

BaCl<sub>2</sub> is used, close to the theoretical amount must be added, for if added in excess it will form a scum itself.

This method cannot, of course, be used in the dry press process, where no water, or at least very little, is added, as the barium or other salts must be used in solution to do the required work.

*Treating the Water.*—When it is necessary to use a water that contains injurious soluble salts, it is simply necessary to precipitate them before adding the water to the clay.

Many good clays are being ruined by bad water, when it needs but a few hours of a chemist's time to rectify the trouble.

*Preventing Scum by Correct Drying.*—Scumming is often caused by incorrect drying of the ware. If ware containing soluble salts is placed in a drier and allowed to sweat slowly, the chances are all in favor of scummed ware, whereas, if the water is carried away from the surface of the ware as fast as it appears this will not often be the case.

It is a remarkable physical fact, not yet fully explained, that where a clay contains soluble salts, they are not deposited on the surface at all, or at least to a less degree, where the drying is steady and rapid, than where it is slow and discontinuous. It seems that rapid drying causes the water to come through the pore channels of the clay as through a filter and a sort of osmosis is set up, by which the saline matters are retained inside the mass of the clay, while the water escapes as vapor from the outside. But where the drying is slow the salts get through this barrier and arrive on the surface plentifully.

It is therefore only necessary that brickmakers, in order to avoid trouble from this source, build good driers and instal in them hygrometers by which their operation can be controlled.

Many other methods are used to prevent this trouble. Some of them, however, have but temporary effects.

One of these is to paint the surface of the scummed ware with oil, which for the time being covers up the scum. This is really practicing a fraud, for while the ware does not show scum when put into the building it shows up as soon as the oil evaporates.

Another method is to paint one surface of the unburned brick with a heavy oil or tar. This prevents evaporation from that surface, the salts being carried to the other surfaces. The oil or tar is burned off in the kiln, leaving a clean face. This, too, is only temporary unless the brick is vitrified, as otherwise the salts will be drawn to the clean surface after a few soakings.

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## THE ELECTROLYTIC DETERMINATION OF ZINC IN ORES.

By GEO. KEMMERER.

Received July 30, 1910.

The investigation was undertaken to ascertain if

the zinc content of an ore could not be accurately and quickly determined electrolytically.

The original plan was to separate the zinc from the other constituents of the ore, as zinc sulphide, by a method similar to the "Modified Waring;" this sulphide was then to be dissolved in a little acid, the hydrogen sulphide boiled out, made alkaline with sodium hydroxide and electrolyzed.

Numerous experiments with an ore of known zinc content, using an electrolyte containing from 7–10 grams of sodium hydroxide, gave high non-concordant results.

About this time E. B. Spear, E. E. Wells and B. Dyer<sup>1</sup> showed that several methods gave high results and Spear<sup>2</sup> stated that the high results were due to zinc oxide or hydroxide deposited with the zinc and suggests that a strong alkaline electrolyte might prevent this, but proved that it is theoretically impossible to deposit all the zinc from such an electrolyte. Harrison Hale<sup>3</sup> determined the zinc content of a pure blend, using an electrolyte containing 15 grams of sodium hydroxide. His results were not high and the average of a large number of determinations was very close to the gravimetric results.

*Experimental.*—The electrolytic cell used consisted of a cylindrical nickel gauge cathode which fitted loosely into a 150 cc. Jena beaker, and a revolving propeller-shaped anode.

The cathode surface was about 160 sq. cm. while the anode was rotated about 600 times per minute.

Weighed pieces of C. P. zinc were dissolved with nitric acid in a 180 cc. flask, 2 cc. of sulphuric acid added and evaporated to dense fumes of sulphur trioxide. After cooling, the contents of the flask were rinsed into a 150 cc. beaker, diluted to 100 cc. and stick sodium or potassium hydroxide added. This heated the solution nearly to boiling and it was electrolyzed at once.

When the deposition was complete the cathode was removed without opening the switch and plunged into a large beaker of water. It was then dried with absolute alcohol, and ether, which had been distilled over sodium, heated to 70–100°, cooled and weighed at once.

The gauze electrodes cool quickly and it is important to weigh at once for on standing the deposits gain in weight.

	Weight of deposit.		Weight after standing in desiccator.	Gain.
1.....	0.2501	Over night.....	0.2505	0.0004
2.....	0.2500	Two hours.....	0.2504	0.0004
3.....	0.2517	One hour.....	0.2521	0.0004

After the electrolysis the solution remaining was always tested for zinc by acidifying with dilute sulphuric acid, cooling to 60° and adding 50 cc. of 10 per cent. solution of potassium ferrocyanide. This test

<sup>1</sup> J. Am. Chem. Soc., **32**, 530.

<sup>2</sup> Ibid., **32**, 533.

<sup>3</sup> Thesis, U. of P., 1908.

as shown by E. B. Spear, E. E. Wells and B. Dyer<sup>1</sup> was found to produce a turbidity with 0.5 mg. of zinc in 200 cc. of solution.

After weighing the deposits, the zinc was dissolved from the nickel cathode in 2-3 per cent. sulphuric acid. By this treatment the cathode loss was kept below 0.5 mg., but it gradually darkened due to a trace of lead in the zinc. After ten to twenty determinations the black deposit was removed by pouring a little nitric acid over the electrode.

With an electrolyte containing from 7-10 grams of sodium hydroxide the results ran as much as 0.9 per cent. high and were not concordant.

When the alkali was increased to 20-25 grams the following results were obtained:

	A.	V.	Time.	Zinc taken.	Zinc found	Error.
1.....	6	4.4	15	0.1762	0.1759	-0.0003
2.....	6	4.2	15	0.2099	0.2019	0.0000
3.....	5	3.8	15	0.3180	0.3184	+0.0004
4.....	5.2	3.8	15	0.3740	0.3743	+0.0003
5.....	5	4.0	15	0.2412	0.2410	-0.0002
6.....	5	4.0	10	0.2502	0.2501	-0.0001
7.....	5	4.2	14	0.2502	0.2500	-0.0002
8.....	5	4.2	15	0.2502	0.2496	-0.0006
9.....	6	4.4	20	0.2149	0.2147	-0.0002
10.....	6	4.4	20	0.2149	0.2144	-0.0005

The deposits were all a beautiful bluish white and in every case the remaining solution showed no zinc present by the ferrocyanide test.

These results seem to justify the application of the method to ore analysis, so a simple carbonate ore was chosen, the zinc content of which had been determined several times before this work was started. It contained 42.35 per cent. zinc, 9 per cent. iron, no lead. It was treated by the modified Waring method given in Low's "Technical Methods of Ore Analysis" as follows:

"After decomposing the weighed sample by acids alone, or aided by fusion, as the case may require, all the zinc is to be brought into solution as sulphate. If nitric acid was used in the decomposition, all traces of it must be expelled by evaporation with hydrochloric and sulphuric acids successively, or by two evaporations with sulphuric acid, finally to abundant evolution of SO<sub>3</sub> fumes. Dissolve the mass in 25-40 cc. of water and add sufficient sulphuric acid to bring the free acid in the solution up to 10 or 15 per cent. Introduce a piece of heavy sheet aluminum and boil 10 minutes, or to complete reduction. Filter and wash through a filter containing a piece of aluminum into a beaker containing a stirring-rod or strip of the same metal, cool, add a drop of methyl orange, and neutralize carefully with sodium bicarbonate to a light straw color. Add, dropwise, dilute formic acid (20 per cent. strength) until the pink color is just restored, then 5 drops more. (Dilute hydrochloric acid, 1 part strong acid to 5 parts water, may be substituted for formic acid when ammonium thiocyanate is to be introduced.) Dilute to about 100 cc. for each 0.1 gram of

zinc possibly present, add, if much iron is present, 2-4 grams ammonium thiocyanate, remove the strip of aluminum, heat nearly to boiling, and saturate with hydrogen sulphide. Allow the pure white zinc sulphide to subside for a few minutes, then filter and wash with hot water."

The zinc sulphide was carefully washed with hot water and dissolved on the filter in a little hot dilute hydrochloric acid. To this solution in the 400 cc. beaker in which the sulphide was originally precipitated 2 cc. of sulphuric acid were added and the whole allowed to evaporate until most of the sulphuric acid was driven off. The zinc sulphate was then rinsed into a 150 cc. beaker diluted to 100 cc., 25 grams of sodium hydroxide added and electrolyzed.

The nickel gauze cathode previously described was used and a current of 6 amperes at a pressure of 4.4 v. was allowed to flow for 15 minutes, while the anode revolved about 600 times per minute.

The results were concordant, but always about 0.3 per cent. high.

Several of these deposits were dissolved, the iron determined colorimetrically and found to be equal to 0.0014-0.0016 gram of iron. When using a 1/2 gram sample of ore this would equal 0.3 per cent.

The sodium hydrate was carefully tested and did not contain more than a trace of iron, so that this large amount must have been carried down with the zinc sulphide.

After numerous experiments it was determined that if 4-5 drops of concentrated hydrochloric acid in place of 5 drops of 1-6, were added to the neutral solution before precipitating the zinc sulphide, that in the presence of ammonium sulphocyanide all the zinc was precipitated as sulphide free from iron.

With this modification the ore containing 42.35 per cent. of zinc, gave the following electrolytic results:

Weight of ore.	A.	V.	Time, min.	Zinc found.	%.
0.5000	5	3	15	0.2116	42.32
0.5007	6	4.2	15	0.2114	42.22
0.4995	6	4.2	15	0.2107	42.18
					Average, 42.24

The next ore was a standard sent out by the New Jersey Zinc Company. The results by various chemists ran as follows: 35.5, 35.57, 35.5, 35.2, 35.5, 35.67, 35.87, 35.7; average, 35.56.

#### ELECTROLYTIC METHOD.

Wt. ore.	A.	V.	Time, min.	Zinc found.	%.
0.5002	6	4.2	15	0.1792	35.83
0.5003	6	4.2	15	0.1783	35.64
0.5002	6	4.2	15	0.1794	35.86
0.5009	6	4.2	15	0.1790	35.73
0.5007	6	4.2	15	0.1790	35.77
					Average, 35.77

Each of these deposits was tested for iron and not more than a trace was found.

<sup>1</sup> J. Am. Chem. Soc., 32, 530-3:

All the results obtained for this ore included those corrected for iron are as follows:

35.73, 35.74, 35.74, 35.57, 35.67, 35.83, 35.64, 35.86, 35.77; average, 35.73.

#### CONCLUSIONS.

This work has proven that zinc can be accurately determined electrolytically; that the results are not high if the electrolyte contains from 20–25 grams of sodium hydroxide and with a current of  $N. D_{100} = 3.1$  A, all the zinc can be deposited; that this method which is shorter than the usual gravimetric procedure gives results fully as accurate.

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### THE DETERMINATION OF FREE ACID IN HYDROGEN PEROXIDE SOLUTIONS.

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Received July 25, 1910.

Sometime ago in the examination of drug samples, I had occasion to analyze practically all of the different makes of hydrogen peroxide to be found on the Kentucky market, and one of the determinations to be made in the analysis of this preparation is the determination of the free acid present.

The U. S. Pharmacopeia, which is recognized by both Federal and State Food and Drugs Acts, as the standard for drugs, defines this preparation as being:

"A slightly acid, aqueous solution of hydrogen dioxide, which should contain, when freshly prepared, about 3 per cent. by weight of absolute hydrogen dioxide, corresponding to about 10 volumes of available oxygen."

Among other tests for purity for this preparation, it states that if to 25 cc. of the solution, 5 cc. of tenth normal potassium hydroxide V. S. be added, and the mixture be evaporated to about 10 cc. and 3 drops of phenolphthalein T. S. be added, not less than 2.5 cc. of tenth normal sulphuric acid should be required to destroy the red color of the solution after continued boiling (limit of free acids).

This does not appear at first glance, to be a difficult determination, but after a few trials, we found that it did not yield correct results, and upon examination it developed surprising possibilities for trouble.

Acids occur in hydrogen peroxide solutions for two reasons: first, as an aid in preservation; second, in order to remove the barium from which the hydrogen peroxide is prepared. Sulphuric, hydrochloric, phosphoric, oxalic, benzoic acids, etc., are the acids likely to be present.

Acetanilid is used in a large number of hydrogen peroxide preparations on the market, as an additional preservative.

The official method for determining the free acid was soon found to be unreliable, giving high results, so in order to locate the source of trouble, the author

prepared a 3 per cent. hydrogen peroxide solution, using perhydrol, a neutral 30 per cent.  $H_2O_2$  solution. This perhydrol was tested for sulphuric, phosphoric, hydrochloric, oxalic acids, etc., and was found to be entirely free from such acids.

The 3 per cent. aqueous solution of hydrogen peroxide thus prepared was used as a basis for preparing the following solutions containing known amounts of sulphuric, hydrochloric, phosphoric, and benzoic acids.

*Solution "A."*—This solution was made by adding sufficient sulphuric acid to the 3 per cent. solution of  $H_2O_2$  so that 25 cc. of the solution thus prepared were exactly equivalent to 2.5 cc. of  $N/10$   $H_2SO_4$ , which is the limit of acid allowed in the U. S. P. article.

*Solution "B."*—This was prepared in the same way as solution "A", using hydrochloric acid. 25 cc. of this solution were equivalent to 2.5 cc.  $N/10$  HCl.

*Solution "C."*—Prepared as in solution "A," 25 cc. of which were equivalent to 2.5 cc.  $N/10$   $H_3PO_4$ .

*Solution "D."*—25 cc. of solution were equivalent to 2.5 cc.  $N/10$  benzoic acid. This solution was prepared as a type of the organic acids likely to be met with in some preparations of hydrogen peroxide found on the market.

*Solution "E."*—This solution was prepared by dissolving 0.040 gram acetanilid, m. p.  $114^\circ C$ . (cor.), in a sufficient amount of the hydrogen peroxide solution to make 100 cc. corresponding to  $\frac{3}{16}$  grain acetanilid per fl. oz., the strength ordinarily used in preserving peroxide solutions.

Solution "E" was prepared to determine what effect the presence of acetanilid would have on the methods used. The solutions thus prepared were analyzed by the following methods:

*First Method.*—The U. S. P. method, which was carried out as follows: 25 cc. of the solutions representing 2.5 cc.  $N/10$  acid were treated with 5 cc.  $N/10$  KOH and evaporated in porcelain to about 10 cc., and three drops of phenolphthalein added and the excess of alkali titrated back, using tenth normal sulphuric acid, and boiling.

*Second Method.*—A modification of the U. S. P. method was used as follows: 25 cc. of the solution equivalent to 2.5 cc. tenth normal acid were treated with 5 cc. tenth normal potassium hydroxide and evaporated on a water bath in a large platinum dish, kept covered with a watch glass, to avoid loss by the rapid disengagement of gas until effervescence ceased and all  $H_2O_2$  was decomposed. Phenolphthalein was then added and the excess of alkali titrated back, using tenth normal sulphuric acid and boiling off  $CO_2$  after each addition of acid.

*Third Method.*—25 cc. of the solution, equivalent to 2.5 cc. tenth normal acid, were titrated in the cold, with tenth normal potassium hydroxide, using phenolphthalein as indicator.