

the rate of stirring, as it was too great for even an approximate counting of the number of turns per minute. This is easily explained when we consider that the force propelling the liquid increases with the current passing through the solution and also with the increase of strength of the magnetic field. Thus when the cell and the coil are connected in series, this force would be approximately proportional to the square of the current. As a matter of fact the rate of stirring would not rise as fast as this, on account of the rapid increase of friction in the liquid with its increasing speed.

It should also be mentioned that the bottom of the cell is preferably not flat, but V-shaped as shown in the cut, in order that a small amount of mercury may form a complete ring on it. If 40 g. of mercury be used, the total weight of the apparatus will be about 100 g. and so within the capacity of an ordinary balance.

Since the requirement of a motor has been one of the most objectionable features of the rapid methods for electroanalysis, it is hoped that this apparatus by avoiding the use of all moving parts, will facilitate the introduction of these methods into practical work.

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## THE RAPID DETERMINATION OF ZINC BY ELECTROLYSIS.

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A great many methods have been proposed for the determination of zinc with the use of stationary electrodes; the use of solutions containing oxalates, citrates, acetates, lactates, formates, cyanides and phosphates being recommended by various authors. The use of a potassium zincate electrolyte is strongly recommended by Amberg<sup>2</sup> who obtained unsatisfactory results with the sodium zincate electrolyte recommended by Millot<sup>3</sup>, v. Foregger<sup>4</sup>, and others. Spitzer<sup>5</sup> has shown that the sodium zincate method gives good results with a nickel gauze cathode, and that while Amberg required 40 g. of KOH for 0.5 g. zinc, the amount of NaOH required is only a few g., barely enough to give a clear solution.

With a rotating anode, using a silver-plated platinum dish as cathode, Exner,<sup>6</sup> Ingham,<sup>7</sup> and Miss Langness,<sup>8</sup> have obtained concordant results

<sup>1</sup> Also published in *Z. angew. Chem.*

<sup>2</sup> *Ber.*, **36**, 2489 (1903).

<sup>3</sup> *Bull. soc. chim.*, **37**, 339.

<sup>4</sup> *Dissertation Bern.*, 1896.

<sup>5</sup> *Z. Elektrochem.*, **11**, 391.

<sup>6</sup> *This Journal*, **25**, 896.

<sup>7</sup> *Ibid.*, **26**, 1269.

<sup>8</sup> *Ibid.*, **29**, 459.

from a sodium zincate solution containing from 2-12 g. NaOH per 100 cc. Exner and Ingham obtained satisfactory though coarsely crystalline deposits from an acetate solution, and Ingham has also recommended the use of a formate electrolyte. Medway<sup>1</sup> has determined zinc from the well known double-oxalate electrolyte, using a rotating cathode. Price and Judge<sup>2</sup> have obtained results at low temperatures with a simple solution of  $ZnSO_4$ , containing sodium sulphate. But in order to precipitate the last traces of zinc they found it necessary to cool with ice the funnel containing the solution. Methods for use with the mercury cathode have also been worked out, but will not be considered here.

In the course of a few preliminary experiments on the rapid determination of zinc with my apparatus for electromagnetic rotation of the electrolyte, I found that an acetate solution yielded a coarsely crystalline deposit of metal which, although adherent enough for washing in a dish electrode, was easily brushed off from the more exposed surface of the gauze cathode. Furthermore, a very high voltage was required (17-19 volts for a current of 4-5 amperes) and the electrolyte soon began to boil violently. The formate and oxalate electrolytes were not tried, as it seemed probable that their behavior would be similar to that of the acetate solution. The use of sodium hydroxide was found to give fine precipitates and to require a uniformly low voltage; it was therefore chosen for this investigation, and about 8 g. of alkali were used per 100 cc. of electrolyte.

In all experiments where the electrolyte was rotated (except those in Table 3) a cylindrical cathode of nickel gauze was used; in most of the others a nickel dish was used. After weighing, the zinc was removed from the cathode by treatment with dilute sulphuric acid. The amount of nickel dissolved with the zinc appeared to depend on the strength of the acid and the length of the treatment, and varied in extreme cases from 0.0 to 10.4 mg. The average loss was about 1 mg. per determination. The height of the cathode was 5 cm. in each case, and its diameter was such that it just fitted inside the beaker used.

The anode was a spiral of 1 mm. platinum wire; it was noticed that it slowly became brown by use, so after being used 5 times it was washed, boiled in nitric acid containing oxalic acid to remove any lead peroxide which might be the cause of the color, dried at 100-110° and weighed. The color did not appear to be affected by the acid treatment. After further use as anode in 20 determinations, it was washed again with water, dried and weighed, when a loss of 0.8 mg. was found. Without further treatment it was used as anode in 46 more determinations, then washed again, dried and weighed. This time a loss of 0.7 mg. was found. The anode was then boiled with a mixture of nitric and oxalic acids,

<sup>1</sup> Z. anorg. Chem., 42, 114; Am. J. Sci., 18, 180.

<sup>2</sup> Chem. News, 94, 18, (1906).

washed, dried and weighed. Its color remained unaltered but it had apparently lost 0.2 mg. During the heating with the acid mixture, it was noticed that, after removing the flame, bubbles of gas were continually disengaged from the wire for some time. As there was found to be practically nothing dissolved, I thought that the platinum oxide, whose presence has been offered as an explanation of the catalytic action of platinum-black, might possibly be the cause of the discoloration.

This oxide, if present, should dissociate at a relatively low temperature, so the spiral was quickly passed through the flame of a blast-lamp. The brown color disappeared at once, leaving the pure white platinum, whose surface appeared a little roughened in comparison to the polished surface of the upper part of the wire, which was new at the beginning of the series of determinations. The spiral was now heated to redness, cooled, and weighed. The loss in weight after heating was found to be 0.5 mg. Another washing with water and alcohol and drying, failed to change the weight. The loss therefore, could not be caused by the difference in the film of water on the wire before and after ignition. Senter<sup>1</sup> has recently investigated the behavior of platinum as anode in acid and alkaline solutions, at a potential however, below that at which gaseous oxygen is evolved. He believes that under these conditions, platinum goes into solution in the presence of acids, as an oxide, while in alkaline solutions he could find no evidence of an oxide in the solution. It would appear possible that in this case the oxide formed by the  $\text{SO}_4$  ions at the anode would be prevented from dissolving by the alkali, and so remain attached to the anode<sup>2</sup>. At least, the rate of solution of the anode appears to be so small as to be negligible in ordinary work.

The cover-glasses and sides of the beaker were washed down with a fine spray of water 5 minutes before the end of the electrolysis, or, in cases where the current was reduced for the second part of the analysis, the washing took place immediately after the reduction of the current.

The experiments 1-3, Table 1, and all in Table 4 were conducted in a 150 cc. beaker at a dilution of about 125 cc. and the solution was not cooled. In all other experiments with the magnetic rotation, the electrolyte had a volume of about 100 cc. and was contained in a 125 cc. beaker. This smaller beaker was surrounded by a spiral of lead pipe through which water could be passed, if desired, in order to cool the electrolyte.

On completion of each determination, the current was reduced to about

<sup>1</sup> Trans. Faraday Soc., 2, 142 (1906), (from an abstract in the J. Chem. Soc., 92, 68 (1907)).

<sup>2</sup> Since this article was written my attention has been called by an abstract in the current number of the J. Chem. Soc., 1907, [2] 698, to an article on the electrolytic oxidation of platinum by C. Marie, in Compt. rend., 145, 117 (July 8, 1907). Marie shows that the oxide formed liberates I from  $\text{KI} + \text{HCl}$ , therefore, he considers it to be a peroxide.

one ampere and the alkaline liquid was drawn off and replaced by distilled water, without breaking the current, care being taken not to expose the zinc deposit to the air till most of the alkali had been removed. The first 200 cc. of the alkaline liquid were reserved for testing, and the washing finished in the usual manner. After rinsing with alcohol the cathode was dried at 100-120°, cooled in a desiccator and weighed.

The alkaline liquid was acidified with sulphuric acid and tested for zinc by the addition of 3-4 cc. of a 10 per cent. solution of potassium ferrocyanide. The test must be allowed to stand 10 minutes if no precipitate appears before that time, as with small amounts of zinc the precipitation does not take place at once. Under these conditions 0.2 mg. of zinc causes a distinct cloudiness in 200 cc. of the solution.

Exner and Ingham obtained concordant results with 5 amperes at 5-6 volts in 15-20 minutes. The average of the results on the same solution seems to have been assumed as correct. In no case do they record that they tested the alkaline liquid remaining after the determination, and the same remark holds true for the later work of Miss Laugness and of Medway.

The experiments in Tables 1 and 2 show that one can get concordant results under varying conditions, which results, nevertheless, are uniformly low. In every case zinc could be detected in the liquid drawn off at the close of the determination. If the testing of this liquid be neglected it would seem that the precipitation of the metal was complete at the end of 35-40 minutes.

TABLE 1.

Electrolysis with Magnetic Rotation,<sup>1</sup> Without Cooling. Nickel Gauze Cathode.

| No. | Solution | Zinc found | Error (mg.) | Amp. | Volt. | Time (min.) | Temperature at start | Temperature at end | Zinc found in solution after electrolysis. |
|-----|----------|------------|-------------|------|-------|-------------|----------------------|--------------------|--|
| 1   | A        | 0.1965     | -1.5        | 7.4  | ..    | 33          | cold                 | ...                | trace                                      |
| 2   | A        | 0.1968     | -1.2        | 5.9  | 4.3   | 34          | warm                 | ...                | trace                                      |
| 3   | A        | 0.1966     | -1.4        | 5.5  | 4.4   | 40          | warm                 | ...                | trace                                      |
| 4   | B        | 0.0912     | -0.9        | 4.3  | ..    | 35          | cold                 | 60°                | trace                                      |
| 5   | B        | 0.0914     | -0.7        | 4.5  | ..    | 50          | cold                 | ..                 | trace                                      |
| 6   | B        | 0.0915     | -0.6        | 6.2  | 4.    | 50          | cold                 | 90°                | (test lost)                                |
| 7   | B        | 0.0916     | -0.5        | 6.5  | 3.6   | 50          | cold                 | 91°                | none                                       |

TABLE 2.

Electrolysis of Solution C with Cooling and Magnetic Rotation of the Electrolyte Nickel Gauze Cathode. Electrolysis Started at Room Temperature.

| No. | Zinc found | Error (mg.) | Amp. | Volt. | Time (min.) | Final temperature | Zinc found in solution after electrolysis |
|-----|------------|-------------|------|-------|-------------|-------------------|---|
| 1   | 0.1770     | -15.8       | 4.4  | 4.4   | 10          | 30°               | much                                      |
| 2   | 0.1920     | - 0.8       | 4.5  | 4.6   | 15          | 37°               | trace                                     |
| 3   | 0.1916     | - 1.2       | 4.4  | 4.6   | 25          | 36°               | "   |
| 4   | 0.1922     | - 0.6       | 4.5  | 4.2   | 31          | 44°               | "   |
| 5   | 0.1925     | - 0.3       | 5.3  | 4.3   | 45          | 50°               | "   |
| 6   | 0.1932     | + 0.4       | 4.5  | 4.1   | 51          | 39°               | bare trace                                |

<sup>1</sup> Using my apparatus for rapid analysis by electrolysis, as described in the preceding paper.

Experiments 4-7 (Table 1) show that with about 5 amperes most of the zinc was precipitated at the end of 35 minutes, but the last traces required 25 minutes more for their removal. The experiments in Table 2 show that under other conditions almost all of the zinc is precipitated at the end of 15 minutes but the last traces are difficult to remove as long as the current density is so high. In comparison with these results the later experiments in Table 5 show the conditions under which the metal may be completely precipitated in 35 minutes.

As it seemed probable that the precipitation of zinc by means of the rotating anode had not been complete in the time given by Ingham and Exner, a series of qualitative experiments were undertaken with a rotating anode and a nickel dish as cathode. For each experiment about 0.2

TABLE 5.  
Qualitative Experiments with Rotating Anode and Nickel Dish Cathode.  
Electrolysis Started at Room Temperature.

| No. | Amp. | Volt. | Time (min.) | Final Temperature | Zinc in solution after electrolysis. |
|-----|------|-------|-------------|-------------------|--------------------------------------|
| 1   | 4.8  | 4.8   | 20          | 40°               | much                                 |
| 2   | 5.   | ...   | 17          | ...               | much                                 |
| 3   | 5.3  | 4.5   | 30          | ...               | trace                                |
| 4   | 5.3  | 5.    | 35          | 53°               | trace                                |
| 5   | 4.9  | 4.8   | 47          | ...               | bare trace                           |
| 6   | 4.9  | 4.8   | 57          | 52°               | bare trace                           |

g. zinc as sulphate was used, and 8 g. of sodium hydroxide. After electrolysis the alkaline solution was drawn off and replaced by distilled water without breaking the current. The results are given in Table 3, and indicate that the precipitation with the rotating anode, under the conditions given by the above-named investigators (except that a nickel dish was used instead of a silver-plated platinum dish) could scarcely be complete in less than an hour, and that in this respect the behavior of the solution is the same with the rotating anode as with the magnetic rotation. The failure to test the liquid remaining at the close of the analysis is one which occurs in very many published investigations of electro-analytical methods, and which can not be too strongly condemned.

A very essential condition in the deposition of zinc seems to be the temperature at which the electrolysis takes place. The importance of this factor in alkaline solutions is shown by the well-known fact that such solutions dissolve zinc very readily, and the more readily, the higher their temperature. In the work of Exner, Ingham and Miss Langness, the temperature was not observed nor its influence considered, although with the current and voltage used the solution must have become quite warm. Amberg, working with potassium hydroxide solutions of much higher concentration, found that if the solution was kept continually at a temperature above 60°, the metal had a strong tendency to precipitate in a spongy form. He found that at 40° the precipitate was of good quality

but that there was no advantage in keeping the solution at that temperature. He, therefore recommends that the solution be heated to 60-70° at the start and then allowed to cool off to room temperature. Spitzer<sup>1</sup> did not study the effect of the temperature, but contented himself with showing that it was unnecessary to heat the solution and that the precipitate obtained at room temperature was very satisfactory. Jene<sup>2</sup>, on the contrary recommends a temperature of 50° for the determination.

My experience is in accord with that of Amberg, that at high temperatures the zinc often deposits in a spongy form, and I also find that, at high temperatures, it is very difficult to deposit the last traces of the zinc. With the use of the higher current-density required for rapid deposition, there occurs another difficulty in that the zinc appears to redissolve much more readily than it does at the same temperature with lower current-densities. Therefore, for about 0.2 g. zinc I have found it advantageous to use a current of about 4.5 amperes for 15 minutes, and then continue the electrolysis 15-20 minutes with 1-2 amperes<sup>3</sup>.

During this latter interval the temperature also falls perceptibly, as the heat-evolution is much smaller. The experiments in Table 2 show that little, if anything, is gained by using the strong current more than 15 minutes, as at the end of that time all but about 1 mg. of the zinc has been precipitated. The temperature also rises steadily in spite of the cooling. If, however, at the end of the first 15 minutes the current is

TABLE 4.

Electrolysis of Solution A with Magnetic Rotation of the Electrolyte, but without Cooling. Nickel Gauze Cathode. Current Reduced during latter Part of the Analysis. Electrolysis Started at Room Temperature.

| No. | Zinc found | Error mg. | Amp.     |          | Volt.    |          | Time (min.) |          |       | Zinc found in solution after electrolysis |
|-----|------------|-----------|----------|----------|----------|----------|-------------|----------|-------|---|
|     |            |           | <i>a</i> | <i>b</i> | <i>a</i> | <i>b</i> | <i>a</i>    | <i>b</i> | total |   |
| 1   | 0.1983     | +0.1      | 5.       | 1.2      | 5.7      | 3.5      | 15          | 22       | 37    | none                                      |
| 2   | 0.1992     | +1.0      | 5.       | 1.3      | ..       | ..       | 15          | 10       | 25    | bare trace                                |
| 3   | 0.1978     | -0.4      | 5.       | 1.2      | 3.9      | 2.8      | 15          | 20       | 35    | none                                      |
| 4   | 0.1909     | -7.3      | 5.       | 1.2      | ..       | 2.7      | 17          | 16       | 33    | much                                      |
| 5   | 0.1988     | +0.6      | 5.       | 1.2      | ..       | 2.8      | 15          | 20       | 35    | none                                      |
| 6   | 0.1914     | -6.8      | 4.3      | 1.2      | 4.1      | 2.6      | 18          | 22       | 40    | much                                      |

reduced to 1 to 2 ampere and the electrolysis continued for about 20 minutes, all the zinc is removed, as shown by experiments 1, 3 and 5 in Table 4, and by Table 5. Experiments 2, 4 and 6 (Table 4) show that the reduction of current-density alone, without cooling, does not always give reliable results, while with both cooling and reduction of current-strength (Table 5) the results are very reliable. In all cases where the current used for electrolysis was reduced to 1 to 2 ampere, the current in the

<sup>1</sup> Z. Elektrochem., 11, 391.

<sup>2</sup> Chem.-Ztg. 1905, 803; Z. Elektrochem., 12, 388, (1906).

<sup>3</sup> In the tables the conditions during the first interval are marked *a*, those during the second, *b*.

solenoid was kept at 4.5-5 amperes by means of an auxiliary circuit, and the rotation of the liquid remained quite vigorous. When only 0.1 g. of zinc is present, the reduction of the current seems to be less necessary (Table 6).

TABLE 5.

Electrolysis of Solution C with Cooling and Magnetic Rotation of the Electrolyte. Current Reduced during Second Part (*b*) of each Determination. Nickel Gauze Cathode. Electrolysis Started at Room Temperature.

| No. | Zinc found | Error (mg.) | Amp.     |          | Volt.    |          | Time (min.) |          |       | Final temperature | Zinc found in solution after electrolysis |
|-----|------------|-------------|----------|----------|----------|----------|-------------|----------|-------|-------------------|---|
|     |            |             | <i>a</i> | <i>b</i> | <i>a</i> | <i>b</i> | <i>a</i>    | <i>b</i> | total |                   |   |
| 1   | 0.1926     | -0.2        | 4.5      | 1.1      | 4.6      | 3.2      | 17          | 23       | 40    | 23°               | none                                      |
| 2   | 0.1930     | +0.2        | 4.5      | 1.2      | 4.6      | 3.1      | 20          | 15       | 35    | 31°               | none                                      |
| 3   | 0.1934     | +0.6        | 4.5      | 1.2      | ..       | ..       | 17          | 17       | 34    | ..                | bare trace                                |
| 4   | 0.1926     | -0.2        | 4.7      | 1.7      | 4.5      | 3.3      | 18          | 18       | 36    | 28°               | none                                      |
| 5   | 0.1944     | +1.6        | 4.7      | 1.7      | 4.2      | 3.6      | 15          | 20       | 35    | 25°               | none <sup>1</sup>                         |
| 6   | 0.1930     | +0.2        | 4.4      | 1.7      | 4.3      | 3.3      | 15          | 17       | 32    | 35°               | none                                      |
| 7   | 0.1926     | -0.2        | 4.4      | 1.7      | 4.3      | 3.5      | 15          | 17       | 32    | 26°               | bare trace                                |
| 8   | 0.1944     | +1.6        | 4.5      | 0.9      | 4.5      | 3.       | 25          | 17       | 42    | 22°               | none <sup>1</sup>                         |
| 9   | 0.1930     | +0.2        | 4.5      | 0.9      | 4.3      | ..       | 15          | 17       | 32    | 28°               | bare trace                                |

<sup>1</sup> Nos. 5 and 8 were precipitated on a rough cathode, were dark-colored and probably oxidized.

TABLE 6.

Electrolysis of Solution B with Cooling and Magnetic Rotation of the Electrolyte. Nickel Gauze Cathode. Electrolyte at Room Temperature at the Beginning of each Determination.

| No. | Zinc found | Error (mg.) | Amp. | Volt. | Time (min.) | Final temperature | Zinc found in solution after electrolysis |
|-----|------------|-------------|------|-------|-------------|-------------------|---|
| 1   | 0.0902     | -1.9        | 5.3  | 4.6   | 30          | 52°               | trace                                     |
| 2   | 0.0908     | -1.3        | 4.3  | 4.4   | 25          | 41°               | trace                                     |
| 3   | 0.0920     | -0.1        | 4.3  | 4.1   | 30          | ..                | none                                      |
| 4   | 0.0924     | -0.3        | 4.5  | 4.5   | 30          | ..                | none                                      |
| 5   | 0.0920     | -0.1        | 4.5  | ..    | 30          | ..                | none                                      |
| 6   | 0.0924     | -0.3        | 4.5  | ..    | 32          | 47°               | none                                      |
| 7   | 0.0910     | -1.1        | 4.5  | ..    | 35          | 45°               | trace                                     |
| 8   | 0.0912     | -0.9        | 4.4  | 4.6   | 32          | 38°               | none                                      |

TABLE 7.

Electrolysis of Solution A with Nickel Dish as Cathode without Cooling or Rotation of Electrolyte. Solution Heated to 40-60° before Electrolysis.

| No. | Zinc found | Error (mg.) | Amp.  | Volt. | Time (min.) | Zinc found in solution after electrolysis |
|-----|------------|-------------|-------|-------|-------------|---|
| 1   | 0.1973     | -0.9        | 1.05  | 3.15  | 165         | none                                      |
| 2   | 0.1986     | +0.4        | 1.1   | 2.95  | 165         | none                                      |
| 3   | 0.1978     | -0.4        | 0.95  | 3.5   | 180         | none                                      |
| 4   | 0.1985     | +0.3        | 0.95  | ..    | 180         | none                                      |
| 5   | 0.1990     | +0.8        | 0.8-1 | ..    | 135         | none <sup>1</sup>                         |

<sup>1</sup> Nickel gauze cathode used.

To show that the rapid method gives results agreeing with those from the ordinary determination, the 5 analyses given in Table 7 were made, using a nickel dish as cathode. The mean of these results is 0.1982 g.

zinc; the mean of the only rapid analyses of solution A where the precipitation was complete (Nos. 1, 3 and 5, Table 4) is 0.1983 g. In the case of the other solutions (B and C) the mean of all the determinations where complete precipitation was assured (except Nos. 5 and 8, Table 5), was assumed to be the correct value and the error calculated on this basis.

The deposit was generally of a fine steel-gray color and metallic luster. It was noticed that the character of the precipitate is very dependent on the surface of the cathode; on one cathode which had been treated for a long time with acids and thus had its surface roughened, the precipitate was always of a dark color and had a tendency to oxidize, as shown by experiments 5 and 8 (Table 5), where this cathode was used.

#### Summary.

1. With electromagnetic rotation of the electrolyte 0.1 g. zinc can be completely precipitated by 4.5 amperes in 30 minutes on a nickel gauze cathode. About 8 g. of sodium hydroxide should be used, and the electrolysis should be conducted at as low a temperature as possible.

2. For quantities of zinc up to 0.2 g. the current-strength should be 4.5 amperes for 15 minutes and then about 1.5 amperes for 20 minutes. (Other conditions are the same as in 1).

3. The testing of the liquid remaining after electrolysis is essential.

4. It is highly improbable that complete precipitation of 0.2 g. zinc can be obtained with 5 amperes in 15-20 minutes, as stated by Exner and Ingham. From the results obtained it would also seem improbable that the concordant results obtained by Miss Languess with 10-13 amperes in 3 minutes represent complete precipitation.

The work on which this and the preceding articles are based was done during the spring and summer of 1907 in the electro-chemical laboratory of the Royal Technical High School at Berlin. I take this occasion to thank Professors von Knorre and Peters, and Dr. Arndt, of that laboratory, for their interest in this work and the many kindnesses shown me during its course.

UNIVERSITY OF MINNESOTA,  
Minneapolis, Minn.,  
Aug. 20, 1907.

### CLAY ANALYSIS—AN EXAMINATION OF THE RESIDUE LEFT AFTER VOLATILIZATION OF THE SEPARATED SILICA WITH HYDRO- FLUORIC AND SULPHURIC ACIDS.

First Paper.

By W. R. BLOOR.

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It has been generally assumed that the residue left after volatilization of the separated silica with hydrofluoric and sulphuric acids in the ordinary process of clay analysis is composed of iron and aluminium oxides and as such is to be added in with them.