.—Two grams dissolved in aqua regia (five per cent. HNO_3 (1.42) and ninety-five per cent. HCl (1.20), and the solution evaporated to dryness. Subsequent procedure was as described above for ferromanganese after the evaporation. Phosphorus, in "insoluble residues" was separated and determined.

Arsenic was added as dry As_2O_3 to the samples when weighed out. The reagents used in the analysis oxidized it to arsenic oxide.

NOTES AND QUERIES ON DR. DUDLEY'S METHOD OF DETERMINING PHOSPHORUS IN STEEL.

BY O. S. DOOLITTLE, CHEMIST, AND ALBAN EAVENSON, ASSISTANT CHEMIST
PHILADELPHIA AND READING RAILROAD COMPANY.

Received February 16, 1894.

THE object of the work outlined in this paper was to ascertain the accuracy of the method proposed by Dr. Dudley for the volumetric analysis of phosphorus in steel, described in *J. Am. Chem. Soc.*, Sept., *1893*, p. 519, and to determine if a separation of phosphorus could be made in the presence of arsenic with a sufficient degree of accuracy for commercial purposes