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ART. XI.—*The Use of Cupric Nitrate in the Voltameter, and the Electro-Chemical Equivalent of Copper*; by FREDERICK E. BEACH.

[Contributions from the Sloane Physical Laboratory of Yale College.]

AMONG the voltameters in common use the silver voltameter gives results of a very high degree of accuracy, but is not conveniently used except for comparatively small currents. On the other hand the copper voltameter from the cheapness of materials and facility of manipulation finds convenient employment in the laboratory. As ordinarily used with the sulphate of copper, it is subject to certain irregularities due to the attack of the copper by the solution under some conditions, and the oxidation of the metal in others. For these reasons as well as for the fact that excellent deposits of metal are obtained from the nitrate of copper, even with great current densities, it seemed probable that this salt could be successfully used in the voltameter. The object of this paper is to show that cupric nitrate has some marked advantages over the sulphate. For purposes of comparison the results and conclusions of different experimenters will be passed in review.

Gore* expresses the opinion that two independent forces act in the solution, one chemical the other electro-chemical. The action of the former is assisted by a rise of temperature. The loss of the anode is greater than the gain of the cathode, but the chemical corrosion of the anode is less than that of a sepa-

* Nature, March 16, 1882.

rate piece of copper without a current. The purely chemical corrosion of the cathode is more than that of the anode. The addition of any considerable amount of sulphuric acid had the effect of diminishing the weight of copper deposited.

Hammerl* as the result of a detailed investigation comes to the following conclusions:

I. No change in the quantity of the deposit was observed when a blank platinum surface was substituted for one which had been covered with a deposit of copper.

II. The change of concentration of the solution caused by the passage of the current and the polarization dependent on it cannot be satisfactorily prevented by agitation. In boiling to agitate the fluid the deposit oxidizes almost completely to CuO, and partially indeed between 40° and 60° C.

III. The highest allowable current strength is 7 amperes per square decimeter. The distance between the plates should not be less than 1.5 cm.

Gray† finds that the highest current-density desirable is one ampere to 50 square centimeters ($= 0.02 \frac{\text{amp.}}{\text{cm}^2}$). He obtains

the ratio $\frac{\text{Cu}}{2\text{Ag}} = 0.2940$ and for the electro-chemical equivalent

of copper $0.0003287 \frac{\text{gm.}}{\text{amp. sec.}}$ when silver is taken as

0.001118. He remarks "This would indicate a value not differing much from 0.0003290." He does not find as did Gore, that loss by chemical action is less when the current is flowing than when it is not. Copper was dissolved in the sulphate at the rate of $0.02 \frac{\text{mgm.}}{\text{cm}^2 \text{ hr.}}$ Addition of sulphuric acid seemed

to retard the loss when the density of the solution was between 1.1 and 1.15.

Gray‡ using a density of the sulphate solution of 1.15 to 1.18 with one per cent free sulphuric acid found that the equivalent depended on temperature and current-density in a manner which is exhibited by the following table. The factor 10^{-7} has been omitted.

Area of cathode in sq. cm. per ampere.	Temperature.				
	2° C.	12° C.	23° C.	28° C.	35° C.
50	3288	3287	3286	3286	3282
100	3288	3284	3283	3281	3274
150	3287	3281	3280	3278	3267
200	3285	3279	3277	3274	3259
250	3283	3278	3275	3268	3252
300	3282	3278	3272	3262	3245

* Wien. Ber., (2), lxxxviii, pp. 273-294.

† Phil. Mag., xxii, p. 289, 1886.

‡ Phil. Mag., xxv, p. 179, 1888.

Vanni* found that a solution of copper sulphate of density 1.12 with one per cent of free sulphuric acid dissolved copper, while a solution neutralized with copper hydrate gave an excess. Combining a liter of the normal solution with a half gram of that containing one per cent of the acid neither a gain nor loss could be observed in the weight of a piece of copper immersed in it.

The mean of six experiments with such a solution showed $\frac{\text{Cu}}{2\text{Ag}} = 0.2938$, whence Cu equivalent = $0.000328\frac{1}{2}$ with a current-density between 0.011 and 0.002.

Cintolesi† observed that the solution of a copper plate in copper sulphate depends on the time and the current strength. In vacuo the amount of copper dissolved is less than in air. Oxygen was believed to have an essential influence on the phenomenon.

Shaw‡ using copper sulphate, and a current-density above $0.025 \frac{\text{amp.}}{\text{cm}^2}$ found as a mean of fifteen experiments that the ratio of $\frac{2\text{Ag}}{\text{Cu}}$ was 3.39983 or Cu equiv. = 0.00032886 .

It thus appears that the behavior of copper sulphate had been thoroughly studied; but no quantitative determination had been made with the nitrate, as far as the writer knows, although it had been stated by Smee and others, that the nitrate would bear a much greater current-density than the sulphate.

The apparatus used in the experiments presently to be considered, may be briefly described as follows: the cathode was made from a piece of electrolytic copper about 2^{mm} thick, by bending it so as to form three sides of a rectangle. This was immersed in copper nitrate contained in a glass beaker. The anode was usually a thin sheet of platinum though copper was occasionally substituted for it. The former was much preferred on account of the ease with which the copper is removed by dipping in nitric acid. After rinsing with water the platinum electrode may be dried by heating to redness in a Bunsen flame. The current was measured by the silver voltmeter when small, and a Thomson Balance in a few instances when the total current was large. The value of the equivalent of silver used in calculating the numbers hereafter given was 0.0011181, the mean of the value 0.0011183 found by Kohlrausch§ and 0.00111794 the one given by Rayleigh.||

* Wied. Annal., x, p. 214, 1891.

† Phil. Mag., xxiii, p. 138, 1887.

‡ Phil. Trans., p. 439, 1884.

§ Beiblätter, xvi, p. 80, 1892.

|| Wied. Annal., xxvii, p. 57, 1886.

It was found early in the course of the work that when the nitrate solution was freshly prepared, it had a tendency to dissolve copper, and that this tendency which was due to the solvent action of the solution itself or the presence of a small quantity of free acid, decreased after the copper electrode had been kept in the solution a sufficient length of time, and that this latter effect seemed to be facilitated by the passage of the current. On the other hand another difficulty to be contended with was the oxidation of the copper deposited after the solution had been used too many times or the current was pushed too far, causing in many cases a darkening or even perceptible blackening of the metal. It was however discovered that the blackening due to oxidation could be prevented by the addition of a small amount of ammonium chloride.

Experiments were now made in which the current density was varied through a considerable range with results which are given in the following table:

No.	Solution.	Current-Density amperes.	Cu. Eq. $\times 10^7$
		cm ²	
1	Cu ₂ NO ₃ nearly neutral without NH ₄ Cl,	0.035	3291
2	“ “	0.065	3291
3	“ “	0.144	3293
4	“ “	0.024	3293
5	“ “	0.83	3305
6	Cu ₂ NO ₃ with NH ₄ Cl,	0.114	3290
7	“ “	0.074	3297
8	“ “	0.076	3298
9	“ “	0.094	3299
10	“ “	0.019	3290
11	“ “	0.048	3297

These values show no dependence on the current-density except No. 5 where the large value of the equivalent is best accounted for by oxidation caused by the excessive current. This deposit was badly fringed at the edge and easily detached. Numbers 1-5, made by repeated use of the same solution, show more uniformity than was at any other time obtained from a solution without ammonium chloride present. Attention may be called to what appears to be evidence of the neutralization of the solvent effect of the nitrate on the copper in the gradual but not always regular increase in the values obtained from the same solution in successive experiments.

Having now obtained a fair control of both the tendency to oxidation and solution, experiments were next undertaken with a view to determining the value of the electro-chemical equivalent. With the exception of Nos. 1-5 already quoted, the

solutions used in obtaining the numbers given in the 1st Series were alike in that they were neutral with respect to the copper and contained NH_4Cl .

First Series.		Second Series.	
No.	Equivalent $\times 10^7$	No.	Equivalent $\times 10^7$
1	3291	33	3294
2	3291	34	3296
3	3293	35	3290
4	3293	36	3293
5	[3305]	37	3295
12	3296	38	3294
13	3297	39	3296
14	[3305]	40	3298
15	3293	41	3293
16	3294	42	3291
17	3296	43	3292
18	3294	44	3302
19	3292	45	3296
20	3300	46	3293
21	3299	47	3294
22	3299	48	3291
23	3291	49	3292
24	3295	50	3293
25	3294	51	3292
26	3292	52	3293
27	3300	53	3292
28	3292	54	3291
29	3296	55	3298
30	3301		
31	3291		
32	3295		

The mean of the First Series, including Nos. 5 and 14, is 3295.6 ± 0.54 . If these experiments be excluded we get 3294.8 ± 0.43 .

Neutralization of the solution in the experiments described had been effected by repeated use. A readier method which suggested itself was to boil the nitrate in order to expel the air, allowing a piece of clean copper to stand in the hot solution until its solvent action had been exhausted. Such solutions were prepared and after the addition of a small amount of NH_4Cl yielded values tabulated in the Second Series, the mean of which is 3293.9 ± 0.4 .

In some cases the solutions employed were used many times so that the tests to which the nitrate has been subjected are in this respect particularly severe. There is good reason for supposing that the numbers would have been more consistent if a fresh solution had been used each time.

It is natural to inquire how the values found agree with the equivalent calculated from the atomic weight of copper.

The last named quantity has been investigated with great care by T. W. Richards* with the following result:

If silver be taken as 108.00, oxygen as 16.000 and bromine 80.007

From	Cu : 2Ag	he finds	Cu = 63.640
	Cu : (2AgBr)		Cu = 63.648
	CuBr ₂ : 2Ag		Cu = 63.643
			<hr/>
			Cu = 63.644

whence we get

$$\frac{\text{Cu}}{2\text{Ag}} = 0.29465$$

and Cu Equivalent = 0.00032944

when silver is taken = 0.0011181

Hence the value here found is substantially in accord with Richards'. In making this comparison it must be borne in mind that the present investigation was not undertaken for the purpose of finding the equivalent of copper but to determine how well the nitrate would serve as the electrolyte in the copper voltameter and that too, throughout a considerable range of conditions. That these conditions when working with such a sensitive metal as copper were sometimes unfavorable to uniformity of result may be sufficient to explain the amount of variation from the mean. The probable error of a single observation in the Second Series is ± 1.9 .

Further experiments were tried to determine the effect of variations in the temperature. Here again it is to be remembered that the solutions were not freshly prepared. A considerable change of temperature either up or down seemed to favor oxidation, but more particularly the latter, probably on account of the increase in concentration of the salt when cooled. Still even this was in great measure prevented by a sufficient addition of the ammonium chloride.

No.	Solution.	Temperature.	Equivalent $\times 10^3$.
56	Cu2NO ₃ with NH ₄ Cl	19°	3296
57	Same	6	3297
58	Same	34	3292
59	Same	29	3321
60	Another solution	18	3291
61	Same	36	3297
62	Same	37	3296
63	Same	6	3313
64	Same	10	3307
65	A different solution	40	3291
66	Same	10	3292

* Proc. Amer. Acad., xxiii, p. 177. Ibid., xxv, p. 212.

From these experiments we may conclude that a moderate change of temperature is not a critical matter.

The First and Second Series were made at the temperature of the room which did not vary much from 19° C.

The following method is recommended for the preparation of the solution: Dissolve copper nitrate, the purest obtainable, in distilled water. Boil for a short time to expel the air and keep at a temperature of 100° C. for an hour or two in the presence of bright metallic copper in order to completely neutralize the solution. When ready for use it should have a density of about 1.53. Add a saturated solution of NH_4Cl at about the rate of 1 drop to 100^{cc} of the nitrate. Just the proper amount of ammonium chloride it is not easy to specify. If too much be present the deposit will discolor on drying; if too little, bubbles will collect on the cathode or the deposit will oxidize in the solution. Perhaps the surest way is to try a preliminary experiment, adding the NH_4Cl till the plate begins to show discoloration on drying.

If the solution is to stand the anode may be left in it. Care should be taken to exclude the air.

On removal from the solution the cathode should be washed thoroughly in running water and drained until it may no longer be said to be wet, after which gentle heat should be cautiously applied until all moisture is removed.

The advantages possessed by the nitrate may be enumerated as follows:

1st. The weight of copper deposited does not appear to depend on the current density.

2d. It permits the use of a high current-density.

The limit is not easily stated. When 0.25 amperes per square centimeter is reached the cathode needs watching, for it will fringe at the edge but does not become powdery.

No way was found to prevent the branching with a high current-density.

A greater amount of NH_4Cl should be present when the current density is increased.

3d. The weight of copper is practically independent of the temperature between 10° and 35° C.

The tendency to oxidation is increased by lowering the temperature but this may be easily counteracted by the addition of more NH_4Cl .

4th. The solution may be used a number of times.

5th. The equivalent agrees to four figures with that calculated from the best chemical determinations, viz:

$$\text{Richards} \quad \text{Eq.} = (3294.4 \pm 0.1) \times 10^{-7}$$

$$\text{First Series} \quad \text{Eq.} = (3294.8 \pm 0.43) \times 10^{-7}$$

$$\text{Second Series} \quad \text{Eq.} = (3293.9 \pm 0.39) \times 10^{-7}$$

The purity of the nitrate as a condition of success is to be emphasized. One specimen tried, which contained nitrite, was absolutely worthless with the foregoing treatment.

To see what CuSO_4 would do under circumstances similar to those in which the nitrate was studied, a saturated solution of the sulphate was rendered neutral by the copper hydrate precipitated on addition of ammonia. NH_4Cl was added until the deposit was as bright and lustrous as that formed in an acid sulphate solution.

Three such experiments yielded

$$\text{Eq.} = 3295 \times 10^{-7}$$

$$\text{Eq.} = 3293 \times 10^{-7}$$

$$\text{Eq.} = 3294 \times 10^{-7}$$

Two other experiments in circuit with the nitrate showed

	Sulphate. gms.	Nitrate. gms.
Copper deposited	0.4722	0.4719
do. do.	0.5671	0.5667

These values tend to confirm the result obtained from the nitrate; at least they do not contradict it.

In conclusion I wish to express my thanks to Professor A. W. Wright, under whose direction the preceding investigation was made, for his many kind and helpful suggestions.

Sloane Physical Laboratory, June 1st, 1893.