

from iron and determined quantitatively, this method is applicable to the analysis of ores and other substances containing large amounts of arsenic.

7. The method may also be used for amounts of arsenic as small as 0.001 milligram, but the apparatus must be made much smaller than that described.

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[CONTRIBUTIONS FROM THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY, LABORATORY OF INORGANIC CHEMISTRY.]

ELECTROLYTIC DETERMINATION OF ZINC.

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Many methods have been proposed for the electroanalysis of zinc,¹ but unfortunately other experimenters have not always been able to get the degree of accuracy that the advocates of a particular method claim it is capable of giving. One of us, while doing some electrolytic determinations of zinc, invariably got high results by several methods. About the same time a paper appeared by Price² in which he stated that the values obtained by all electrolytic methods for zinc are too high. The object of this and the succeeding article was to determine, if possible, the magnitude and cause of the error.

The following methods were investigated:

1. The sodium acetate method.
2. The potassium oxalate method.
3. The sodium, or potassium hydroxide method.

The endeavor was made to follow the directions given in the literature as closely as possible while testing each method. Unfortunately, the instructions are sometimes incomplete, especially with regard to the factors, current density, current in amperes and area of cathode surface. It is not sufficient to give the current density, or the current in amperes alone. Two of these factors should be given from which the third can be calculated.

Over 200 determinations with the above methods have been made and it has been found that when the zinc was completely precipitated the results were invariably too high.

The effect of varying the following factors was also investigated:

1. Nature and concentration of the electrolyte.
2. Form and material of the cathode.
3. Current density.

¹ "Electro-analysis," E. F. Smith. *Elektroanalytische Schnellmethoden*, Fischer, "Die Chemische Analyse," Band 4-5.

² *Chem. News*, 94, 18 (1906), and 97, 89 (1908).

4. Temperature.

The following tables contain a few results that are typical of those obtained during this investigation:

Preparation of the Solution.—The zinc solutions were made by dissolving a weighed amount of pure zinc (0.2–0.4 gram) in 4 cc. of nitric acid (1.2) and evaporating almost to dryness, after the addition of about 2 cc. of concentrated sulphuric acid. The zinc sulphate was dissolved in water, the electrolyte in question added and the solution made up to the necessary volume. At the completion of the electrolysis zinc was always tested for in the remaining liquid by the methods given in the last part of this article.

In the following tables under "Kind of electrode" A is a rotating (500 revolutions to the min.) copper gauze. B is a platinum dish plated with copper. C is a platinum crucible on which the zinc was directly precipitated. D was a stationary platinum plate covered with a light deposit of copper. E was a stationary, silver gauze.

SODIUM ACETATE METHOD.

No.	Vol. of soln.	NaOAc in g.	HOAc drops, 30 per cent.	N. D. Amps.	Time in mins.	Kind of electrode.	Zinc taken.	Zinc obtained.	Error. Per cent.	Remarks.
33	60	3	6	3.5	25	A	0.2229	0.2250	+0.9	Temp. 40–60°
34	60	3	6	3.5	25	A	0.2229	0.2250	+0.9	"
37	60	8	15	2.5	20	A	0.2229	0.2245	0.7	"
38	80	3	15	5–6	30	B	0.2548	0.2552	0.2	Some Zn lost
39	60	3	6	3	30	A	0.2676	0.2690	0.5	T. 25
40	60	3	6	3	30	A	0.2676	0.2706	1.1	"
43	60	1	..	2	30	A	0.2278	0.2290	0.5	2 g. Na ₂ SO ₄ added
44	60	1	..	2	30	A	0.2440	0.2462	0.9	"
45	60	1	10	2	30	A	0.2482	0.2492	0.4	"
51	60	1	..	5–6	30	C	0.1645	0.1673	1.7	"
52	60	1	..	5–6	30	C	0.1780	0.1810	1.7	"
53	60	1	..	5–6	35	C	0.2080	0.2096	0.7	"

POTASSIUM OXALATE METHOD.

No.	Vol. of soln.	K ₂ C ₂ O ₄ in g.	N. D. Amps.	Time in mins.	Kind of electrode.	Zinc taken.	Zinc obtained.	Error. Per cent.	Remarks.
19	60	4	4	30	A	0.2393	0.2452	+2.5	Temp. 40–50°
20	60	4	4	30	A	0.2596	0.2632	1.4	"
21	110	4	3–5	35	A	0.2575	0.2608	1.3	Temp. 20°
22	110	4	3–5	35	A	0.2663	0.2705	1.6	"
29	60	10	5–6	60	A	0.2229	0.2242	0.6	60° cooled toward end
30	60	10	5–6	30	A	0.2229	0.2241	0.6	"

POTASSIUM HYDROXIDE METHOD.

No.	Vol.	KOH in g.	N.D.	Time in mins.	Kind of electrode.	Zinc taken.	Zinc found.	Error. Per cent.	Remarks.
3	125	5	5	30	A	0.3344	0.3397	+1.5	
4	125	5	5	30	A	0.3042	0.3120	2.5	
8	125	3	3.3	30	A	0.3164	0.3171	0.2	
10	125	3	3.3	30	A	0.3352	0.3363	0.3	Cooled towards end
11	125	7	0.6	180	D	0.3042	0.3170	4.0	
12	125	7	0.5	180	D	0.3939	0.4040	2.5	
13	125	0.3	0.5-5	25	A	0.2545	0.2569	1.1	KOH added a few drops at a time
14	125	0.3	0.5-5	25	A	0.2495	0.2519	0.9	
15	125	4	3.5	30	E	0.3464	0.3483	0.5	Cooled towards end
16	125	4	3.5	30	E	0.3487	0.3503	0.4	"

When the deposits are good the error is very much smaller than when they are loose and coarse-grained. One of these bad deposits was obtained and analyzed in the following manner: C. P. zinc was made the anode and a platinum plate the cathode in a sodium hydroxide solution. The current was made high enough to cause the zinc to tree on the cathode and fall off. As fast as this occurred the zinc was removed, washed with water and dried at 150°. About 3 grams were prepared in this manner. On further heating at 150° for 4 hours only a very slight increase in weight (0.6 mg.) took place. Two samples of 1 gram each were analyzed by the ammonium phosphate method and one by the carbonate² method. The per cent. of zinc obtained was 88.38, 88.13, 88.17, respectively. The causes for this error are discussed in the following article.

The Detection of Small Quantities of Zinc.—In order to determine when all the zinc is deposited it is necessary to have a convenient and accurate test. The delicacy of the tests for zinc is greatly reduced by the presence of large amounts of the salts of organic acids, *e. g.*, oxalates, where complex zinc salts may be formed, and doubtless many investigators have been misled because of the failure to take cognizance of this fact. Some of these tests have been investigated as follows:

A dilute solution of zinc sulphate (1 cc. contained 1 mg. Zn) was made by dissolving pure zinc in nitric acid, adding sulphuric acid and evaporating just to dryness. Solutions similar to those used in the electrolysis in contents and volume were then made and the delicacy determined by finding the least quantity of zinc that would give a precipitate with the

¹ Talbot, "Quantitative Chemical Analysis," page 64. Dakin, *Z. anal. Chem.*, 39, 273 (1900).

² Treadwell and Hall, "Analytical Chemistry," Vol. 2, page 117 (1904).

reagent in question. The results are summed up in the following paragraphs in which the concentrations of zinc are given in milligrams per liter.

Freshly prepared ammonium sulphide is not a good testing reagent for zinc at room temperatures. Ten mg. sometimes produces no turbidity. The delicacy is improved somewhat by raising the temperature to 50–60°. The objection to polysulphide is the precipitation of sulphur.

Hydrogen sulphide is a very satisfactory reagent. In a neutral solution of zinc sulphate 1 mg. of zinc may be detected at 50–70°. The limit at the same temperature is about 4 mg. if 100 cc. 0.90 ammonia are added. At 10°, with 40 cc. of 0.90 ammonia present, 10 mg. of zinc will not produce any turbidity for several minutes. Hydrogen sulphide, with or without ammonia, is not a delicate test for zinc when large amounts of potassium oxalate are present.

Potassium ferrocyanide is very satisfactory at a temperature between 50 and 70°. The solution should be made acid with 10–15 cc. of sulphuric acid (1.84) and potassium ferrocyanide added until the concentration is about 25 grams per liter. Under these conditions 0.5 mg. of zinc will produce a turbidity even in the presence of large amounts of the salts of organic acids.

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ON THE CAUSES OF THE HIGH RESULTS IN THE ELECTROLYTIC DETERMINATION OF ZINC.

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It has been shown in the previous article that the electrolytic determination of zinc by several methods is attended by high results. The cause must then be due to the presence of some foreign substance in the deposit such as:

1. Enclosure of liquid.
2. Salt precipitated with the zinc.
3. Hydrogen adsorbed or deposited as hydride.
4. Metal deposited with the zinc.
5. Zinc oxide or hydroxide deposited with the zinc.

The first part of this article consists of a detailed consideration of the above-named possibilities and the conclusion is finally reached that the formation of zinc oxide, or hydroxide, is the real cause of the high results. The second part deals with theoretical considerations.

The method of preparation of the solutions to be electrolyzed and the experimental conditions during the electrolysis were, except where otherwise stated, the same as in the preceding article.