

Honigmann method. Attention may also be called to the fact that while in the methods of Honigmann, Orsat, and Hempel, the same potassium hydroxide is used repeatedly, in the Bunte and Elliot methods the reagent cannot be used twice, these methods being thus extremely wasteful.

In the determination of carbon monoxide the superiority of the Hempel method, both in accuracy and speed, is even more marked. Better results than those cited can be obtained with both the Orsat and Elliot apparatus but only by greatly prolonging the time.

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THE ELECTROLYTIC DETERMINATION OF CADMIUM.

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ABOUT a year ago Max Heidenreich¹ published an article in which he reviewed methods proposed by one of us (S) for the electrolytic determination of certain metals. In some instances he confirmed the observations of Smith, but in most cases differed with him. Recently S. Avery and Benton Dales² announced that so far as the determination of cadmium was concerned their "result was in complete harmony with the experiments of Heidenreich." In consequence of these experiences with the electrolytic methods suggested by Smith for the determination of cadmium, we have repeated them and offer new results obtained by us.

It was in 1878³ that Smith stated that "0.1450 gram of cadmium oxide was dissolved in acetic acid, the excess of the latter expelled upon a water-bath and the platinum crucible then about half filled with water, and * * * connected with the negative pole of a two-cell Bunsen battery * * *. The deposition of the cadmium was regular * * * a perfectly crystalline, grayish white layer." The precipitation was complete in about three hours. The experiment was repeated, but a bichromate battery was substituted for the Bunsen cells. At the time when these

¹ *Ber. d. chem. Ges.*, 29, 1555.

² *This Journal*, 19, 380.

³ *Proc. Am. Phil. Soc.*, November, 1878.

trials were made, current strength in definite units was not given, hence subsequent workers have met with difficulty in repeating some of the early work, and perhaps that may account for the failure to precipitate cadmium from the solution of its acetate. We have sought to obtain the original working conditions given by Smith, have stated them in definite units, and append results obtained by their observance.

Experiment 1.—0.1329 gram of cadmium oxide was dissolved in acetic acid, the solution was evaporated to dryness, and the residue dissolved in thirty cc. of water. The liquid was then heated to 50° C., and electrolyzed with a current of 0.02 ampere for thirty-seven sq. cm. of cathode surface. Voltage, 3.5. The metal was completely precipitated in four hours. It was crystalline and perfectly adherent. There was no evidence of sponginess. The hot, acid liquid was siphoned off and replaced by water without interrupting the current. We found that the period of precipitation could be diminished and very good results be obtained by adding one gram of ammonium acetate to the solution when the current had acted for an hour. The quantity of metallic cadmium present in this particular experiment was 0.1162 gram, while that actually found equaled 0.1158 gram.

Experiment 2.—0.1332 gram of oxide, treated precisely as outlined in Experiment 1, gave 0.1164 gram of adherent, crystalline metal instead of 0.1165 gram.

With these results before us we see no cause why the deposition of this metal from its acetate solution should be condemned. Neumann¹ mentions it as being possible, and Yver² even used an acetate solution in the electrolytic separation of cadmium from zinc.

Smith³ published experiments made by him on the precipitation of cadmium from solutions containing free sulphuric acid. As this method seems not to have proved satisfactory in the hands of Heidenreich, and of Avery and Dales we have repeated the work and offer the following experiments as evidence in favor of the Smith method:

Experiment 1.—0.1270 gram of cadmium oxide was dissolved in two cc. sulphuric acid, sp. gr. 1.09, and the solution then

¹ Theorie und Praxis der analyt. Elektrolyse, p. 129.

² Bull. Soc. Chim., 34, 18.

³ Am. Chem. J., 2, 41.

made up with water to thirty cc. It was heated to 50° C., and electrolyzed for a period of four and one-half hours with a current of 0.08 ampere for thirty-seven sq. cm. cathode surface. Voltage 2.5. The deposit weighed 0.1105 gram instead of 0.1111 gram. It was crystalline and adherent. Tendency to sponginess was not observed. The acid liquid was siphoned off before interrupting the current. The filtrate showed no signs of cadmium when tests were made for it.

Experiment 2.—In this trial 0.1358 gram of cadmium oxide was dissolved and treated as in Experiment 1. The deposit of metal weighed 0.1181 gram instead of 0.1188 gram.

We have never experienced any difficulty in the application of this method, and are also pleased to observe that Neumann¹ gives an example confirming the early recommendation of Smith. It is this: "die Lösung von 0.3 gram Kadmiuni sulfat in 150 cc. Wasser mit 1 bis 2 cc. verdünnter Schwefelsäure versetzt, wird auf 70 bis 80 Grad C., erwärmt und bei diesem Temperatur durch Ströme von 0.6 bis 1 Ampere zersetzt. Die Spannung schwankt zwischen 2.5 bis 5 Volt Der Niederschlag ist silberweiss."

Our experiences with the precipitation of cadmium from a phosphoric acid solution will be reserved for a subsequent communication.

We regard the double cyanide solution² as the best adapted for the deposition of cadmium. Further evidences of this are the many atomic weight determinations made of this metal, in which this particular solution was employed.³

The first suggestion for the electrolytic separation of copper from cadmium was also made by Smith.⁴ He demonstrated that in the presence of free nitric acid copper was deposited in satisfactory form, while the cadmium continued in solution. Heidenreich,⁵ in speaking of this method, which has received frequent confirmation, remarks: "eine Reihe von Versuchen, Kupfer von Kadmiuni aus einer freie Salpetersäure enthaltenden Lösung zu trennen, führten zu keinem befriedigenden Ergeb-

¹ *Loc. cit.*

² *Ber. d. chem. Ges.*, 25, 779.

³ *Ztschr. anorg. Chem.*, 1, 364; *This Journal*, 18, 1022.

⁴ *Am. Chem. J.*, 2, 43.

⁵ *Loc. cit.*

nisse." In reply to this we offer the following experiments:

Experiment 1.—To a solution containing 0.3893 gram of copper sulphate (= 0.0988 gram of copper) and 0.1152 gram of cadmium oxide (= 0.0985 gram of cadmium) were added two cc. of nitric acid, sp. gr. 1.43. The total dilution of the solution equaled 100 cc. It was heated to 50° C., and electrolyzed with a current $N. D._{100} = 0.10$ ampere. Voltage 2.5. The metal was completely precipitated in three hours. It was bright in color and satisfactory in every respect. It weighed 0.0988 gram and did not contain cadmium.

Experiment 2.—A solution containing the same quantity of copper and 0.1203 gram of cadmium oxide, when treated exactly as in Experiment 1, gave 0.0987 gram of copper. It was free from cadmium.

To these results we would add the observation of Neumann:¹ "Am einfachsten is zur trennung von Kupfer und Kadmium immer die Verbindung der mit *freier Saltpetersäure* versetzten Lösung beider Salze."

Heidenreich maintains that the separation of copper from cadmium succeeds "sicherer aus einer mit *Schwefelsäure* versetzten Lösung." This solution had been previously recommended by Smith,² and his observations were confirmed by Freudenberg.³

The results recorded in the preceding paragraphs justify us in saying that cadmium can be successfully determined electrolytically when working either with its acetate or sulphate, and that its separation from copper in the presence of nitric acid is in every respect satisfactory.

The failure of Heidenreich to precipitate uranic oxide by means of the current will be considered later.

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ON THE REACTIONS BETWEEN MERCURY AND CONCENTRATED SULPHURIC ACID.

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MANY text-books class the reactions between copper and concentrated sulphuric acid along with mercury and sul-

¹ *Elektrolyse*, p. 169.

² See *Electrochemical Analysis*, 2nd. Ed., p. 108.

³ *Ztschr. phys. Chem.*, 12, 97.