CVI.—*The Estimation of Zinc as Zinc Ammonium Phosphate and Zinc Pyrophosphate.*

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THE method of estimating zinc as zinc ammonium phosphate was first recommended by Tamm (*Chem. News*, 1871, **24**, 148), and has since been investigated by Clark (*J. Soc. Chem. Ind.*, 1896, **15**, 866), Gooch and Austin (*Amer. J. Sci.*, 1898, **6**, 223), and notably by Dakin (*Zeitsch. anal. Chem.*, 1901, **39**, 273).

As Dakin's procedure was closely followed in the experiments of which the results are given in table III, and was found to yield very satisfactory results when a pure zinc solution was used, a brief description may be given.

Dakin's Method.—The acid zinc solution, contained in a platinum basin, is almost, but not quite, neutralised with ammonia, diluted to 150 c.c., and warmed on the water-bath. To the warm solution ammonium phosphate is added, the weight of the ammonium phosphate being about ten times the probable weight of the zinc. The precipitate, which is amorphous at first, quickly changes to a fine crystalline precipitate of zinc ammonium phosphate, ZnNH_4PO_4 . This change takes place more quickly in presence of a considerable amount of ammonium salts.

The solution is heated for fifteen minutes on the water-bath, and set aside for some time. The precipitate is filtered through a Gooch crucible, washed with 1 per cent. ammonium phosphate until free from chloride, and then several times with alcohol or cold water. It is dried at 100–105°, and weighed as ZnNH_4PO_4 , or, after ignition with exclusion of flame gases, as $\text{Zn}_2\text{P}_2\text{O}_7$.

Dakin also states that where large amounts of ammonium salts are present, it is preferable to ignite directly to the pyrophosphate, owing to the difficulty of removing these salts completely by washing.

Low ("Technical Methods of Ore Analysis," 1911, p. 301) recom-

mends the use of microcosmic salt as precipitant, and to the solution after neutralisation with ammonia he adds 1 c.c. of acetic acid. In some experiments in this laboratory his method was followed, and as the results were sometimes accurate and sometimes very unsatisfactory, a systematic investigation of the method appeared desirable, as it was evident that some slight variation in the conditions of precipitation was the source of the large error.

Effect of Acidity on the Character of the Precipitate.—The error noted above was found to be due to precipitation in a solution which was too acid. The precipitate obtained from a neutral solution or one which contained only a trace of free acetic acid was homogeneous, consisting of pure zinc ammonium phosphate. The precipitate obtained from a solution to which 1 c.c. of glacial acetic acid had been added after neutralisation was found, by microscopic examination, to be a mixture of three substances. One portion was amorphous, and consisted of zinc hydroxide or a basic phosphate; a second portion had the characteristic crystalline form of zinc ammonium phosphate; the third portion consisted of groups of needle-shaped crystals, which tended to arrange themselves in tufts round a common nucleus. These crystals imparted to the precipitate its characteristic flocculent appearance. It appeared probable that these crystals were sodium zinc phosphate, and experiment confirmed this supposition. An almost homogeneous precipitate of zinc sodium phosphate was prepared by addition of sodium phosphate to a pure zinc sulphate solution. The crystals thus obtained showed the crystalline arrangement described above.

Zinc sodium phosphate is readily hydrolysed; even on washing with cold water it becomes transformed into amorphous zinc hydroxide or a basic phosphate.

When zinc is precipitated from an acid solution, some zinc remains in solution, but the error from this source is small in comparison with the total error.

EXPERIMENTAL.

In all experiments, the amount of zinc present was known from the weight of pure zinc sulphate taken.

Precipitation with Microcosmic Salt in Acid Solution.—Table I shows the large error introduced by precipitation in a too strongly acid solution. In these experiments, the zinc was precipitated with microcosmic salt, the solution neutralised with ammonia, and 1 c.c. of glacial acetic acid added. The precipitate was ignited and weighed. Column IV gives the weight of zinc on the assumption that the residue was pure zinc pyrophosphate.

TABLE I.

No.	Zn taken.	Wt. of ppt.	Zn found.	Error.
1	0.1389	0.2676	0.1148	- 0.0241
2	0.1599	0.2892	0.1241	0.0358
3	0.2195	0.4198	0.1801	0.0394

The large error is due to the false assumption that the residue was zinc pyrophosphate. Since zinc sodium phosphate forms part of the precipitate, one would expect high results. The results in practice are low, since zinc sodium phosphate is largely hydrolysed by the wash-water, the final residue being largely zinc hydroxide, or a basic salt.

Precipitation with Microcosmic Salt in Slightly Acid Solution.—To prevent precipitation of the hydroxide, it is necessary to keep the solution on the acid side of neutrality. Table II gives the results obtained by precipitation with microcosmic salt. After addition of the microcosmic salt, the solution was neutralised with ammonia and then made faintly acid with acetic acid. The precipitate was ignited and weighed as pyrophosphate.

TABLE II.

No.	Zn taken.	Zn ₂ P ₂ O ₇ .	Zn found.	Error.
1	0.1993	0.4658	1.1999	+ 0.0006
2	0.1909	0.4462	0.1915	0.0006
3	0.2229	0.5218	0.2239	0.0010

It is evident that accurate results are obtainable by precipitation with microcosmic salt, but, as there is less liability to error, we regard precipitation with ammonium phosphate as preferable.

Precipitation with Ammonium Phosphate.—Table III shows the results obtained by Dakin's method, that is, precipitation with ammonium phosphate in neutral or faintly acid solution. The first half of the table gives the zinc estimated as ZnNH₄PO₄, the second half as Zn₂P₂O₇. In No. 5 a platinum vessel was used, and the precipitate showed a tendency to adhere to the sides of the vessel, a difficulty which was not experienced with glass vessels unless a large quantity of ammonium salt was present.

TABLE III.

No.	Zn taken.	ZnNH ₄ PO ₄ found.	Zn found.	Error.
1	0.1722	0.4708	0.1726	+ 0.0004
2	0.2015	0.5516	0.2022	+ 0.0007
3	0.1839	0.5038	0.1846	+ 0.0007
4	0.2017	0.5520	0.2023	+ 0.0006
5	0.1636	0.4452	0.1632	- 0.0004
6	0.1588	0.4336	0.1590	+ 0.0002
7	0.1778	0.4854	0.1779	+ 0.0001

TABLE III (*continued*).

No.	Zn taken.	Zn ₂ P ₂ O ₇ found.	Zn found.	Error.
1	0·1722	0·4037	0·1732	+0·0010
2	0·2015	0·4706	0·2019	+0·0004
3	0·1839	0·4298	0·1844	+0·0005
4	0·2017	0·4716	0·2023	+0·0006
5	0·1636	0·3794	0·1628	-0·0008
6	0·1588	0·3716	0·1595	+0·0007
7	0·1778	0·4156	0·1783	+0·0005

These results show that accurate results are obtained with a pure zinc solution if Dakin's procedure is closely followed. Inaccurate results, however, will be obtained (1) if the solution is alkaline, or (2) if the solution contains any free mineral acid or more than a trace of free acetic acid.

As commercial "ammonium phosphate" is not always the same salt, it is preferable to neutralise with ammonia after addition of ammonium phosphate, and then add 1 c.c. of dilute (about 2*N*) acetic acid. With this procedure it is immaterial whether one uses an acid phosphate or the normal phosphate.

Precipitation with Potassium and Sodium Phosphates.—The precipitate obtained when potassium or sodium phosphate is added to a zinc salt in neutral solution behaves like zinc ammonium phosphate, being amorphous at first, but crystallising on keeping. The peculiar crystalline appearance of zinc sodium phosphate has already been noticed; the potassium compound is rather finer-grained than zinc ammonium phosphate. Both zinc potassium phosphate and zinc sodium phosphate remain unchanged on further heating after their water of crystallisation has been driven off. Experiments were carried out to see whether these salts would be suitable forms in which to estimate zinc. The results with potassium proved nearly quantitative, those with sodium were very low. The zinc was completely precipitated in both cases, and the error was apparently due to the fact that both salts are hydrolysed by the subsequent washing water, for phosphate could always be detected in the filtrate even after prolonged washing, although no zinc was dissolved. In the case of zinc potassium phosphate, the loss due to hydrolysis was slight, but increased the more thorough the washing. This will be seen from the following table, where Nos. 1 and 2 show the results after washing about six to eight times, Nos. 3 and 4 show the effect of longer washing, and Nos. 5 and 6 the effect of very prolonged washing. The final washings in all cases contained phosphate, but no zinc. Zinc potassium phosphate is therefore not a suitable form in which to estimate zinc.

TABLE IV.

Precipitation with Potassium Phosphate in Neutral Solution.

No.	Zn taken.	ZnKPO ₄ found.	Zn found.	Error.
1	0.1775	0.5392	0.1767	-0.0008
2	0.1629	0.5124	0.1680	0.0009
3	0.1909	0.5774	0.1893	0.0016
4	0.1555	0.4694	0.1539	0.0016
5	0.1790	0.5364	0.1758	0.0032
6	0.1659	0.4998	0.1639	0.0020

Precipitation with Ammonium Phosphate in Presence of Sodium and Potassium Salts.

Whilst the sodium and potassium compounds are not suitable forms in which to estimate zinc, the fact of their formation must be taken into account when precipitating in presence of sodium and potassium salts, for, as might be expected, a mixture of zinc ammonium phosphate and zinc potassium phosphate or zinc sodium phosphate is precipitated. Sodium salts do not present much difficulty, as they can be completely removed in a single precipitation, provided the solution is not too acid and a sufficient quantity of ammonium salt is added. Even when large quantities of sodium salts are present, they can be removed in this way. For example, 5.0 grams of sodium chloride were added to a zinc solution. The zinc was precipitated by ammonium phosphate after addition of 10 grams of ammonium chloride. The precipitate was ignited and weighed as pyrophosphate. Zn taken=0.1965; Zn found=0.1963.

Potassium salts are not removed so easily. A single precipitation, even in presence of a large quantity of ammonium salts, is insufficient to prevent partial precipitation of the potassium salt; a double precipitation is necessary, and a large amount of ammonium chloride must be added before each precipitation. A reference to table VI will show that, for complete removal of potassium, it was necessary to add 10 grams of ammonium chloride before each precipitation.

When such large quantities of ammonium salts were present, the precipitate was found to adhere strongly to the sides of the glass beakers used, and could not be completely removed by rubbing. In such cases the traces were dissolved in a little hydrochloric acid and reprecipitated. Dakin has pointed out that when zinc ammonium phosphate is precipitated in presence of large amounts of ammonium salts, it is impossible to remove all the ammonium salts by washing; in all such cases, the precipitate was therefore ignited and weighed as pyrophosphate.

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Table V gives the results of estimations in presence of potassium salts. Nos. 1, 2, and 3 were precipitated once. With Nos. 4 and 5 the given amount of ammonium chloride was added before precipitation with ammonium phosphate. The precipitate was collected, washed two or three times, and redissolved in a small quantity of hydrochloric acid. This solution was then neutralised, and the zinc precipitated as before, but without addition of ammonium chloride.

TABLE V.

No.	Zn taken.	KCl added.	NH ₄ Cl added.	Zn found.	Error.
1	0.1726	1.0	none	0.1904	+0.0178
2	0.1844	2.0	„	0.2036	0.0310
3	0.1772	3.0	10 grams	0.1920	0.0148
4	0.1576	3.0	10 „	0.1640	0.0064
5	0.1882	3.0	10 „	0.1950	0.0068

These results indicate that the amount of potassium in the precipitate may be reduced (1) by a double precipitation, and (2) by adding a large quantity of ammonium chloride before precipitation. Some experiments were therefore tried on the effect of a double precipitation with addition of ammonium chloride before each precipitation. The results are given in table VI. The fourth column gives the amount of ammonium chloride added before both the first and second precipitation.

TABLE VI.

No.	Zn taken.	KCl added.	NH ₄ Cl added.	Zn found.	Error.
1	0.1778	0.5	5.0	0.1775	-0.0003
2	0.1735	1.0	5.0	0.1745	+0.0010
3	0.1724	1.0	10.0	0.1722	-0.0002
4	0.1418	1.5	10.0	0.1415	-0.0003
5	0.1556	2.0	10.0	0.1559	+0.0003
6	0.1475	3.0	10.0	0.1472	-0.0003

Accurate results are therefore obtainable in presence of potassium by means of a double precipitation with addition of 5 to 10 grams of ammonium chloride before each precipitation.

Composition of Precipitated Zinc Ammonium Phosphate and Zinc Potassium Phosphate.—According to Tamm and Dakin, the composition of the precipitated ammonium salt is anhydrous ZnNH_4PO_4 , but Low gives it as $\text{ZnNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$. Experiments on the salt, dried in the air for an hour on a porous plate, showed that constant weight was obtained at 110° , the salt having lost only 0.15 per cent. of its weight; it is therefore anhydrous zinc ammonium phosphate, since the monohydrate would lose 9.2 per cent. by weight on drying. At 150° the salt begins to decompose, leaving

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the pyrophosphate. Ammonia is freely evolved as the temperature reaches 200° . A sample of precipitated zinc potassium phosphate was dried in the air and weighed. On heating, it became anhydrous at 105° , the loss of weight corresponding with four molecules of water. Precipitated zinc potassium phosphate is therefore probably $\text{ZnKPO}_4 \cdot 4\text{H}_2\text{O}$, but owing to the difficulty of preparing it in a state of purity this result cannot be considered conclusive.

Summary.

The phosphate method for the estimation of zinc has been investigated to find the reason for occasional unsatisfactory results. It was found that salts of the composition ZnNaPO_4 and ZnKPO_4 are formed if the solution contains sodium or potassium salts. Precipitation with microcosmic salt yields inaccurate results unless special care is taken to neutralise the solution or to render it very slightly acid with acetic acid after precipitation. In the presence of sodium salts, correct results are obtained by precipitation with ammonium phosphate in neutral solution, after addition of 5 to 10 grams of ammonium chloride. If potassium is present, ammonium chloride must be added before precipitation of the zinc with ammonium phosphate, the precipitate re-dissolved, more ammonium chloride added, and the zinc reprecipitated as before. The precipitate must be ignited and weighed as pyrophosphate.

If due attention is paid to these points, one obtains a crystalline precipitate which is easily manipulated. For a pure zinc solution no more satisfactory method could be desired; in presence of sodium or potassium (more particularly the latter), the method is less satisfactory, but yields accurate results.

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