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THE USE OF A MERCURY CATHODE IN ELECTROCHEMICAL ANALYSIS.

BY EDGAR F. SMITH.

Received June 26, 1903.

THE suggestion of precipitating metals in the form of amalgams was first made (1880) by Wolcott Gibbs,[1] who described a new scheme for the electrolytic determination of metals, before the National Academy of Sciences, in which scheme he recommended weighing out in a small beaker a definite amount of metallic mercury which was, by means of a platinum wire, connected with a battery and made the cathode, while in the salt solution, contained in the beaker, was suspended a strip of platinum, serving as the anode. The currents used varied greatly in strength. Salts of mercury, tin and cobalt were apparently decomposed, their respective metals being precipitated upon or in the mercury cathode. Quantitative results do not appear. The author of this method believed that possibly sodium and potassium might be separated in this manner and Professor Hunt remarked that the "process came with the beauty and force of a revelation."

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[1] *Chem. News*. **42**, 291.

Three years later (1883) Wolcott Gibbs[1] again directed attention to "the employment of mercury as negative electrode, the positive electrode being a plate of platinum........... It was found possible to separate iron, cobalt, nickel, zinc, cadmium and copper so completely from solutions of the respective sulphates that no trace of metal could be detected in the liquid.......... the author had in view both the determination of the metal by the increase in weight of the mercury, and in particular cases of the molecule combined with the metal, either by direct titration or by known gravimetric methods." The experiments were purely qualitative, such being, in the author's opinion, sufficient to establish the correctness of the principle involved.

In 1886 Luckow,[2] cognizant of the difficulties attending the determination of zinc in the electrolytic way, described a course for this purpose which consisted in weighing out in a platinum dish a quantity of metallic mercury or its oxide, introducing the zinc salt solution and then electrolyzing, when the zinc, combined with the mercury, spread over the inner surface of the dish as a beautiful, adherent amalgam.

Nothing further was done towards the development of the ideas outlined in the preceding paragraph until 1891, when Vortmann[3] described, at considerable length, the determination of several metals in the form of amalgams. His plan consisted in adding a weighed quantity of mercuric chloride to the solution of the salt to be electrolyzed, the metals being then precipitated together. The results were quite interesting and seemed to offer decided advantages, but later experience demonstrated that, except in a few cases, this method of analysis, as elaborated by Vortmann, was in nowise superior to the usual procedure in determining metals electrolytically.

A few months later, in the same year (1891), Drown and McKenna,[4] striving to find a method suitable for the estimation of small amounts of aluminum in the presence of a preponderance of iron, had recourse to the suggestion of Wolcott Gibbs. They accordingly weighed a beaker containing a layer of mercury (the cathode), and introduced into the solution of the metals a platinum plate (the anode). The current was allowed to act through the

[1] *Am. Chem. J.*, **13**, 571.

[2] *Chemiker-Zeitung*, **9**, 338 and *Ztschr. anal. Chem.*, **25**, 113.

[3] *Ber. d. chem. Ges.*, **24**, 2749.

[4] *J. anal. Chem.*, **5**, 627.

night and the iron was completely precipitated in the mercury. The aluminum remained in the slightly acidulated solution. These chemists encountered several difficulties in pursuing this course. The platinum wire projecting into the mercury often had iron precipitated upon it, so that it became necessary to weigh the wire, enclosed in a glass tube, together with the beaker of the mercury. Further, much annoyance was experienced in the efforts to dry the amalgam and obtain constant weights.

The preceding paragraphs comprise all that is to be found in the literature of electrochemical analysis, relating to amalgams and the use of mercury as a cathode in metal precipitations.

The thought of the writer had many times dwelt upon the facts mentioned above until at length it was determined to conduct a series of experiments with mercury as cathode, to establish two points: (*a*) The determination of the negative radical in various salts as well as the metals combined with them, and (*b*) the possibility of effecting the separation of certain metals.

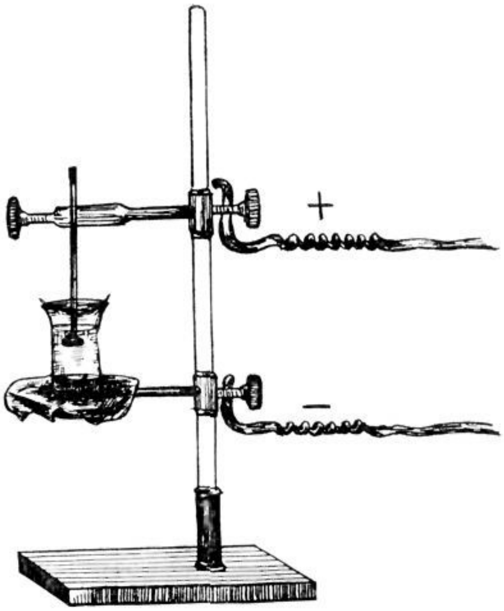

Fig. 1.

To this end, practically the same device as that used by Drown and McKenna was adopted. Into the mercury, serving as cathode, there extended a glass tube from the lower end of which projected a carbon pencil, 1 mm. in length. This pencil of carbon was preferable to the platinum wire; metals did not adhere to it and, therefore, it was not necessary to weigh it together with the beaker and the mercury. The glass tube was nearly full of mercury, into which dipped a copper wire connected with the negative binding-post. Such was the form of apparatus first used.

I. ELECTROLYSIS OF SULPHATES.

The sulphate first chosen was that of copper. A weighed amount of the salt was dissolved in water; the volume of its solution, when introduced into the apparatus mentioned above, equaled about 50 cc. It was electrolyzed at the normal temperature with the conditions given below. Sometimes during the electrolysis "copper trees" appeared on the surface of the mercury cathode (22 sq. cm. in area). They disappeared on gently shaking the beaker. This agitation was sufficient to make them amalgamate. When the liquid had become colorless, it was carefully siphoned into a beaker, its place being taken by distilled water. The washings accumulated in this manner equaled about 500 cc. The current was then interrupted. The sulphuric acid in the liquid conveyed away by the siphon was determined by titration with a tenth-normal sodium carbonate solution. The mercury cathode containing the copper was dried first with bibulous paper and then by standing for a number of hours over sulphuric acid, after which it was weighed.

Number.	Time. Hours.	Ampere. $N.D._{100}$.	Volts.	Cu present. Gram.	Cu found. Gram.	Cu present. Per cent.	Cu found. Per cent.	H_2SO_4 present. Gram.	H_2SO_4 found. Gram.	SO_4 present. Per cent.	SO_4 found. Per cent.
1	5	0.02–0.10	2.25–5.0	0.1512	0.1495	25.30	25.02	0.2352	0.2355	38.55	38.50
2	3½	0.08–0.12	4.25–5.5	0.1512	0.1499	25.30	25.08	0.2352	0.2347	38.55	38.47
3	4½	0.08–0.12	3.5–4.0	0.3024	0.3002	25.30	25.11	0.4704	0.4694	38.55	38.47
4	4½	0.10–0.13	4.0–4.5	0.3024	0.2986	25.30	25.00	0.4704	0.4723	38.55	38.80

The anode in Experiments 1, 2 and 3 was a strip of platinum foil, while in Experiment 4 it was a spiral of platinum.

It will be observed that, so far as the results are concerned, those relating to the metal fall below the theoretical requirement, while in the case of those bearing upon the acid they approximate theory more closely. Difficulty was experienced in drying the amalgam. Drown and McKenna had the same trouble. It seemed at first that it might prove detrimental to the general adoption of the method in ordinary analysis. It was, however, successfully overcome, for it was found that the amalgam could be washed with alcohol and ether, thus removing the final traces of water.

and that not more than fifteen minutes would then be necessary for the drying of the metal. A number of carefully conducted tests established this point. Mr. W. M. Howard of this laboratory also devised the following plan to eliminate the use of the anode of Drown and McKenna, as well as the carbon pencil.

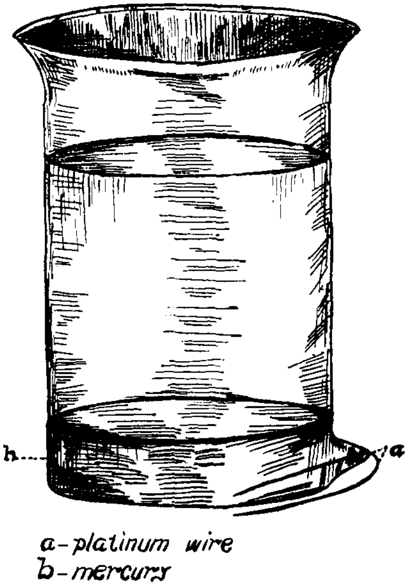

Fig. 2.

It is an extremely simple contrivance, consisting of a small beaker (50 cc. capacity), near the bottom of which there is introduced, through the side, a thin platinum wire. Internally it dips into the mercury, while externally it touches a disk of sheet-copper on which the beaker rests and which is connected with the negative electrode of a cell, thus making the mercury the cathode. By adopting this device and by washing the amalgam with alcohol and ether, the two chief disturbing factors were removed. Thus, on subsequently electrolyzing a copper sulphate solution containing 22.61 per cent. Cu and 41.20 per cent. SO_4, there was obtained

(*a*) 21.61 per cent. Cu	41.23 per cent. SO_4.
(*b*) 21.70 " " "	41.23 " " "

and on substituting a nickel sulphate solution, using a current of 0.05 to 0.06 ampere and 4 volts, the results were

30.41 per cent. Ni	50.75 per cent. SO_4.
30.40 " " "	50.76 " " "

while the theoretical requirements were

30.40 per cent. Ni	50.70 per cent. SO_4.

With zinc sulphate, a current of 0.26 ampere and 6 volts acted for six hours, giving

(*a*) 24.27 per cent. Zn	36.71 per cent. SO_4.
(*b*) 24.37 " " "	36.61 " " "

while the quantities present were

24.30 per cent. Zn	36.60 per cent. SO_4.

In sphalerite, the zinc determined volumetrically equaled 65.7 per cent., while a second portion of the same mineral rapidly decomposed with nitric acid and evaporated with hydrochloric acid, furnished a solution, which on electrolyzing with a mercury cathode showed 65.6 per cent. Zn.

In ferrous ammonium sulphate, electrolyzed in the same fashion, the following percentages of iron were found: 14.26, 14.28, 14.33, 14.19, 14.25 per cent., the theoretical being 14.28 per cent.

Additional data might be given to show that with a mercury cathode it is possible to electrolyze sulphates like those mentioned above and thus determine both the metals and the molecules with which they were in combination. It is needless to add that from such metals phosphoric acid, also, might be easily separated and determined in this way.

For quite a while the writer had been striving to effect, in the electrolytic way, the separation of iron from uranium. On observing the readiness and completeness of the precipitation of iron in the mercury, steps were at once taken to try this method in the hope of effecting the above separation. One-tenth of a gram of each metal was present in the solution in the form of sulphate. To this was added 0.25 cc. of 50 per cent. sulphuric acid and the liquid then electrolyzed with a current of 0.25 to 0.5 ampere and 6 to 8 volts for four and one-half to five hours. The iron was precipitated free from uranium. The separation was repeated several times with like satisfactory results. It may also be added that quantitative separations of iron from titanium, from zirconium and from thorium were made and the results were most satisfactory. In these separations the pressure did not exceed 5 volts with a cathode surface of 22 sq. cm. The precipitation of the iron was finished in five hours, although several trials were conducted through the night.. The ordinary temperature prevailed in the separations. The quantity of each metal present was 0.1 gram. The found percentages of iron from titanium were 14.15, 14.20 and 14.21 per cent.; of iron from zirconium, 14.28 and 14.42 per cent.; of iron from thorium 14.31, 14.38 and 14.32 per cent., instead of the required 14.28 per cent.

II. THE ELECTROLYSIS OF METALLIC NITRATES.

Having ascertained that sulphates could be completely analyzed as indicated in the preceding paragraphs, it was only natural to turn to nitrates. Previous experience had taught that in such cases the acid radical instead of being released as such was reduced to ammonia. But this, it was believed, could be readily estimated if, before commencing the electrolysis of the nitrate, a definite volume of sulphuric acid of known strength should be added. When the electrolysis was finished, the free residual sulphuric acid could be titrated and the difference between its quantity and that originally introduced would give a difference which was combined with the ammonia. It would be a mere matter of calculation to arrive at the quantity of nitric acid previously combined with the metal. Guided by this thought a trial was instituted. The theoretical amount of metal was deposited in the mercury cathode, but upon titrating the sulphuric acid a volume of tenth-normal sodium carbonate equivalent to it was not only consumed, but in addition a volume sufficient to neutralize the nitric acid in union with the metal. In other words, the nitric acid had not been reduced to ammonia. It will be recalled that Vortmann[1] described a method for the determination of nitric acid which consisted in reducing the acid to ammonia in the presence of copper sulphate and sulphuric acid. This knowledge led to several repetitions of the experiment with like results, *viz.*, complete precipitation of the metal and liberation of the nitric acid. Nickel nitrate was the salt more particularly studied, although other nitrates showed a like behavior:

Nickel present. Per cent.	Nickel found. Per cent.	NO_3 present. Per cent.	NO_3 found. Per cent.
20.27	20.06	42.61	42.24
....	20.07	....	42.02
....	20.28	....	41.70
....	20.28	....	....

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[1] *Ber. d. chem. Ges.*, **23**, 2798.

These results were obtained with a current of 0.1 to 0.2 ampere and 3 to 3.5 volts. The time allowed was six hours. Search was made for ammonium salts but none were found, from all of which it would appear that the mercury cathode allowed of the complete determination of the acid and metal portions of nitrates, as well as of sulphates.

III. ELECTROLYSIS OF HALIDES.

Could the haloid acids be similarly determined? Several years ago Vortmann[1] published an account of the estimation of iodine in potassium iodide. Later Specketer[2] announced an electrolytic separation of the halogens. In neither instance was the estimation of the associated metal considered.

To begin, the writer set himself the problem of determining the sodium and the chlorine in ordinary salts. The small beaker, pictured on p. 887, was used. At first, silver-plated strips of platinum were made to serve as anodes. Very soon it was found that, as silver chloride was produced on these plates and loss took place in the drying of the same, anodes of platinum gauze coated with silver would answer better. It very shortly became evident that the chlorine was quantitatively deposited on these anodes. The method of procedure then became this: About 50 grams of pure mercury were put into the beaker, which was then weighed. The aqueous solution of a weighed amount of salt was introduced, the volume of liquid equaling about 40 cc. In this solution the weighed, silver-coated, platinum gauze was suspended. The current was then permitted to pass at the ordinary temperature. Almost immediately the silver began to darken in color from the lower edge of the gauze upwards. When this ceased, the decomposition was assumed to be at an end, whereupon the gauze was raised from the solution, rinsed with water and further washed with alcohol and ether. It was weighed after drying for a short time. For the gauze, a platinum spiral was substituted in the residual liquor in the beaker; the current was reversed, the layer of mercury being made the anode, when the sodium was rapidly driven into the water. All this occupied about twenty minutes, after which the alkaline liquor was titrated with standardized acid.

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[1] *Ztschr. Electrochem.*, **1**, 137; **2**, 169.

[2] *Ztschr. Electrochem.*, **4**, 539.

A solution of salt, containing 0.0606 gram of chlorine and 0.0390 gram of sodium, gave:

Number.	Cl. Gram.	Na. Gram.
1	0.0606	0.0389
2	0.0610	0.0384

Six hours were allowed for the decomposition. The current showed 0.0325 to 0.03 ampere and 2 volts.

On electrolyzing a solution of barium chloride, in the same way, there were obtained

Ba. Per cent.	Cl. Per cent.		Ba. Per cent.	Cl. Per cent.
55.87	28.69	instead of	56.14	29.09
56.07	29.31		....	....

Strontium bromide was analyzed with just as much success. The same is true of other halides. Perhaps it may be well to add that both sodium chloride and barium chloride were electrolyzed successfully without the use of the mercury cathode. A flat, platinum spiral was made to take its place. The alkaline liquor, observing proper current conditions, did not interfere with the deposition of the halogen upon the silver gauze. The thought occurred that in this behavior there was a method of preparing caustic if only some other metal than silver could be applied as anode to take up the chlorine. Numerous experiments in this direction were made, but they resulted negatively.

In this work the writer had the aid of Messrs. William Blum, Raymond Wells, W. M. Howard, and Claude Poole, to each of whom his thanks are here expressed.

In conclusion it may be remarked that the hints which have been developed by this use of a mercury cathode are numerous. The separations of iron from uranium, titanium, zirconium and thorium point to other possibilities where this metal is separated with difficulty, more especially the rare earth metals. Further, there is a noticeable difference in the decomposition pressure of bromides of the alkaline earth metals, so that it would seem as if in a mixture of them this method would yield sharper determinations than we are by force of circumstances obliged to accept. The analysis of barium chloride or of common salt in the electrolytic way was not dreamed of in the years of the development of electrochemical analysis. In 1865 the metal copper was first determined electrolytically. Since then many other metals have been brought into the circle of experimentation, but it is only now in the present—a period nearly forty years later—that interest is being taken in the determination of acidulous groups by the help of the current. To the writer, the possibilities that suggest themselves with other halides than those of the alkali and the alkaline earth metals seem great, and it is his hope that he may be permitted to continue studies in this direction for a little while longer.

UNIVERSITY OF PENNSYLVANIA.

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METAL SEPARATIONS IN THE ELECTROLYTIC WAY.

BY EDGAR F. SMITH.

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THE purpose of this communication is to submit the results obtained in trying to effect the separation of silver, mercury and copper from selenium and tellurium. These gaps in electrochemical analysis existed with two exceptions, *viz.*, silver from selenium, and copper from tellurium, and as the separations were needed both for practical reasons and also to extend and complete the possible range of applicability of the current in analysis, they were tried with evident success, as shown in the sequel.

SILVER FROM SELENIUM.

(*a*) *In Alkaline Cyanide Solution.*—In the *Zeitschrift für anorganische Chemie*, 31, 393 and This Journal, 25, 225, appeared Meyer's account of a method of determining the atomic weight of selenium, which consisted in electrolyzing silver selenite in cyanide solution. The results were so very concordant that there can be little question as to the completeness of the separation of the two metals. Working conditions were not given by Meyer, hence it was thought advisable to give those which in this laboratory proved very satisfactory for this particular separation. They appear in the following lines:

Silver present	0.1341 gram.
Sodium selenate present	0.2500 gram.
Potassium cyanide	3 grams.
Total dilution	150 cc.
$N.D_{100}$	0.02 ampere.
Pressure	2.5 volts.
Temperature	60° C.
Time	6 hours.
Silver found	0.1333 gram.