Methods are described for preparing and keeping pure sodium amalgam and anhydrous ethyl amine, and of measuring the true potential of the amalgam of an oxidizable metal in aqueous solution.

BOSTON, MASS., June 24, 1910.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY.]

THE ELECTROLYTIC DETERMINATION OF CHLORINE IN HYDROCHLORIC ACID WITH THE USE OF A SILVER ANODE AND A MERCURY CATHODE.

BY JACOB S. GOLDBAUM AND EDGAR F. SMITH.

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With the introduction of the silver anode and mercury cathode, many new and interesting determinations and separations have been effected.

Much attention has been paid in this laboratory to this phase of electroanalysis, and exact and satisfactory results have been obtained.[1]

Recently there appeared an article by Gooch and Read[2] on the "Electrolytic Determination of Chlorine in Hydrochloric Acid, with the Use of the Silver Anode." From this communication it would seem that upon extending the analysis of chlorides, in neutral aqueous solution, to the determination of chlorine in free hydrochloric acid, the method as presented in previous communications from this Laboratory yields values which are "very irregular and always low." It is, therefore, proper to consider the question raised by Gooch and Read, and to submit additional evidence, together with some of the details of procedure.

Experiments were made with hydrochloric acid precisely as described by Gooch and Read, and behaviors similar to those noted by these chemists were observed; that is, the electrolysis resulted, not only in the fixation of chlorine at the anode and the liberation of hydrogen at the cathode, but also in a secondary decomposition, which gave rise to the production of hypochlorites. As a consequence, some of the silver of the anode dissolved in the electrolyte, and at times appeared at the cathode. The fixation of the oxygen at the anode was likewise observed and, indeed, when this oxygen was driven off, low and non-concordant results were obtained. Now, in these experiments a platinum cathode was employed and with the exception of a single determination, the experiments performed by Gooch and Read were with a platinum cathode, whereas, in all the work done in this laboratory on the fixation of anions, a mercury cathode has been employed. Indeed, Gooch and Read were really not using "similar means," and the criticism of the original method because of the failure of an altered arrangement is hardly fair. Hence, it is only natural that we should try the effect of a silver anode and mer-

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[1] THIS JOURNAL, 29, 447, 1445, 1455, 1460; *Ibid.*, 30, 1706.

[2] *Am. J. Sci.*, 544 (1909).

cury cathode in the analysis of hydrochloric acid, and to this end, experiments were accordingly conducted.

The platinum gauze anode was plated with silver from a potassium silver cyanide electrolyte. It is true, as stated in the article by Gooch and Read, that there is a possibility of the retention of some soluble cyanide in the gauze, even after the plated anode has been treated with boiled water, and subsequently ignited gently. We have been aware of this fact, however, for several years, and while making no mention of it, have succeeded in obviating the difficulty by dipping the freshly plated silver gauze in dilute hydrochloric acid, washing it thoroughly with distilled water, and then igniting it to incipient redness in a low Bunsen flame. By this means, any admixed cyanide is destroyed. The solution undergoing analysis could not then become contaminated by material derived from the plating bath. Care should be taken not to ignite the anode too strongly in the Bunsen flame, as it is most desirable that the silver should not fuse, and that its porous nature should be preserved. A complete retention of the chlorine is favored by these means, whereas with a smooth silver surface there is a possibility that molecular chlorine may be liberated, with a consequent production of hypochlorites and chlorates.

Another fact, known to us for some time, is the secondary formation of oxide upon the anode along with the halide. To obviate its disturbing effect upon the weight of the anode, we have had recourse to a home-made electric oven heated to 300°. Silver oxide is completely decomposed at 250°, giving off oxygen and leaving metallic silver, so that at the end of an electrolysis the anode is at once placed in an oven with the temperature mentioned for a period of ten or fifteen minutes, when nothing will remain but silver and silver chloride, so that the increase in weight of the anode would represent only the weight of the added halogen. These and certain other perfections of our original procedure in the analysis of halides in the double cup, which have come as results of experience, will be more fully described in a later communication relating to the determination of the atomic weight of chlorine in the electrolytic way.

During analysis, the anode should not be placed too near the cathode. By observing this point a too-high current density will be avoided and one need not fear a possible loss due to the loosely adherent silver halide because of its too-rapid formation. It is advisable with the pressure usually employed (2.5–5 v.) with the double cup to place the anode at least 15 mm. from the level of the mercury. No turbidity of the electrolyte will then follow.

The hydrochloric acid used in the determinations which appear in this paper was standardized by the well-known precipitation method with silver nitrate. The residue from 40 cc. of the solution, containing

0.1418 gram of hydrogen chloride, weighed 0.0001 gram. Only freshly distilled water was used for dilution. In the first two determinations, a "double-cup" was used, but since in the case of hydrochloric acid this presented no advantage over a cell with a single compartment, the latter was employed for the subsequent determinations. This cell consisted of an ordinary beaker, 6 cm. in diameter and 8 cm. high, containing a layer of pure mercury 3 mm. deep. Cathode connection was made with the mercury by means of a platinum wire sealed in a glass tube. The anode was the usual disk gauze type. It made 300 revolutions per minute. The total dilution of the electrolyte was 90 cc. The liquid remaining in the beaker after the current was interrupted was found in every case to be neutral to methyl orange, and when tested with silver nitrate and with starch, and potassium iodide, hypochlorous acid or hypochlorites were invariably absent. In experiments 3 and 4 the electrolyte showed a slight turbidity, due to the fact that the electrodes were too close. In all other determinations the liquid remaining after the electrolysis was perfectly transparent and clear. The liquid from determinations 8 and 9 was evaporated to dryness and gave no appreciable residue. The mercury used for cathode had been distilled several times and was carefully examined for silver before and after the electrolysis, but none was found. Hence there was no transference of the metal from the anode to the cathode.

	Chlorine taken in HCl. gram.	Time. Min.	V.	A.	Chlorine found.	Error.
1	0.0709	20	2.5–5.0	0.85–0.01	0.0707	—0.0002
2	0.0709	22	2.5–5.0	0.80–0.005	0.0710	+0.0001
3	0.1418	28	2.5–5.0	0.95–0.01	0.1410	—0.0008
4	0.1418	30	2.5–5.0	0.95–0.015	0.1406	—0.0012
5	0.0709	20	2.5–5.0	0.85–0.005	0.0703	—0.0006
6	0.1418	30	2.5–5.0	0.80–0.005	0.1418	+0.0000
7	0.1418	35	2.5–5.0	0.75–0.005	0.1416	—0.0002
8	0.0709	20	2.5–5.0	0.75–0.005	0.0709	±0.0000
9	0.0709	20	2.5–5.0	0.80–0.005	0.0707	—0.0002
10	0.0709	23	2.5–5.0	0.65–0.01	0.0710	+0.0001
11	0.1418	35	2.5–5.0	0.80–0.005	0.1420	+0.0002

From the foregoing tests it would appear that the electrolytic determination of chlorine in hydrochloric acid by means of a silver anode and mercury cathode is not only possible but is, moreover, extremely accurate and reliable.

Since the preceding determinations were made, W. B. Coleman, a student in this laboratory, carried out a series of determinations of bromine in hydrobromic acid. The results obtained by him are submitted in the following table. These results confirm those obtained with chlorine and prove beyond question that this method of analysis is reliable and exact.

HYDROBROMIC ACID.

Br present in gram.	V.	A. N.D.$_{80}$.	Time. Min.	Br found in gram.	Remarks.
0.0700	4	0.4 –0.01	35	0.0685	Solution turbid after electrol.
0.0700	4	0.4 –0.02	35	0.0683	Solution turbid after electrol.
0.0700	3	0.35–0.01	35	0.0698	Clear solution.
0.0700	3	0.35–0.002	50	0.0699	" "
0.0700	3	0.35–0.002	50	0.0697	" "
0.0700	3	0.35–0.003	50	0.0698	" "
0.0700	3	0.35–0.003	50	0.0696	" "
0.0700	3	0.35–0.001	50	0.0700	" "
0.0700	3	0.35–0.001	50	0.0696	" "

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[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY.]

ELECTROLYTIC SEPARATIONS.

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During the last three years there have been carried out in this laboratory certain metal separations in the electrolytic way, which may be of interest to those who are engaged in work of this character, so that it seems only proper that the results should be brought together in a single communication. The following paragraphs give in sufficient detail all the data necessary for those who may have occasion to repeat the separations. Thus, the separation of mercury from nickel was conducted in the presence of sulphuric acid. The anode consisted of a flat platinum spiral, which was rotated. The cathode was an ordinary platinum dish. With 0.1437 g. of mercury, and 0.2772 g. of nickel in the presence of 0.1 cc. of concentrated sulphuric acid, a current of N. D.$_{100}$ = 0.3 amp. and a pressure of 2.9 volts there was precipitated in the course of thirty-five minutes 0.1436 gram of mercury. Again, 0.2876 g. of mercury was separated from 0.1386 g. of nickel in the presence of 0.1 cc. of concentrated sulphuric acid, by the means of a current of N. D.$_{100}$ = 0.3 amp. and a voltage of 2.8 in a period of forty minutes. Six additional separations with conditions like those just indicated resulted similarly, so that we may regard this as a satisfactory procedure for the separation of mercury from nickel. The deposits of mercury were in every instance examined for nickel, but it was not found.

In the separation of bismuth from nickel 0.2772 g. of nickel and 0.2640 g. of bismuth, in the presence of 1 cc. of concentrated sulphuric acid, were exposed to the action of a current of N. D.$_{100}$ = 0.3 amp. and 2.2 volts for forty-five minutes. The deposit of bismuth weighed 0.2642 g. It was free from nickel. Six additional experiments resulted similarly. The deposits of bismuth, however, were not coherent, and the greatest care was required in washing them to avoid loss of the metal.