

The idiosyncrasies of the silver coulometer have been further investigated by Richards and Anderegg,¹ and Hulett and Vinal.²

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INCLUSIONS IN THE SILVER VOLTAMETER DEPOSITS.

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1. Introduction.

In a previous paper³ on the voltameter a brief discussion of the question of inclusions of foreign materials in the silver voltameter deposits was given, together with a short résumé of other papers on this subject and a few experiments which had been made at the Bureau of Standards. It was pointed out that, in so far as the international ampere is concerned, the value assigned to the electrochemical equivalent of silver by the London Conference has been generally accepted by the various National laboratories as applying to the silver as we find it deposited in the voltameter, without reference to any inclusions that it may contain. This is not a serious matter because the uniformity of the results obtained by the National laboratories working together, indicated that the inclusions must be very small or very constant in amount and the International committee was enabled to fix the voltage for the Weston normal cell with sufficient accuracy for present purposes. But it was also stated in the reference mentioned above that it is important, if possible, to eliminate any error due to the inclusions, in order that we may know what deviation there is, if any, from the value assigned to the electrochemical equivalent of silver (1.11800 mg. per coulomb).

The earliest experiments of the Bureau on the inclusions in the silver were few in number and were not considered conclusive. Only one deposit was heated to incandescence and that was from an electrolyte in

¹ THIS JOURNAL, 37, 675 (1915).

² J. Phys. Chem., 19, 173 (1915).

³ "The Silver Voltameter," Part IV, by Rosa, Vinal, and McDaniel, *Bull. Bur. Standards*, 10, 516, reprint No. 220.

which impurities were purposely introduced. Its result had, therefore, no significance so far as the value derived for the Weston normal cell was concerned, since only pure electrolytes were used for that purpose.

We have now carried out at the Bureau some further experiments, principally to determine the loss of weight of the deposits when heating them to temperatures of 600° or more. These will be recorded in the present paper, and also a few experiments bearing on the question of the anode liquid.

Richards and Anderegg¹ have recently made determinations of the inclusions of foreign material in the silver deposits. They found the inclusions in their deposits to be very variable and large enough to be a serious source of error in the silver voltameter determinations. They recommended as a safe and convenient method for determining these inclusions that the platinum cups containing deposits should be heated to dull redness in a flame and reweighed.² The resulting loss in weight they attributed to the expulsion of foreign material in the deposit. We have repeated this part of their work and we have extended the experiments to include comparisons with the effect when similar deposits are heated in an electric furnace. Van Dijk³ has previously used a furnace for this purpose. Our furnace was considerably larger than his, so that we could heat our regular platinum cathodes in it.

We found the losses on glowing the deposits to be only 0.004% on the average and fairly constant. We also found that both these methods of heating the deposits are subject to a source of error. In order to drive the inclusions out of the deposited silver a temperature of about 600° has been used and there is necessarily more or less alloying of the silver with the platinum cup. On removing this silver there is left behind a stain of platinum black. This may be so slight as to be hardly noticeable, but if deposits are made without entirely removing the stains the deposited silver does not accurately represent the quantity of electricity that has passed through the voltameter and if such a deposit is heated to dull redness the observed loss in weight depends more on the loss of adsorbed material from the platinum black than on the expulsion of inclusions from the deposited silver. This source of error was not mentioned by previous observers.

2. Apparatus Employed.

(a) **The Electric Furnace** was designed and built by Prof. G. A. Hulett for this work and we are greatly indebted to him for the use of it. It

¹ THIS JOURNAL, 37, 15 (1915).

² Essentially the same method has been previously described and used by Lord Rayleigh and Mrs. Sedgwick, *Phil. Trans.*, 175, 430 (1884); Jaeger and von Steinwehr, *Z. Instrumentenk.*, 28, 354 (1908); Boltzmann, *Sitzb. Akad. Wiss., Wien, IIA*, 121, 1060 (1912).

³ *Ann. Physik*, 19, 263 (1906).

was constructed from a glazed porcelain beaker and the heating coils of nichrome wire were wound not only on the sides and bottom, but there was also a heating coil in the porcelain cover in order to provide as uniform a temperature inside as possible. Temperature measurements were always made by a platinum platinum-rhodium thermocouple which had been calibrated at this Bureau. The thermocouple passed into the furnace through a porcelain tube in the center of the cover. The outside of the furnace consisted of two concentric hollow cylinders of metal and asbestos. The double air space thus provided gave ample heat insulation to make the furnace efficient for temperatures not exceeding 750°. The top of the furnace was of glazed porcelain rings, one of which supported the interior parts. The outside dimensions of the furnace are 21 cm. diameter by 27 cm. high, and the inside dimensions are 9 cm. diameter by 16 cm.

The platinum cups, one at a time, were lowered into the furnace with platinum-tipped tongs and rested on a network of platinum wires woven in a perforated porcelain plate. The cups were covered with glazed porcelain crucible tops to prevent the accidental falling of any particles into them when putting the thermocouple in place. The electric current was applied gradually by steps of one ampere at intervals of a few minutes until the maximum current of 7.7 amperes was reached. After each heating the furnace was allowed to cool to about 300° before opening it.

The furnace was designed with a view of avoiding the difficulties of metal contamination sometimes encountered with platinum wound furnaces.¹ To test this an empty platinum cup was heated four times and weighed after each heating with the results given in Table I.

Date. 1915.	Wt. of cup. G.	Δ. [Mg.	Treatment of cups.
July 23.....	38.496887	—0.019	Washed and dried 160°
	942	+0.036	Heated to 650°
	897	—0.009	Heated to 648°
24.....	897	—0.009	Heated to 646°
	Mean, 38.496906	±0.018	

Each of the four determinations given in Table I is subject to the same experimental error in so far as the weighings are concerned. Since the deviations are by small amounts the results show that the heating to a high temperature was without effect on the weight of the cup.

(b) **For Heating by the Flame Method**, the platinum cups were supported on a quartz triangle and covered with a small glazed porcelain evaporating dish. The room was darkened and the cup heated quickly and as uniformly as possible to a very dull red with a Bunsen burner held

¹ *Proc. Am. Acad. Sci.*, 38, 460 (1903).

in the hand. We made a number of determinations on empty platinum cups to determine the effect of heating. The following results, Table II, give the weight after each heating to about 600°:

Date.	Wt. of large cups. G.	Δ. Mg.	Wt. of small cups. G.	Δ. Mg.	Treatment of cups.
June 10.....	80.293412	+0.004	38.495585	+0.003	Washed, dried and glowed
	404	-0.004	579	-0.003	Heated to dull redness
Mean, 80.293408		±0.004	38.495582	±0.003	
June 11.....	80.293183	+0.068	38.494855	+0.047	Washed and dried at 160°
	113	-0.002	805	-0.003	Heated to dull redness
	082	-0.033	788	-0.020	Heated to dull redness
12.....	083	-0.032	786	-0.022	Heated to dull redness
Mean, 80.293115		±0.034	38.494808	±0.023	
Average Δ's of both sets,		±0.024		±0.017	

The results of Table II show very little change, if any, in the weight of the empty cup due to heating them to redness. In all the succeeding work the empty cups were glowed each time before weighing them.

When heating the cups with silver deposits to dull redness, the porcelain dish serving as a cover for the cup was examined for any traces of volatilized silver, but none was ever seen nor was any found by chemical tests. During the heating process the observer listened for the "series of small explosions" mentioned by Richards and Anderegg,¹ but this phenomenon was never observed.

(c) **The Silver Voltmeters** were the same instruments as used in the previous work at the Bureau of Standards together with the voltmeters previously used in the Princeton laboratory. To these were added two silver cups identical in size and shape with the Princeton platinum cups. It has generally been thought impossible in the past to use silver cups, partly because the deposit cannot readily be removed and the cup restored to its original condition, and partly because of inconstancy of weight when heated. Both of these objections were mentioned by Lord Rayleigh.² Recently it has been found in the work at Princeton that silver deposited on *highly polished silver* may be scraped off with the greatest ease, although it adheres sufficiently well for the usual washing operations. The deposit after being washed was scraped down while still wet with a small silver "hoe." This has afforded a ready means of determining the inclusions between the crystals and the cup and of saving deposits for further examination for inclusions. Prof. Hulett has kindly permitted us to make use of his silver cups in this way.

The electrolytes used in these experiments were generally of a very high

¹ *Loc. cit.*, p. 9.

² *Phil. Trans.*, 175, 411 (1884).

degree of purity and the silver nitrate was prepared either by the methods¹ previously described by the Bureau or by the Princeton method. The electrolyte was always tested for its acidity and for reducing agents.

The cups were weighed on the same balances described by Rosa, Vinal, and McDaniel,² but these balances were mounted in a new balance room, similar, however, to that used before.

3. The Alloying of Silver and Platinum.

Nearly all the previous observers who have tried heating the silver deposits have mentioned the alloying of the silver and platinum at a temperature corresponding to dull redness, and Van Dijk³ has described the black stain left on the platinum cup after the silver has been removed. Others have not mentioned this, probably because the stain was almost invisible if the alloying was slight. None of the previous authors seem to have been aware of the significance of this alloying and of the black stain; for example Richards and Anderegg⁴ say, "Such heating slightly alloys the two metals * * * * *". This complication, of course, had not the slightest effect upon the quantitative experiment."

Time, as well as temperature, is a very important factor in alloying. Rapid heating to a given temperature for a short time may produce little effect, but it becomes very pronounced as the time of heating is increased, as we found on using the electric furnace. A cup heated to 625° for thirty minutes in the furnace was much more alloyed than a similar cup heated to 675° in the same furnace and immediately allowed to cool.

When the deposits are removed from the alloyed cups by electrolysis or nitric acid, a brown stain remains on the platinum if the cups have been heated for only a short time with the flame, or a heavy, dark brown or black stain in the case of cups heated for a longer time in the furnace. We were unable to remove this stain completely by scrubbing without a considerable abrasion of the platinum surface and it persisted even after the cups were carefully washed and dried at 160°. If the cups were heated to bright redness in a Bunsen flame the slight stains completely disappeared, but their capacity to make trouble was only slightly lessened. Early in our work we found that this change in color from brown or black to gray was accompanied by a marked change in weight of the cup. This change in weight may be as small as 0.1-0.2 mg. in the case of cups that have been very slightly alloyed or it may amount to milligrams in case of heavily alloyed cups. The following figures give the change in weight as we have observed it for a few cases:

¹ *Bur. Standards Bull.*, 9, 537, reprint No. 201; *Trans. Am. Electrochem. Soc.*, 22, 372 (1912).

² *Bur. Standards Bull.*, 9, 174, reprint No. 195.

³ *Arch. Néerland. des. sci.*, [II] 10, 277 (1905); *Ann. Physik*, 19, 265 (1906).

⁴ *Loc. cit.*, p. 15.

TABLE III.

Change in weight due to glowing a cup stained by the alloying of silver and platinum after cleaning and drying at 160°.

Date. 1915.	Loss in wt. Mg.	Character of stain.
July 27.....	0.180	Very slight brown stains
	0.220	Very slight brown stains
Aug. 6.....	0.672	Brown stains
	0.643	Brown stains
Sept. 23.....	1.083	Brown stains rather prominent.
Oct. 2.....	4.89	Heavy black stain

The cause of this phenomenon seems to be the expulsion of adsorbed material in the brown or black stains. These stains we believe to be platinum black. The nature of this material adsorbed by the platinum black has not yet been determined, but experiments will shortly be made to identify it. The disappearance of the stains when heated was more apparent than real, since the platinum black was converted into platinum gray and was, therefore, hardly visible on the gray surface of the platinum cup itself. The stains show their marked catalytic power when brought in contact with hydrogen peroxide. Even in cases when the alloying has been so slight that the platinum black stains are invisible we have found that the actual presence of the stains can be shown by making a test with peroxide. In this test the peroxide was made to cover both platinum black and the bare platinum surface of the cup at the top. The bubbles formed quickly in the platinum black region and not noticeably over the bare platinum. There was a sharp line of demarcation between the decomposing peroxide and the remainder at the point where the top of the silver deposit had been. We have also tried this experiment on a cup which had been heavily alloyed by heating in the furnace and in this case we found that the prominent brown stains caused a great evolution of bubbles in the peroxide. In another case the platinum black stains which had been converted into platinum gray by glowing the cup were tested. Here the effect was much less marked than in a companion cup which had been similarly treated in every way except that it had not been glowed. We think this indicated that the stains were really platinum black.

In the case of moderately alloyed cups, with polished inner surfaces, the brown stains often showed the position and size and shape of each individual crystal of silver. But as the alloying was increased by longer heating it was possible to see the alloy spread out into the spaces between the crystals of silver, so that when the silver was removed the brown stains had merged together forming one continuous stain all over the inner surface of the cup. We have examined these stains under a high power microscope and found them to be essentially a surface phenomenon.

It seemed desirable to investigate the change in weight of this platinum

black in its relation to temperature and, therefore, we heated a cup to successively higher temperatures, weighing it after each heating. As a trial we washed and weighed it three times, heating it to 151° to see how well the weighings might be expected to repeat themselves. The cup contained only a medium amount of the stain and was not an extreme case.

TABLE IV.

Wt. of cup minus counterpoise. Mg.	Temperature. ° C.	Decrease in wt. Mg.	Remarks.
+0.276	151	...	Heated in electric oven
+0.236	151	...	Heated in electric oven
+0.247	151	...	Heated in electric oven
+0.123	231	0.130	Heated in electric oven
+0.044	400	0.079	Heated in electric furnace
-0.660	600	0.704	Color changed to gray
-0.718	660	0.058	Heated in electric furnace
-0.830	760	0.112	Heated in flame, temp. estimated
Total, 1.083			

These results are shown graphically in Fig. 1.

We next considered the question of the effect this layer of platinum black or platinum gray has upon the silver deposited and what role it played in the determination of the inclusions by the method of heating as advocated by Lord Rayleigh and later by Richards. From the above results we concluded that a cup containing a trace of platinum black, on which silver has been deposited, if heated to dull redness will show a loss in weight that cannot properly be assigned to the liberation of inclusions in the silver alone. Yet all previous observers, with little or no precautions to insure against the presence of the platinum black, have assumed the observed loss in weight to represent the liberated inclusion from the silver deposit. It is also obvious that if the platinum black is present the losses observed when making determinations of the inclusions by heating will be found to be very variable and their magnitude will depend upon the amount of platinum black present and its previous heat treatment. On the other hand if the cup had been glowed before making the deposit of silver, so that the platinum black is converted to platinum gray, it is less probable that subsequent heating of the silver deposit will show large or variable losses in weight. We have made a special test of this point in the case of two cups both coated with platinum black from previous alloying with silver. One of these was glowed before making the deposit of silver and the other was treated in the usual way, that is, washed and dried at 160°. Aside from the question of relative weights of the two deposits, which will be discussed farther on, we give here the observed losses in weight when the two cups with identical deposits were heated:

Cup that had been glowed before making the deposit, lost 0.06 mg.

Cup that had not been glowed, lost 4.89 mg.

This, of course, is an exaggerated case, but shows the possibility of error in the assumption made by previous observers as mentioned on page 502.

We concluded that if the cup has been thoroughly glowed previously to making the deposit that a subsequent determination of the inclusions will represent fairly the change in weight of the deposit. For if we take the mean of thirteen determinations given in Table VI, in which the

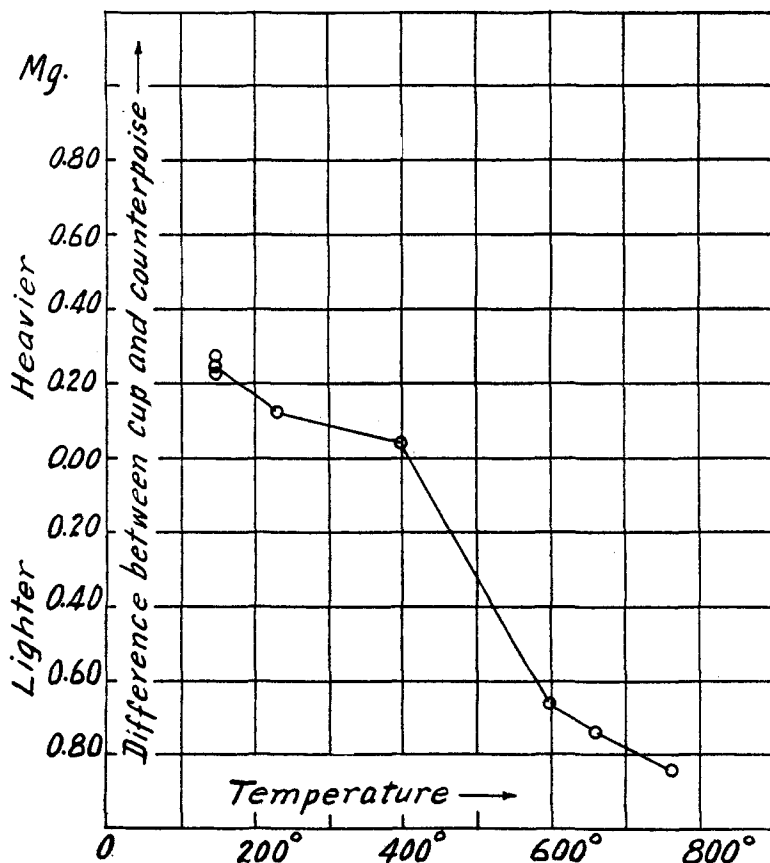


Fig. 1

cup contained a small amount of platinum black previously glowed, and compare it with twelve determinations made with cups which were entirely free from the platinum black or platinum gray before making the deposit, we find the difference in estimated inclusions to be only 0.0006% which is within the experimental error.

4. Effect of Alloying on the Amount of Silver Deposited.

The first intimation which we had that the presence of platinum black or platinum gray in the voltameter would cause serious errors in the quantity of silver deposited was in an early experiment when two cups that had been heavily alloyed, but subsequently glowed, showed deposits more than two milligrams lighter than the other cups. It was this experiment that first suggested the nature of the stains on the platinum and led us to experiment with them. Since then we have made special experiments to determine the general effect of previous alloying of the cups on subsequent deposits of silver.

TABLE V.

Effect of platinum black and platinum gray on the mass of silver deposited (deposits dried at 160°).

Date. 1915.	Cup.	Deposit. Mg.	Condition of the cup.	
Aug. 12.....	38	4249.23	Normal voltameter, no alloy	
	27	4249.19	Pt black removed by aqua regia	
	28	4250.61	A heavy layer of platinum black	
	18.....	93	4207.80	Normal voltameter, no alloy
		92	4207.33	Slightly alloyed and glowed
		27	4207.68	Pt black removed by aqua regia
Oct. 2.....	39	4207.49	Slightly alloyed and glowed	
	1	4207.58	Pt black removed by aqua regia	
	11	4207.64	Pt black removed by aqua regia	
	27	27	4233.03	Alloyed and glowed, platinum gray
		28	4234.35	Heavy layer of platinum black
	38	4233.58	Normal voltameter, no alloy	

It thus appears that a cup that had been alloyed and hence contains the platinum black stains gave an apparently heavier deposit than normal if it had not been glowed, or a lighter deposit than normal if it had been glowed previously to making the deposit. This was not understood at first since we thought that the light weight of the deposit might be due to the catalytic effect of the platinum gray on the hydrogen ions present in the solution, and it was, therefore, expected in the experiment of Aug. 12th that cup No. 28 would show a still lighter deposit. As a matter of fact the deposit was much too heavy and this was confirmed by the same cup in the experiment of Oct. 2nd. The difficulty was explained when we heated cups No. 27 and No. 28 of the last experiment to a dull red. No. 27 lost 0.060 mg.; No. 28 lost 4.89. That is, the deposit in No. 28 was in reality much the lightest, although apparently heavy, owing to material probably adsorbed by the platinum black.

Careful measurements of the acidity of the electrolyte were made and checked for the experiment of Oct. 2nd. It was found that the acidity increased considerably in the case of the cup with platinum black, somewhat less for the cup with platinum gray and none at all for the standard cup.

The acidities were as follows:

Initial acidity of electrolyte.....	7×10^{-6} acid
Final acidity No. 27, platinum gray.....	10×10^{-6} acid
Final acidity No. 28, platinum black.....	15×10^{-6} acid
Final acidity No. 38, normal cup.....	6×10^{-6} acid

Table V shows that when the platinum cup containing the platinum black is cleaned with cold concentrated aqua regia, and rubbed, the deposits are in agreement with those in cups which have never been alloyed with silver. This cleaning process, however, removes a considerable amount of the platinum. In exaggerated cases this is as much as a gram. For this reason it appears doubtful whether a moderate amount of scrubbing would suffice for the complete elimination of the platinum black. Richards and Anderegg, for example, mention scrubbing the cups and say that the crucibles lost a few tenths of a milligram each time. Our work would lead us to expect a much greater loss than this if the platinum black, even for only a slight alloying, be entirely removed. Cleaning the cups in this way is inconvenient and destructive to the cup. We do not find it necessary to make inclusion determinations for every deposit of silver and to do so would speedily ruin the platinum cups.

5. Estimation of Inclusions in Deposits from Pure Electrolytes.

Table VI shows the observed losses in weight of deposits from pure electrolytes, the purity being judged by the standards of purity previously published by the Bureau.¹ All such deposits which were heated according to the method described by Richards and Anderegg are included in this table. In no case was platinum black present, but in some cases slight amounts of platinum black had been converted over into platinum gray before making the deposits. This is immaterial, as we showed on page 503, but these cases are noted in the table. All deposits which were heated in the electric furnace are also included in the table, with the exception of two in the experiment of July 20th. For unknown reasons these were discordant with all the other results of the table and they are therefore omitted. They would affect the mean result by only 0.0005% if they were included.

The inclusions expelled by heating the silver, therefore, seem to be about 0.004%. Richards and Anderegg² apply a correction of 6% for the solids they estimate to remain from the inclusions, but 6% of 0.004% is too small to consider.

It is interesting at this point to compare the results which have previously been obtained by methods similar to those used in this paper. We give in Table VII an analysis of earlier results compared with our own. In general these results had to be computed from the original data con-

¹ *Bur. Standards Bull.*, 9, 524, reprint No. 201.

² *Loc. cit.*, p. 18.

TABLE VI.—ESTIMATION OF INCLUSIONS BY HEATING THE DEPOSITS.

Date. 1915.	Cup.	Method of heating.	Temper- ature. ° C.	Number of heatings.	Total loss in wt. Mg.	Loss in wt. %.	Platinum gray pres- ent or not.	Remarks.
June 14	95	Flame	..	2	0.130	0.0032	No	Silver nitrate prepared by B. S. methods
	39	Flame	..	2	0.186	0.0045	No	Silver nitrate prepared by B. S. methods
16	95	Flame	..	3	0.220	0.0055	Yes	Silver nitrate prepared by B. S. methods
	39	Flame	..	3	0.300	0.0075	Yes	Silver nitrate prepared by B. S. methods
24	95	Flame	..	3	0.181	0.0041	Yes	Silver nitrate as purchased not quite pure
	92	Flame	..	3	0.129	0.0029	No	Silver nitrate prepared by B. S. methods
	27	Flame	..	3	0.205	0.0047	No	Silver nitrate prepared by B. S. methods
	28	Flame	..	3	0.279	0.0064	No	Silver nitrate as purchased not quite pure
July 9	95	Flame	..	2	(+)0.007	(+)0.0002	Yes	Silver nitrate prepared by the Princeton method
	92	Flame	..	2	0.013	0.0003	Yes	Silver nitrate prepared by the Princeton method
	27	Furnace	625	2	0.048	0.0011	Yes	Silver nitrate prepared by the Princeton method
	28	Furnace	625	2	0.028	0.0007	Yes	Silver nitrate prepared by the Princeton method
	I	Furnace	625	2	0.166	0.0040	No	Silver nitrate prepared by the Princeton method (Cup not previously glowed)
	II	Furnace	625	2	0.115	0.0028	No	Silver nitrate prepared by the Princeton method (Cup not previously glowed)
20	95	Flame	..	I	0.161	0.0037	Yes	Silver nitrate prepared by the Princeton method
	92	Flame	..	I	0.116	0.0027	Yes	Silver nitrate prepared by the Princeton method
	I	Furnace	623	I	0.322	0.0073	Yes	Silver nitrate prepared by the Princeton method
	II	Furnace	623	I	0.254	0.0058	Yes	Silver nitrate prepared by the Princeton method
Aug. 9	92	Flame	..	I	0.333	0.0079	Yes	Silver nitrate prepared by the Princeton method
18	27	Furnace	625	I	0.240	0.0057	No	Silver nitrate prepared by the Princeton method
	I	Furnace	630	I	0.111	0.0026	No	Silver nitrate prepared by the Princeton method
	II	Furnace	625	I	0.169	0.0039	No	Silver nitrate prepared by the Princeton method
Oct. 2	27	Flame	..	I	0.060	0.0014	Yes	Silver nitrate prepared by B. S. methods
13	27	Flame	..	I	0.251	0.0057	No	Silver nitrate prepared by B. S. methods
	28	Flame	..	I	0.238	0.0054	No	Silver nitrate prepared by B. S. methods

Mean, $0.0040\% \pm 0.0018\%$

Probable error, 0.0015% for single observation; probable error, 0.0003% for mean result.

Mean flame determinations, 0.0041% ; mean furnace determinations, 0.0038% .

tained in the various papers. Thus in the case of Lord Rayleigh's Table II we have computed the percentage loss in weight of the deposit for all deposits made from silver nitrate not contaminated with acetate. For Richards and Anderegg's work we have included all the results given in their Table III and have averaged them together.

TABLE VII.

Summary of Results Obtained by Heating the Silver Deposits in the Platinum Cups to Expel Inclusions.

Year.	Observers.	Extreme values. %.		Range. %.	Mean result. %.	No. of observations.
1884	Rayleigh & Sedgwick ¹	0.000	-0.030	0.030	0.010	24
1902	Richards and Heimrod ²	-0.003	-0.030	0.027	0.018	12
1906	Van Dijk ³	+0.009	-0.006	0.015	0.000	7
1908	Jaeger and von Steinwehr ⁴ .	+0.002	-0.005	0.007	0.0008	18
1912	Boltzmann ⁵	+0.0026	-0.0087	0.0113	0.0023	19
1915	Richards and Anderegg ⁶ ...	-0.0039	-0.0352	0.0313	0.0142	27
1915	Vinal and Bovard ⁷	+0.0002	-0.0079	0.0081	0.0040	25

It is readily seen from Table VII that the results classify themselves in two groups. On the one hand we have Lord Rayleigh and Mrs. Sedgwick, Richards and Heimrod, and Richards and Anderegg; on the other hand we have Van Dijk, Jaeger and von Steinwehr, Boltzmann and the present authors. So far as Lord Rayleigh and Mrs. Sedgwick are concerned, it must be remembered that they were working with the filter paper voltameter and, therefore, their electrolyte was impure, which we think will account for a high value for the inclusions. Whether we include their results or not, the fact remains that Richards and his co-workers stand alone in finding the largest inclusions and in having the largest variation between his extreme values. The most consistent results, that is, those having the smallest difference between the extreme values are the results of Jaeger and von Steinwehr. These are closely followed by the results of the present paper and by the results of Boltzmann and Van Dijk. If we group these four series together we have 69 fairly consistent determinations, of the inclusions of which the mean is 0.0023%, weighting each of the four results according to the number of observations on which it is based. Richards' 39 observations, on the contrary, give a mean result of 0.0154% or nearly seven times larger than the mean of the other observers. Just how much effect the platinum black has had in the results of these previous observers we shall not attempt to say,

¹ *Phil. Trans.*, (A) 175, 438 (1884).

² *Z. physik. Chem.*, 41, 323 (1902).

³ *Ann. Physik*, 19, 266 (1906).

⁴ *Z. Instrumentenk.*, 35, 226 (1915).

⁵ *Sitzb. Akad. Wiss., Wien*, 121, 1062 (1912).

⁶ *THIS JOURNAL*, 37, 16 (1915).

⁷ This paper.

but it is evident that in the case of Van Dijk, Jaeger or von Steinwehr and Boltzmann it was very small. The last named mentions glowing the cup each time before making a deposit and this would nullify the effect of the platinum black so far as determining the inclusions is concerned, as we have shown.

The voltameters used in the researches that showed very small inclusions have varied greatly in size. The smallest cup was Van Dijk's which held only 30 cc. and the largest were our own, some of which held over 300 cc.

Smith, Mather, and Lowry heated a few deposits, but not to as high a temperature as in the case of the results recorded in Table VII; they are, therefore, not mentioned in this connection. This is also the case with a few other observers whose methods have differed in principle from the methods of this paper.

6. The Value of the Faraday.

The Bureau¹ published some years ago a value for the absolute electrochemical equivalent of silver which was obtained by the same silver voltameters used in the present work and an absolute current balance. This value was 1.11804 mg. per coulomb. Subsequently this was revised² to 1.11805 mg. per coulomb. Whichever of these values is taken, if we apply as a correction the estimated inclusions as found in the preceding section, it appears that 1.11800 mg. per coulomb, which was adopted by the London Electrical Congress of 1908 as the value for the electrochemical equivalent in determining the International ampere, is in reality also the closest figure that we can assign as an absolute value to this constant and is probably correct to within a few parts in one hundred thousand. We do not know the value for the atomic weight of silver with this degree of accuracy. It is only expressed to five significant figures, but taking the present international value 107.88 we find the value of the Faraday to be

$$96,494.$$

In a recent paper by Vinal and Bates³ the value 96,500 is recommended for general use and this recommendation still holds good. The correction for inclusions found in the present paper will account for only four out of twenty-one parts in 100,000 difference between the results of the silver and iodine voltameters of their work. Additional experiments are now being made in the Princeton laboratory in which some of the deposits obtained during the present investigation will be analyzed. After these results have been obtained a more extensive discussion of the Faraday will be given.

¹ *Bur. Standards Bull.*, 8, 367, reprint No. 171.

² *Ibid.*, 10, 477, reprint No. 220.

³ *Ibid.*, 10, 449, reprint No. 218.

7. Additional Experiments on the Deposits.

(a) **Successive Heatings of the Deposits.**—It will be noted in Table VI that some of the deposits were heated more than once. This was to determine how completely the inclusions are expelled by one heating. Our experiments showed that about 90% of the total loss in weight occurs the first time that they are heated.¹ The second and third heatings show small changes, which are sometimes slight gains in weight instead of losses.

(b) **Effect of Heating Deposits to an Abnormally High Temperature.**—Two deposits were heated by a flame to a temperature estimated at 700° after being heated to dull redness. The resulting loss in weight was observed.

Percentage of deposit, 0.0017 and 0.0006. Mean, 0.0011%.

One deposit was heated in the furnace to 675° after having been twice heated to 625°; the result was an apparent gain in weight of 0.0011%.

Effect of Prolonged Heating of the Deposit.—When the deposits are heated with the Bunsen burner the time that the deposit is at a high temperature is very brief, but in the case of the furnace the cup and deposit are over 600° for at least 7 minutes. The agreement of these two methods of heating shows that the time is not significant, but as a further test we baked a deposit for the second time in the furnace for 1/2 hour at 625° and found the loss in weight to be only 0.0004%.

It is fortunate that the time for heating can be made so short because the trouble with the alloy of silver and platinum is much lessened.

(c) **Heating the Deposit after Removal from Cathode.**—Two samples A and B of silver deposits from pure electrolytes were removed from the silver cathodes as described on page 499. These were dried at 160° in a small platinum dish previously washed, dried, and glowed. After weighing they were heated in the same platinum dish to dull redness with a Bunsen burner. We give in Table VIII these two values, together with the values obtained by heating the deposits on platinum of the same run according to the method described by Richards, or in the furnace. Two deposits of the run of July 9th, which are given in Table VI, are omitted here because the platinum cups were not previously glowed, and two deposits also on June 24th made with a different electrolyte.

TABLE VIII.

Estimations of inclusions in silver scraped from the cathode.

Date. 1913.	Sample.	Loss in wt. %.	Cup.	Loss in wt. %.	Mean. %.	Difference, sample minus cup. %.
June 24.....	A	0.0045	92	0.0029	0.0038	+0.0007
			27	0.0047		
July 9.....	B	0.0008	95	(+)0.0002	0.0005	+0.0003
			92	0.0003		
			27	0.0011		
			28	0.0007		

¹ Boltzmann (*Loc. cit.*) also obtained a similar result.

The agreement of these two results is better than was to be expected.

(d) **The Inclusions between the Crystals and the Surface of the Cup.**—Richards and Andregg¹ note that platinum cups with rough interior surfaces considerably increase the inclusions. It, therefore, seemed worth while to examine this point closely because of the excellent agreement of results obtained by Hulett and Vinal,² although one used platinum cups with rough interior surfaces and the other smooth surfaces. In the present work Cups I and II had rough interior surfaces and 27 and 28 became roughened after cleaning with the aqua regia, so we may readily classify the results given in Table VI according to the character of the interior surface of the cup. This is done in Table IX.

TABLE IX.

Comparison of inclusions in voltmeters with rough and smooth surfaces.

Smooth surfaces (% loss in weight on heating):

0.0032, 0.0045, 0.0055, 0.0075, 0.0041, 0.0029, 0.0047, 0.0064, +0.0002, 0.0003, 0.0011, 0.0007, 0.0037, 0.0027, 0.0079. Mean, 0.0037%.

Rough surfaces (% loss in weight on heating):

0.0040, 0.0028, 0.0073, 0.0058, 0.0057, 0.0026, 0.0039, 0.0014, 0.0057, 0.0054. Mean, 0.0044%.

The difference is thus only 0.0007%, which is within the experimental error, and, therefore, we may say that the inclusions on smooth and rough surfaces are, so far as our experiments go, the same.³

As to the magnitude of the inclusions between the crystals and cup, we were enabled to form an estimate using the silver cups in which the silver can be so easily scraped from the cathode while the cup is filled with conductivity water.

The general procedure was to wash these deposits until further washing produced no change in the conductivity of the water used. Then a platinum cup similar to the cups in use was filled, after washing, with the same conductivity water and stood beside the cup under test. A large glass plate was interposed between the observer and the cups while the silver was scraped down, so that during the three to five minutes required the breath of the observer might not contaminate the water in the cups. As soon as the scraping was complete the conductivity of the water in the cup under test and the blank also were immediately measured in a conductivity cell of the pipet form.⁴ The net result found represents the increase due to the silver nitrate liberated by scraping the silver and also all other causes of increase of conductivity, except the effect of temperature which was under control. Consequently the values found are maximum values

¹ *Loc. cit.*, p. 16.

² *Bur. Standards Bull.*, 11, 557, reprint No. 240.

³ Compare Jaeger and von Steinwehr, *Z. Instrumentenk.*, 35, 233 (1915).

⁴ This was the same cell used by Hulett and Vinal, *Bur. Standards Bull.*, 11, 558, reprint No. 240.

and the silver nitrate calculated from the increase in conductivity is probably too large. In the first experiment the value found is considerably larger than in the others. This is probably due to imperfect technique before we learned the best way of doing the experiment. The results are given in Table X.

TABLE X.
Inclusions between crystals and cup.

Date, 1915.	Cup.	Equivalent AgNO_3 for increase in conductivity. Mg.
Aug. 9.....	VI	0.04 (omitted from mean)
	V	0.01
" 18.....	V	0.0052
	VI	0.0078
Mean, 0.0076 mg., 0.0002% of the deposit		

The amount of silver nitrate trapped behind the crystals is, therefore, very small and consequently it is not surprising that Table VIII shows so close an agreement between the inclusions determined for the silver removed from the cathode and otherwise.

(e) **Inclusions in Silver Deposits from Less Pure Electrolytes.**—In two experiments we used electrolytes manifestly less pure than in the other experiments. For one of these we purposely added filter paper to the electrolyte and in the other the impurity manifested itself by a considerable volume effect which, being larger than the average experimental error, we regard as evidence of impurity. These results are given in Table XI.

TABLE XI.

Estimated inclusions by heating the cups with deposits from impure electrolytes.

Date, 1915.	Cup.	Loss in wt. %.	Remarks.
July 2.....	95	0.0067	Filter paper put in electrolyte
	92	0.0118	Filter paper put in electrolyte
	27	0.0071	Filter paper put in electrolyte
	28	0.0097	Filter paper put in electrolyte
28.....	95	0.0106	Volume effect of 7 in 100,000
	92	0.0102	Volume effect of 7 in 100,000
	27	0.0118	Volume effect of 7 in 100,000
	28	0.0095	Volume effect of 7 in 100,000
	1	0.0102	Volume effect of 7 in 100,000
	2	0.0093	Volume effect of 7 in 100,000

Mean, 0.0097

The inclusions, therefore, appear to be more than twice what was found in the case of pure electrolyte. This is in accord with the view expressed by the Bureau¹ several years ago that the presence of impurities of a colloidal nature which break up the crystalline structure of the silver will increase the inclusions in the deposited silver.

¹ *Bur. Standards Bull.*, 10, 517, reprint No. 220.

TABLE XII.
Analysis of deposits with reference to the volume effect.

Date. 1915.	Size.	Deposit before heating. Mg.	Δ . Large— small. Mg.	Deposit after heating. Mg.	Δ . Large— small. Mg.	Remarks.
June 14	Large	4095.69	+0.12	4095.56	+0.17	} Silver nitrate as purchased } Filter paper in electrolyte Note volume effect
	Small	4095.57		4095.39		
16	Large	3975.84	+0.21	3975.62	+0.29	
	Small	3975.63		3975.33		
24	Large	4375.07	+0.07	4374.94	+0.14	
	Small	4375.00		4374.80		
	Large	4375.25	+0.15	4375.07	+0.25	
	Small	4375.10		4374.82		
July 2	Large	4221.87	+0.97	4221.59	+0.99	
	Small	4220.90		4220.60		
	Large	4222.46	+1.53	4221.98	+1.46	
	Small	4220.93		4220.52		
9	Large	4180.13	\approx 0.00	4180.14	+0.06	
	Small	4180.13		4180.08		
	Large	4180.09	-0.04	4180.08	-0.02	
	Small	4180.13		4180.10		
28	Large	4339.94	+0.28	4339.48	+0.33	
	Small	4339.66		4339.15		
	Large	4339.84	+0.34	4339.40	+0.31	
	Small	4339.50		4339.09		
Total Δ 's,			+3.63		+3.98	

(f) **The Volume Effect.**—Richards and Anderegg,¹ explaining the volume effect, attribute it to a surface effect and claim the inclusion to be greater in the larger cups, so that when both large and small cups are heated the resultant deposits are in agreement. We have examined all our experiments with this point in view and we give in Table XII an analysis of all those in which a comparison of our large and small cups (No. 92 and No. 95 large size, No. 27 and No. 28 small size) was made with subsequent heating, except for the experiment of July 20th, in which, as we stated on page 505, the results with the small cups were anomalous. This table includes the results of deposits from pure solutions in which the volume effect was very small or absent altogether and also the results of deposits from impure solutions in which the volume effect is large. The table shows that heating the deposits to expel the inclusions did not make the difference between large and small deposits any less² as Richards' theory would call for, but on the other hand the difference became a trifle larger, on the average 0.03 mg. for each comparison which is perhaps as good

¹ *Loc. cit.*, p. 16.

² Examining the results of Lord Rayleigh and Mrs. Sedgwick we find the same thing. Their large cup deposits lost 0.013% and their small cup deposits lost 0.009%. The difference between these results is well within their experimental error.

an agreement as could be expected. Richards' results could, however, be explained on his theory by the assumption that the platinum black from previous heatings was not entirely eliminated before making the deposit. In such a case for two cups equally alloyed the amount of platinum black would be proportional to the surface of the cup. This, even with pure electrolyte, would probably show an apparently heavy deposit in the large cup as our results on page 504 indicate and this deposit would also lose the most on heating to a high temperature, hence the two deposits would appear to draw together. The results of Table XII emphasize the previous viewpoint of the Bureau that the purity of the salt used for the electrolyte is the determining factor in the volume effect.

8. Experiments on the Anode Liquid.

Many lines of evidence led the Bureau to the conclusion stated in Part I¹ of the recent voltameter papers that the effects of the supposed anomalous substance formed at the anode during electrolysis were in reality due to impurities present in the solution, as for example filter paper. The Bureau has not found it necessary to change this view, but in the present work we have tried two further experiments on the anode liquid.

The first experiment was suggested to us by the remark of Richards and Anderegg² that the reasons most observers had failed to find this peculiar compound in the anode liquid, is because they delayed testing for it until the compound had become oxidized and vanished. Accordingly, we drew four 10 cc. samples of the dense anode liquid (17%, the original electrolyte was 10%) from inside the porous cups of the voltameters of Aug. 18th. The electrolyte of this experiment was quite pure as judged by the permanganate, acidity and volume effect tests. The four samples of anode liquid were taken within one minute after the electrical circuit was broken. Each was put in a stoppered glass tube and acidified, then one cc. of 0.001 *N* KMnO_4 was added to each tube and all shaken to mix the contents. The whole operation consumed less than five minutes. The times required for the permanganate color to fade were noted. They were

42; 52; 70; 70; mean, 59 minutes.

We do not think that our anode liquid contained the oxidizable compound spoken of by Richards, else the color of so small a quantity as 1 cc. of 0.001 *N* KMnO_4 would hardly be expected to last for an hour.

Our second experiment on the anode liquid was suggested by the use of the alundum porous cups in an experiment described by Richards and Anderegg.³ They used the porcelain porous cup to hold back the anode compound and the very porous alundum cup to let it through. We thought

¹ *Bur. Standards Bull.*, 9, 151, reprint No. 194.

² *THIS JOURNAL*, 37, 686 (1915).

³ *Ibid.*, 37, 685 (1915).

that a slightly different arrangement of the porcelain and alundum cups would perhaps throw more direct light on the matter. A previous experiment showed that our alundum cup permitted water to pass through its pores about sixty times as fast as it passed through our porcelain (Pukal) porous cups.

We arranged three voltameters. One was a normal voltameter with the ordinary porous cup, the second was similar to the first except that an alundum porous cup was used in place of the porcelain porous cup. The third had a porcelain porous cup fitting snugly inside of an alundum porous cup. The alundum and porcelain cups were all prepared similarly and as described by the Bureau.¹ According to the theory of Richards, the deposits in the first and third voltameters should agree and both be lighter than the deposit in the second, but on the other hand if the heavy anode compound with excess silver is non-existent then the second and third should agree and if heavier than the first this shows that the alundum cups are responsible for introducing impurities into the solution. The results of this experiment were as follows:

	Mg.
The first (normal voltameter).....	4327.08
The second (alundum cup).....	4327.38
The third (alundum cup with porcelain porous cup inside).....	4327.44

These results, therefore, tend to confirm the previous views of the Bureau that the anode reactions produce no effect whatever in the quantitative measurements² of the silver deposited.

This work has been done at the Bureau of Standards under the direction of Dr. E. B. Rosa. We have also been fortunate in having the help of Prof. G. A. Hulett. The investigation is being continued under the direction of Prof. Hulett by one of the present authors (Bovard) in the Princeton laboratory.

9. Summary.

(1) We have heated a number of silver deposits to temperatures slightly above 600° both with a flame and in an electric furnace and have found the losses in weight to indicate inclusions of foreign matter in the deposits to be 0.0040% on the average for pure electrolyte and higher for impure electrolytes.

(2) We have found that such heating of the deposits produces an alloy of silver and platinum, which, when the silver is dissolved, leaves a layer of platinum black that may lead to serious errors the next time the cup is used if proper precautions are not taken.

(3) We are led to conclude that the most accurate absolute value for the electrochemical equivalent of silver is 1.11800 mg. per coulomb and,

¹ *Bur. Standards Bull.*, 9, 185, reprint No. 194.

² Boltzmann (*Loc. cit.*) made experiments on the anode liquid and also found it without effect on the deposited silver.

therefore, the value of the Faraday becomes 96,494 absolute coulombs, but for general purposes 96,500 as a round number is recommended.

(4) Inclusions in silver deposits made on smooth platinum surfaces are the same to within the experimental error as when the deposits are made on matte surfaces.

(5) Inclusions between the crystals and cup have been measured by an application of the conductivity method and are found to be a negligible part of the total inclusions which, with pure solutions, were about four parts in a hundred thousand.

(6) In cases where the deposit in large cups exceeds that in small cups (that is where the "volume effect" is appreciable) we do not find that strong heating of the deposits diminishes the difference.

(7) Two experiments on the anode liquid support the Bureau's previous conclusions as to the non-existence of the heavy anode ion.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE JOHNS HOPKINS UNIVERSITY.]

**STUDIES OF THE VAPOR PRESSURE OF SOLUTIONS.
THE LOWERING OF THE VAPOR PRESSURE OF WATER PRODUCED BY
DISSOLVED POTASSIUM CHLORIDE.**

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Introduction.

In a preliminary article¹ the authors described a static method for the study of the vapor tension of aqueous solutions, and gave a sufficient amount of experimental material to demonstrate its reliability. Although these results were apparently very good, when judged by the agreement among the different determinations made on a given solution at various times, extending over periods of several weeks, the authors were not positive that the results obtained were the true vapor tension depressions of the solutions investigated. For this reason certain alterations have been made in the apparatus as originally described. In its improved form it is believed that the apparatus is capable of giving the vapor tension depressions of aqueous solutions correctly to 0.001 mm. or less; and in the present article the authors purpose to describe these alterations in detail and with as little repetition of the portion contained in the first article as will make the description clear. The accompanying illustrations, in which all essential details of the apparatus are given, will assist in making clear such points as are not described here in detail. The measurements on potassium chloride solutions recorded in

¹ THIS JOURNAL, 36, 2439 (1914); also *Z. physik. Chem.*, 89, 155 (1914).