VII. DETERMINATION OF ZINC AS PYROPHOSPHATE.

By Geo. C. Stone, Ph. B.

Sometime since I had occasion to analyze a sample of water said to contain the tailings from an amalgamating mill. The analysis of the suspended matter only added up about eighty-eight per cent. I tried boiling the filtrate from the magnesia with KOH, this threw down a fine, crystalline, white precipitate; on making a qualitative examination of this I found it contained ZnO, and P_2O_5. On weighing the precipitate and calculating the amount of ZnO. it contained, supposing it to be $Zn_2 P_2 O_7$, I found it eleven and a fraction per cent., which made my analysis add up very close to one hundred per cent. This led me to experiment with phosphate of zinc with the following results.

If a mixture of an acid solution of a zinc salt and an alkaline ortho-phosphate is exactly neutralized with ammonia, the zinc is precipitated as a bulky, flocculent double phosphate of zinc and ammonia, easily soluble in acids or ammonia, and slightly soluble in potassic hydrate. If the solution in ammonia is boiled, thedouble. phosphate reprecipitates as a fine, crystalline white precipitate, very slightly soluble in ammonia, and almost absolutely insoluble in water. If the boiling is continued till the free ammonia is all driven off, the precipitation is complete. On drying and igniting this precipitate the zinc is obtained as pyrophosphate $Zn_2 P_2 O_7$.

This method of determining zinc has several advantages over the one commonly employed, of precipitating as sulphide, dissolving in hydrochloric acid, reprecipitating as basic carbonate, igniting and weighing as oxide.

First.—It is much quicker, as it is not necessary to let the precipitation stand, and there is only one precipitation.

Second.—The precipitate settles rapidly, filters quickly, does not run through the filter, washes easily, dries quickly, brushes off the paper easily and completely when dry, and is very difficult to reduce.

Third.—The presence of ammonia salts does not interfere with the completeness of the precipitation.

In all of which particulars its behavior is quite the reverse of that of either the sulphide or basic carbonate.

Fourth.—The pyrophosphate contains only 42.76 per cent. of zinc, while the oxide contains 80.25 per cent. so that an error in weighing makes much less difference in the result.

Fifth.—The phosphate does not need any purification, whereas the oxide frequently contains silica.

On the other hand the phosphate bumps badly while boiling out the ammonia ; and the precipitate sticks pretty tightly to the beaker. If the solution is kept rather dilute and only just enough ammonia is added to redissolve the precipitate first formed, and the solution is frequently stirred, the bumping will not give much trouble. The precipitate that sticks to the beaker is best removed by dissolving in a few drops of HCl, adding a little $NaNH_4HPO_4$, making just alkaline with NH_4OH and boiling till the free ammonia is expelled.

Experiment I.—Was made more to test the behavior of the phosphate of zinc and to see if the results agreed, than to test the absolute accuracy of the method. 0. 2 grms. of zinc,coated with oxide, were dissolved in H_2SO_4 and a few drops of HNO_3, the solution was diluted to about 300 cc., an excess of $NaNH_4HPO_4$ added, and just enough NH_4OH to re-dissolve the precipitate first formed. The solution was then boiled till there was no longer any smell of NH_3, filtered, washed thoroughly with hot water, dried, ignited and weighed. Gave :

A $Zn_2P_2O_7$ 0.4627 grms.=Zn 0.1979 grms.
B $Zn_2P_2O_7$ 0.4624 grms.=Zn 0. 1977 grms.

A was filtered as soon as the NH_3 was expelled. B was allowed to stand in a warm place for three hours after boiling.

Experiment II.—0.2 grms. of zinc ore, mainly oxide, was dissolved in HCl, HNO_3 and H_2SO_4, evaporated till the HCl and HNO_3 were expelled, diluted, filtered, the iron separated as basic acetate, dissolved and reprecipitated by a large excess of NH_4OH, the filtrates combined and evaporated to about 300 cc., an excess of $NaNH_4HPO_4$ added and the zinc determined as in I. In a second portion of 1. 0 grm. the iron was separated as above,the zinc precipitated by H_2S in a boiling acetic acid solution, let stand, filtered, washed, dissolved in HCl, reprecipitated as basic carbonate by Na_2CO_3, ignited and weighed as oxide. Gave :

A $Zn_2P_2O_7$ 0.3441 grms. Zn 0.1471 grms.=73.55 per cent
B $Zn_2P_2O_7$ 0. 9149 grms. Zn 0.7341 grms.=73.41 " "

Experiment III.—0.2 Grms. ferruginous blende treated as in II and gave :

A $Zn_2P_2O_7$ 0.2721 grms.=Zn 58.17 per cent
B $Zn_2P_2O_7$ 0.2716 grms.=Zn 58.07 " "

The analysis was afterwards completed and gave :

Zn (average of 2 determinations)	58.12	per	cent
Fe " " "	7.61	"	"
Insoluble silicious matter	1.43	"	"
S calculated to give Fe S and Zn S	32.96	"	"
Total,	100.12		

Experiment IV.—1.0 grm. $Zn(C_2H_3O_2)_2\ 2\ H_2O$ dissolved in water, excess of $NaNH_4HPO_4$ and NH_4OH added, the NH_3 expelled by boiling and the zinc determined as before. Gave :

A $Zn_2P_2O_7$ 0.6953 grms.=Zn 29.78 per cent
B $Zn_2P_2O_7$ 0.6974 grms.=Zn 29.82 " "

The theoretical percentage is 29.68.

Experiment V.—To test the influence of alkaline and ammonia salts :

0.5 grms. $Zn(C_2H_3O_2)_2 2\ H_2O$, 2.0 grms. $Na_2\ CO_3$, 2.0 grms. NH_4Cl, and 5.0 grms. $Na\ C_2H_3O_2$
the zinc determined as before gave :

A $Zn_2P_2O_7$ 0.3484 grms. = Zn 29.78 per cent.
B $Zn_2P_2O_7$ 0.3469 grms. = Zn 29.66 per cent.

Experiment VI.—As the phosphate of zinc is soluble in NH_4OH, while the phosphates of lime, magnesia, and manganese are insoluble in it, it seemed probable that the zinc could be separated by means of this reaction. The following experiments were tried to test this : 0.5 grm. $Zn(C_2H_3O_2)_2\ 2\ H_2O$, 0.1 grm. Mn_3O_4, 0.1 grm. $CaCO_3$ and 0.1 grm. $MgSO_4\ 7H_2O$ were dissolved in HCl excess of $Na\ NH_4HPO_4$ and NH_4OH added and let stand cold for eighteen hours, the clear solution filtered off, the precipitate dissolved in HCl, reprecipitated by NH_4OH and a few drops of $Na\ NH_4HPO_4$, filtered, washed with cold dilute NH_4OH, the NH_3 boiled out, and the zinc determined as before, gave:

A $Zn_2P_2O_7$ 0.3444 grms. = Zn 29.46 per cent.
B $Zn_2P_2O_7$ 0.3451 grms. = Zn 29.52 per cent.

The phosphates of manganese and lime clogged the filter and showed a tendency to run through it. To get good results the solution must be rather dilute (400 to 500 cc.).

Experiment VII.—0.5 grms. $Zn(C_2H_3O_2)_2\ 2H_2O$ and 0.5 grms. $MgSO_4\ 7H_2O$, treated as in the last experiment, gave:

A $Zn_2P_2O_7$ 0.3453 = Zn 29.54 per cent.
B $Zn_2P_2O_7$ 0.3451 = Zn 29.52 per cent.

Experiment VIII.—As phosphate of lime filters very slowly and is very difficult to wash, I tried precipitating the lime as oxalate in a rather dilute solution, decanting, dissolving in HCl, reprecipitating, and determining the zinc in the filtrate as phosphate. 0.5 grms. $Zn\ (C_2H_3O_2)_1\ 2H_2O$ and 0.25 grms. $CaCO_3$ taken, gave:

$Zn_2P_2O_7$ 0.3429 grms. = 29.32 per cent.

Experiment IX.—1,365 grms. $Zn_2P_2O_7$, heated to redness for about half an hour, weighed 1.365 grms.

Experiment X.—0.4 grms. zinc ore, containing about 14 per cent. SiO_2, 20 per cent. Fe_2O_3, 12 per cent. $CaCO_3$, and 16 per cent. MnO. A. Iron separated as basic acetate, dissolved and reprecipitated. Manganese precipitated by Br. Excess of $NaNH_4HPO_4$ and NH_4OH added, the solution decanted from the lime, precipitate, dissolved and reprecipitated by a large excess of NH_4OH, filtered and washed with dilute NH_4OH, using a filter pump, the excess of NH_3 boiled out, and the zinc ignited and weighed as $Zn_2P_2O_7$.

A. $Zn_2P_2O_7$ 0.2760, Zn 0.1179 = 29.47 per cent.

B. Iron precipitated as basic acetate, dissolved and reprecipitated by a large excess of NH_4OH, the filtrates combined, made strongly acid with $HC_2H_3O_2$, the zinc precipitated by H_2S in a boiling solution, filtered, dissolved in HCl and $KClO_3$, reprecipitated by Na_2CO_3, ignited, and weighed as ZnO, gave:

B. ZnO 0.1466, Zn 0.1176 = 29.40 per cent.

Experiment XI.—0.4 grms. ore similar to the last, treated in the same way, gave:

A. $Zn_2P_2O_7$ 0.2468 Zn 0.1055 = 26.37 per cent.
B. ZnO 0.1303 Zn 0.1045 = 26.15 per cent.

Experiment XII.—0.4 grms. ore similar to the last, treated in the same manner, gave:

A. $Zn_2P_2O_7$ 0.2390, Zn 0.1022 = 25.55 per cent.
B. ZnO 0.1294, Zn 0.1030 = 25.75 per cent.

The results of the separations are not as good as I could wish; but I intend to continue the experiments, in hopes of improving on them.

RESUME:

	Substance Analyzed.	Grms. used.	Grms Zn found.	REMARKS.
Expt. I.	Impure Zinc.	0.2	0.1979	
	" "	0-2	0.1977	
" II.	Zinc Ore.	0.2	0.1471	Weighed as Zn_2 P_2 O_7
	" "	1.0	0.7341	" " ZnO
" III.	Blende	0.2	0.11634	
	"	0.2	0.11614	
" IV.	$Zn(C_2H_3O_2)_2$ $2H_2O$	0.1	0.2978	Theory requires 0.2968 grms Zn.
" V.	"	0.1	0.2982	+2 grms. N H_4 Cl+2 grms. Na_2 CO_3+5 grms. Na C_2 H_8 O_2
	"	0.5	0.1489	
" VI.	"	0.5	0.1484	+0.1 grm. $Mn_3.O_4$+0.1 grm. $CaCO_3$+0 1 grm. Mg SO_4. $7H_2O$
	"	0.5	0.1473	
" VII.	"	0.5	0.1476	+0.5 grms. Mg SO_4. 7 H_2 O
	"	0.5	0.1477	
" VIII.	"	0.5	0.1476	+0. 25 grms. $CaCO_3$ Separated as oxalate.
	"	0.5	0.1466	
" IX.	$Zn_2P_2O_7$	1.365	1.365	Ignited for half an hour.
	Zinc Ore	0.4	0.1179	Weighed as Zn_2 P_2 O_7
" X.	" "	0.4	0.1176	" " ZnO
	" "	0.4	0.1055	" " Zn_2 P_2 O_7
" XI.	" "	0.4	0.1046	" " ZnO
	" "	0.4	0.1022	" " Zn_2 P_2 O_7
" XII.	" "	0.4	0.1030	" " ZnO

Since making the above experiments, I have found that Hugo Tamm(*Chem, News* XXIV, p. 148) has proposed to weigh zinc as the double phosphate of zinc and ammonia, Zn NH_4 PO_4, which, of course, necessitates the use of a weighed filter. His method is as follows: Make acid solution of a zinc salt alkaline with N H_4O H, then barely acid with HCl and add a solution of Na_2 HPO_4 heat nearly to boiling for a few minutes, filter, wash, dry at 100°C. and weigh as Zn NH_4 P O_4.

He states that there is invariably a loss when the double phosphate is converted into pyrophosphate by ignition ; but from the results of my own experiments, I should say the loss was due to his precipitate being formed in an acid solution, in which I have found the double phosphate to be quite soluble. The greater quantity of zinc found when weighing the double phosphate was probably due to insufficient heat in the drying. He uses the atomic weight of 65.5 for zinc ; using 65, the one now generally accepted, his results would all be low.

The composition of pyrophosphate of zinc is as follows :

2 Zn	130	42.763	per cent.
2 P	62	20.395	“
7 O	112	36.842	“
$Zn_2P_2O_7$	304	100.000	

or,

2 ZnO	162	53.29	per cent.
$P_2\ O_5$	142	46.71	“
			“
$Zn_2P_2O_7$	304	100.00	

Nickel and cobalt form phosphates which behave precisely like the corresponding zinc salt ; both, however, are strongly colored, and so can readily be distinguished from phosphate of zinc.

VIII. METHYL VIOLET TEST PAPER.

By T.O'Connor Sloane A. M., Ph. D.

Several years have passed since it was first proposed to use methyl violet as an indicator or test for mineral acids in the presence of organic acids. Since it has also been used as a coloring matter for test paper it occurred to me that a few notes on the preparation and use of the paper would be of interest.

I tried solutions of methyl violet of different strength in dyeing paper. A solution of one part of violet in four thousand parts of water was found to be sufficiently strong. A solution of double this strength gave a very good color.

Using paper dyed with the first solution I performed the following experiments:

One cc. of concentrated hydrochloric acid was mixed with him one hundred cc. of water. The acid was of sp. gr. 1.197 corresponding to about 40 per cent. acid; the solution therefore was of four one thousands strength or four-tenths of one per cent.

A piece of paper dipped in this solution did not show the reaction except on drying ; then it came out perfectly. A piece made from a violet solution of half the strength showed a little; this acid seemed therefore to be close upon the limits of sensibility for an immediate reaction.

It will also be noticed that the more weakly colored paper was slightly more sensitive ; on drying the darker paper shows as well or better.