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A VOLUMETRIC DETERMINATION OF ZINC INVOLVING A QUANTITATIVE PRECIPITATION OF ZINC AMMONIUM PHOSPHATE

BY

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CHAPTER I

INTRODUCTION

The necessity of a precise method for the determination of zinc is evident after reading the report of the Sub-Committee on Zinc Ore Analyses(3), which shows the wide discrepancies encountered in the determination of zinc by methods in ordinary use. Their report showed results from forty-two chemists ranging from 12.20 per cent to 39.22 per cent on a sample of zinc ore containing 18.16 per cent of zinc.

The difficulties to be met by various methods used to determine zinc are twofold: the quantitative precipitation of zinc sulfide in a form suitable for rapid filtration and washing, and the subsequent conversion of this precipitate to a definite compound(5). There has been considerable work done on these two main difficulties.

Zinc may be precipitated as the sulfide from a solution in which the pH is maintained between 2 and 3. Zinc sulfide is not precipitated completely from more acid solutions and is gelatinous and difficult to filter when precipitated from less acid solutions. The proper hydrogen ion concentration can be obtained by a formate-formic acid buffer(5), a sulfate-sulfuric acid buffer(6), a chloracetate-chloracetic acid buffer(7), or a citrate-citric acid buffer(2). The use of any of these buffers allows a maximum precipitation of zinc sulfide, and the first difficulty encountered has been reduced to the extent where it is now regarded as a minor difficulty.

Various methods are now being used for determining zinc once it is obtained in the form of zinc sulfide. It can be determined:

1. by converting zinc sulfide to zinc sulfate or zinc oxide;

$$ZnS + H_2SO_4 \xrightarrow[500^\circ]{} ZnSO_4 + H_2S$$

$$ZnS + air(O_2) \xrightarrow[1000^\circ]{} ZnO + SO_2$$

2. by converting zinc sulfide to zinc ammonium phosphate monohydrate, converting the monohydrate to the anhydrous form by drying at 105°C;

$$Zn^{++} + 2NH_4^+ + HPO_4^{--} + H_2O \longrightarrow ZnNH_4PO_4 \cdot H_2O + NH_4^+ + H^+$$

$$ZnNH_4PO_4 \cdot H_2O \xrightarrow[105^\circ]{} ZnNH_4PO_4 + H_2O$$

3. by converting the zinc ammonium phosphate to zinc pyrophosphate;

$$2ZnNH_4PO_4 \xrightarrow[1000^\circ]{} Zn_2P_2O_7 + H_2O + 2NH_3\uparrow$$

4. volumetrically, by precipitating the zinc sulfide as zinc potassium ferrocyanide.

No particularly good, direct volumetric method is known for determining zinc. The method now being used involves the precipitation of the ferrocyanide,

$K_2Zn_3[Fe(CN)_6]_2$,

$$3ZnCl_2 + 2K_4Fe(CN)_6 \longrightarrow K_2Zn_3[Fe(CN)_6]_2\downarrow + 6KCl$$

The end point can be determined by using uranyl nitrate as an external indicator: portions of the uranyl nitrate are placed in the depressions of a spot plate and from time to time during the titration a drop of the solution is removed and added to the uranyl nitrate. At the equivalence-point, the excess of ferrocyanide gives a chocolate-colored precipitate of uranyl ferrocyanide, $(UO)_2Fe(CN)_6$. This procedure is slow, inconvenient, and introduces positive and negative errors above those that would be expected in a precise volumetric determination. The positive error occurs at the end point, amounting to 0.5-0.7 ml. Tyler(10) showed that the precision average per cent deviation from mean, using uranyl nitrate as external indicator or diphenylbenzidine as internal indicator, is wholly unsatisfactory for a precise determination of zinc.

It is the object of this thesis to propose an indirect volumetric method of determining zinc which is simpler and more accurate than the standard method used today, namely, the ferrocyanide method. The method proposed in this paper is somewhat similar in principle to that used by Trykov(9), where the zinc ammonium phosphate is dissolved in excess 0.1 N nitric acid and the excess acid is titrated with 0.1 N sodium hydroxide.

CHAPTER II

THEORETICAL DISCUSSION

Zinc may be precipitated as a double salt by adding to its nearly neutral solution an excess of diammonium hydrogen phosphate. The acid formed during the precipitation reacts with excess of the preceipitating agent to form ammonium dihydrogen phosphate. These two phosphates, which are present as a buffer, keep the solution at the proper pH.

$$Zn^{++} + 2Cl^{-} + 2(NH_4)_2HPO_4 + H_2O \longrightarrow ZnNH_4PO_4 \cdot H_2O + NH_4H_2PO_4 + 2NH_4Cl$$

Table 1 shows the effect of pH on the quantitative precipitation of zinc ammonium phosphate. From this it has been found that the precipitation of zinc is accurate within $\pm$ 0.4 mg. of zinc if the solution has a pH between 5.1 and 7.6 after the precipitation. The optimum pH is 6.6. A two-hour heating period in a covered beaker automatically adjusts the acidity to the proper range(1). Too low a pH value prevents the existence of a sufficient quantity of tertiary phosphate ion, PO_4^{---}. On the other hand, it is readily soluble in a solution of too high a pH value. In such solutions, the ammonium ion is converted partially to its conjugate base, NH_3, which forms a complex cation with zinc, $Zn(NH_3)_4^{++}$. After the

TABLE 1

EFFECT OF pH ON THE PRECIPITATION OF ZINC AMMONIUM PHOSPHATE (1)

Number	Zinc Had, g.	Zinc Found, g.	Difference mg.	Relative Mean Error Parts per 1000	pH
1	0.0881	0.0798	-8.3	-80	4.2
2	0.0877	0.0874	-0.3	- 3	5.1
3	0.0880	0.0876	-0.4	- 4	5.4
4	0.0877	0.0876	-0.1	- 1	5.4
5	0.0882	0.0879	-0.3	- 3	6.2
6	0.0888	0.0888	0.0	0	6.4
7	0.0889	0.0890	+0.1	0	6.4
8	0.0887	0.0884	-0.3	- 3	6.4
9	0.0548	0.0548	0.0	0	6.6
10	0.0726	0.0726	0.0	0	6.6
11	0.0363	0.0363	0.0	0	6.7
12	0.0717	0.0716	-0.1	- 1	6.7
13	0.0817	0.0818	+0.1	+ 1	6.9
14	0.0888	0.0891	+0.3	+ 3	7.1
15	0.0885	0.0887	+0.2	+ 2	7.4
16	0.0892	0.0896	+0.4	+ 4	7.6
17	0.0883	0.0863	-2.0	-20	7.8
18	0.0887	0.0844	-4.3	-50	7.9
19	0.0884	0.0793	-9.1	-99	8.3

container. On adding a strong solution of sodium hydroxide, it was believed that complete reaction would take place and the liberated ammonia would diffuse into the solution of hydrochloric acid. The results obtained were very low and inconsistent. This was due, in large part, to incomplete reaction brought about by the lowness of the temperature.

The second method involved distillation of ammonia. The precipitate of zinc ammonium phosphate is placed in a flask and a sufficient amount of water and alkali are added. Upon heating this mixture, complete reaction occurs and the ammonia is distilled and absorbed in a large quantity of boric acid, which does not need to be measured accurately(11).

$$ZnNH_4PO_4 + 5NaOH \longrightarrow Zn(OH)_4^{--} + PO_4^{---} + NH_3\uparrow + 5Na^+ + H_2O$$

A borate ion is liberated for each molecule of ammonia absorbed.

$$NH_3 + HBO_2 \longrightarrow NH_4^+ + BO_2^-$$

This solution is then titrated with standard hydrochloric acid.

$$NH_4^+ + BO_2^- + H^+ + Cl^- \longrightarrow NH_4^+ + Cl^- + HBO_2$$

and the weight of nitrogen calculated. This gives the weight of zinc because there is an atom of zinc to every atom of nitrogen and by multiplying the weight of nitrogen by the conversion factor, $\frac{Zn}{N}$ (4.67), the weight of zinc can be obtained.

A possible theoretical error encountered, other than the precipitation of zinc ammonium phosphate, would be in the titration stage. The titration of ammonia in boric acid solution, with the aid of methyl red indicator, is based on the fact that in presence of boric acid the indicator develops its acid color in an intermediate intensity, corresponding to the acidity of the boric acid solution, and that this color is markedly changed in intensity by small amounts of alkali or acid(11). During the titration of ammonia, the yellow solution develops a reddish color as the equivalence point is approached and upon continued addition of acid the red color becomes progressively clearer and deeper, finally reaching a maximum well beyond the equivalence point. There is at no time a sharp color change, but at the equivalence point, the intensity of the red color is identical with that of the boric acid-methyl red solution similarly diluted.

As a matter of convenience, and to be sure of the presence of the same quantity of methyl red in both comparison solution and titrated solution, the methyl red should be added to the whole supply of boric acid solution.

The comparison solution has the same concentration of boric acid as the titrated solution at the equivalence point but lacks the ammonium chloride. Therefore, the ionization constant of the boric acid and the hydrogen ion concentration of the titrated solution are greater than that for the comparison solution. The maximum difference in pH between the comparison solution and the titrated solution due to this cause is no more than 0.1 of a pH unit, which is equivalent to 0.01 ml. of a 0.1 N hydrochloric acid solution(8). For most purposes, this error may be neglected. It is possible, however, to eliminate the difference in pH of the two solutions by adding an amount of ammonium chloride to the comparison solution which would contain the same concentration as that of the ammonium chloride present in the titrated solution after titration. Hence, the ionic strength of the two solutions would be equal, and consequently, there would be no difference in the pH values. The calculated amount of ammonium chloride that would be in the comparison solution could be determined from the theoretical weight of ammonium in zinc ammonium phosphate.

CHAPTER III

EXPERIMENTAL PROCEDURE

The procedure followed for the precipitation of zinc was essentially that found in Reiman, Neuss, and Naiman, "Quantitative Analysis." A known amount of zinc sulfide was dissolved in 25-30 ml. of warm concentrated hydrochloric acid. The solution was gently boiled to expel the hydrogen sulfide and then cooled. One drop of methyl orange was added, and the solution neutralized with 6 N ammonium hydroxide. Carefully, 1 N hydrochloric acid was added until the indicator turned pink. The solution was then diluted to 200 ml., heated to 90°C, and added, with constant stirring, an excess of a solution of di-ammonium hydrogen phosphate, i.e., about ten times the theoretical amount necessary to combine with the zinc. Generally, 25 ml. of freshly prepared 2 M solution of the precipitant was sufficient. A flocculent precipitate of zinc phosphate first formed, kept the solution hot, but below boiling, until this substance changed to the crystalline zinc ammonium phosphate, which settled rapidly to the bottom of the beaker. Usually ten to twenty minutes was required for this change. The solution was allowed to digest on a water bath for thirty minutes. Unless the solution was nearly neutral before adding the diammonium hydrogen phosphate, the pH would not be correct for a quantitative precipitation. A check of the pH at this point was made by adding a few drops of bromothymol-blue. The pH was within the acceptable limits if the indicator assumed any shade of green. The precipitate was then filtered through a filtering crucible, washed once with freshly prepared 0.1 M secondary ammonium phosphate solution, and then twice with 50 per cent alcohol.

While the precipitate dried, an apparatus similar to that used in the Kjeldahl determination was set up. A steam trap was connected to the Kjeldahl flask. Its purpose was to prevent any of the alkaline solution from being carried as a spray into the condenser. The receiving flask should be a 400 ml. beaker, marked to indicate the level to which it should be filled to hold 200 ml. Fifty ml. of 0.6 M boric acid, containing methyl red, was put into the flask. The lower end of the condenser was fitted with a rubber stopper to which was attached a bent adapter which extended nearly to the bottom of the flask.

The precipitate of zinc ammonium phosphate was then placed into the Kjeldahl flask and 150 ml. of water added, some of which was used to wash out the crucible containing the precipitate. To this mixture, 100 ml. of 10 N sodium hydroxide was introduced by means of a funnel, a few marble chips added and distillation begun. Steam distillation was recommended for the separation of ammonia because this method avoids the tendency of the alkaline solution to bump. The process must be constantly watched in order to prevent temperature changes which might cause the mixture from the receiver to be drawn back into the Kjeldahl flask. When the volume in the receiving flask reached 200 ml., the adapter was disconnected, flame removed, and the condenser and adapter rinsed out with distilled water, allowing the washings to run into the receiver. The contents of the receiving flask were titrated with 0.1 N hydrochloric acid and the weight of nitrogen calculated. This calculation was based on the theoretical per cent of nitrogen present in zinc ammonium phosphate.

CHAPTER IV

DISCUSSION OF RESULTS

Since this problem was not directly concerned with the separation of zinc from interfering metals, all of the samples used were zinc sulfide of high grade purity. The writer was well aware of the possible errors that would be involved in the separation of zinc, and believed that, by improved technique, the results obtained in this paper would have differed very little from those that would have been obtained if separation of zinc by the standard methods had been encountered. The results shown on Table 2 were obtained from the same sample of zinc sulfide as the results shown on Tables 3 and 4.

Table 2 gives the results of a number of analyses made as described in the experimental procedure. The results of analyses that failed because of improper control of conditions are not included. It is believed that the data in Table 2 are representative. The average error was ± 2.4 parts in a thousand. The results in Tables 3 and 4 are those of two standard gravimetric methods: conversion to zinc ammonium phosphate, and conversion to zinc oxide, with an average error of ± 2 and ± 1 parts in a thousand, respectively.

There are positive and negative errors involved

TABLE 2

VOLUMETRIC DETERMINATION OF ZINC INVOLVING A QUANTITATIVE PRECIPITATION OF ZINC AMMONIUM PHOSPHATE

Number	Weight of Nitrogen g.	Zinc Found g.	Zinc Had g.	Difference mg.	R.M.E. Parts per 1000
1	0.0801	0.3738	0.3740	-0.2	-0.6
2	0.0650	0.3036	0.3042	-0.6	-2
3	0.0754	0.3522	0.3526	-0.4	-1
4	0.0673	0.3143	0.3149	-0.6	-2
5	0.0947	0.4423	0.4433	-1.0	-2
6	0.0609	0.2845	0.2852	-0.7	-2
7	0.0614	0.2867	0.2873	-0.7	-2
8	0.0785	0.3665	0.3683	-1.8	-5
9	0.0705	0.3294	0.3305	-0.9	-3
10	0.0725	0.3384	0.3376	+0.8	+2

TABLE 3

DETERMINATION OF ZINC BY PRECIPITATION AS ZINC AMMONIUM PHOSPHATE

Weight of $ZnNH_4PO_4$ g.	Zinc Found g.	Zinc Had g.	Difference mg.	Relative Mean Error Parts per 1000
1.3388	0.4907	0.4916	-0.9	-2
0.9643	0.3534	0.3526	+0.8	+2
1.1963	0.4384	0.4392	-0.8	-2
0.8611	0.3156	0.3149	+0.7	+2
1.0047	0.3682	0.3691	-0.9	-2

TABLE 4

DETERMINATION OF ZINC BY CONVERSION TO ZINC OXIDE

Weight ZnO g.	Zinc Found g.	Zinc Had g.	Difference mg.	Relative Mean Error Parts per 1000
0.6538	0.5253	0.5245	+0.9	+1
0.7982	0.6413	0.6407	+0.7	+1
0.3559	0.2859	0.2861	-0.2	-1
0.4194	0.3369	0.3370	-0.1	0
0.3978	0.3196	0.3198	-0.2	-0.6

in this method. As stated above, the various determinations were started with samples of zinc sulfide, eliminating a possible positive error, which could be an abnormal composition of the precipitate, due to the presence of excessive amounts of ammonium salts in the solution, or excessive amounts of sodium or potassium ions(12). Negative errors, some of which are unavoidable but may be held to a minimum, are:

1. Failing to expel hydrogen sulfide from original sample causes a precipitation of zinc sulfide when the solution is adjusted to the proper pH value. This error can be avoided by gently boiling the solution ten to fifteen minutes, or until the odor of hydrochloric acid fumes are predominant.

2. Incomplete precipitation of zinc ammonium phosphate. By carefully adjusting the pH of the solution to the point where a half-drop of 1 N hydrochloric acid is sufficient to turn the indicator from yellow to red, this error can also be avoided.

3. Solubility loss during the washing process. Unavoidable if water is used, but this error may be taken into account since the solubility of zinc ammonium phosphate in water is known.

4. Transferring of precipitate.

5. Volatization of some ammonia before the Kjeldahl flask is attached to the distillation apparatus.

6. Failure to match the color of titrating solution with that of the boric acid-methyl red solution similarly diluted. This error can be minimized by proper lighting, white background, and by using the same stock solution for the adsorption flask and comparison buffer.

CHAPTER V

SUMMARY

1. An indirect, volumetric method, making use of the volatization of ammonia brought about by the partial decomposition of zinc ammonium phosphate, was proposed for determining the percentage of zinc in an ore.

2. A comparison was made in the titrating stage between the standard method used today and the method proposed in this paper.

3. The results obtained by the writer's method were compared to the results of two standard gravimetric methods.

4. Although this paper was concerned with the determination of zinc, it is well to note that this method is applicable to any element forming the ammonium phosphate salt. Magnesium, manganese, cobalt, berrillium, cadmium, and uranium could therefore be determined by the method proposed in this paper.

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