Studies on Silver Coulometer.

by

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Introduction.

Previous to the starting of this investigation there had been
extensive studies and experiments made with the silver cou-
lometer, dating back to the fundamental work of Rayleigh and
Sedgwick[1] in 1883, when the coulometer first became an accurate
instrument for the measure of electric current. The present
investigation was undertaken in order to throw light upon a
matter which had received no attention in the numerous articles
published on the silver coulometer.

In the discussion which followed Duschak and Hulett's[2] work
on the silver coulometer the point was made by Mr. Hering[3]
that, since platinum is known to contain oxygen in some form,
it seems possible that dissolved oxygen may play some part in
the deposition of silver, and it would naturally follow that
abnormal weights might be caused thereby.

Platinum is known to take up oxygen either in solution or as a
compound, forming an oxygen electrode in equilibrium with the
oxygen in the electrolyte. On passing a current through a
solution of silver nitrate the main reaction at the cathode would
be the deposition of silver, but some of the current would go to
the removing of the oxygen, and, since 8 grams of oxygen are
equivalent to 107.88 grams of silver, it follows that there might
be a deficit in the amount of silver deposited, an amount which
might easily admit of measurement. It seemed possible that

[1] The literature of the coulometer is particularly reviewed by Guthe, Bull. No. 3,
Bureau of Standards, 1905, page 347, and by Smith, Mather and Lowry. Phil.
Trans., **207**, 545. Rayleigh and Sedgwick; Phil. Trans., **175**, 111 (1884).

[2] Duschak and Hulett: Trans. Am. Electrochem. Soc., **12**, 257 (1907).

[3] Hering: Trans. Am. Electrochem. Soc., **12**, 293 (1907); Bose: Chem. Ztg., **26**,
67 (1902).

information on this question could be obtained by using as a cathode cup some metal such as gold, which does not measurably absorb oxygen.

Considerable work has been done on the silver coulometer in vacuo and in solutions saturated with nitrogen, which means the exclusion of oxygen, and, while the evidence is not conclusive (most experimenters have observed a heavier deposit where oxygen has been excluded), this might be explained by the foregoing assumption.

The type of coulometer used by us was essentially the same as that used by Duschak and Hulett. Two of the cups were made of gold and two of platinum, each containing a porous cup to retain the heavy anode liquid. These were run in series, with the idea of comparing the silver deposited on platinum and on gold, in order to determine whether gold could be substituted for platinum as a cathode and thereby overcome the influence which might be caused by the oxygen in the platinum.

We soon found that the purity of the materials used in making up the electrolyte affected the deposits, and also that the inclusions in the deposited silver had to be taken into consideration, so this investigation really involved several important questions, and has resulted in two independent researches. Since it soon developed that the slight impurities in the electrolyte caused measurable variations in the weight of the silver deposited, it seemed probable that this variation in the weights might be due to the variation in the impurity included by the deposited silver. A very careful study of inclusions in electrolytic silver was taken up by Mr. J. S. Laird, and a method developed for the accurate determination of these inclusions, as described in a separate paper. Our first problem was to get a standard reproducible silver nitrate solution.

Incidentally we obtained some information from the suggestions of Richards[4] and others that a complex ion is formed at the anode, and that when this anolyte comes in contact with the cathode the deposit of silver is too heavy. In testing this point we arranged two coulometers in series, in which we maintained by the use of syphons the catholyte and anolyte at such levels that in each cathode cup the flow of the liquid would be towards the opposite pole.

[4] Richards, Collins and Heimrod; Proc. Am. Acad., **35**, 123 (1899).

We also attempted to substitute "Alundum" cups made of pure Al_2O_3 for the porous porcelain cups, since these permitted an easier flow of liquid and lessened the resistance.

In series with most of these experiments we ran a coulometer of the Rayleigh type, using the filter paper inclosed anode. We also experimented with electrolytes of different degrees of purity.

Apparatus Used.

Each cathode cup was 10 cm. high, 5 cm. in diameter, and weighed 72 grams. The cups were so adjusted as to weigh within 0.001 gram of each other, the advantage of this being that one tare would suffice for all of the cups and the exact differences in weight could be determined with the rider. The cathode cups Nos. *1* and *2* were of platinum, while *3* and *4* were of pure gold. These cathode cups were handled with tongs at all times. They were thoroughly cleaned with sea sand, also chemically, and washed, after which they were heated to redness for ten minutes in an electric furnace. This final treatment produced a surface on the gold cups to which the silver adhered so tenaciously that it could not be readily detached. Since the deposits were to be saved, this treatment was abandoned. When, however, the cathode cups were placed in wooden molds, and the internal surfaces made smooth with a blood-stone burnisher, then cleaned as stated above and heated in an electric furnace at 160° for thirty minutes, it was found that this treatment gave a gold surface from which the silver deposits could generally be removed with a platinum spatula. The deposits in the platinum cups could always be removed with ease.

The weighings were made under the same conditions as those described by Duschak and Hulett, the only difference being that the swing divisions were read through a small telescope fixed in the balance case. Duplicate weighings could be made to 0.02 mg. with certainty. Care was always taken that temperature equilibrium had been established in the balance case, and the cups were always placed on the pans with long tongs. The weights were calibrated, and at each weighing the temperature, barometer and hygrometer were noted. The anodes were made of "atomic-weight" silver, the purification of which is described elsewhere. The silver was melted in a porcelain cru-

cible and cast into cylindrical sticks 6 cm. by 1 cm. in a mold made of pure graphite which had previously been heated to redness for thirty minutes. These anodes were suspended by platinum wires which served as electrical connections. The four cathode cups were cleaned, adjusted to the same weight by removing a little from the top of the heavier ones, cleaned as described above, cooled in separate vacuum desiccators, and finally weighed.
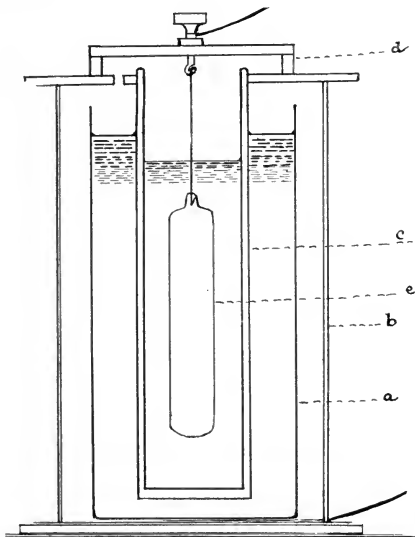
Fig. 1.

The cathode cups were now set up ready for a run, on circular pieces of plate glass the bottoms of which had been previously paraffined and on the top of which had been placed several pieces of filter paper to insure perfect insulation. The cathode cups (a) as shown in Fig. 1 were surrounded by glass jackets (b) which extended 2.5 cm. above the cups, and the glass cylinders were covered with pieces of glass provided with two holes, those in the center being just large enough to hold the porous cups (c),

while those at the side and through which the catholyte was introduced were smaller. On the glass cover rested a hard rubber bridge (d) from which the anode (e) was suspended as indicated in the figure. In series with these four coulometers we ran one of the Rayleigh type, modeled after the specifications prepared by the National Academy of France. The Rayleigh bowl was 9 cm. by 4 cm. deep.

The porous cups were exact copies in size and texture of the Berlin "Pukel" filter tubes except that the upper 3 cm. were vitreous. They were 2.5 cm. in diameter by 12 cm. long, and when placed in position extended to within 0.75 cm. of the bottom of the cathode cups. These porous cups were treated with concentrated nitric acid, and then water was allowed to flow through them continuously until the last trace of nitric acid had been removed. At no time were they glowed or allowed to dry out. During a run the anolyte was removed at intervals with a constant level pipette and the catholyte added, so that the electrolyte was always flowing into the porous cups towards the anode. After an experiment had been completed the silver crystals were loosened with a platinum spatula and sealed in test tubes which had previously been glowed. This silver was examined by Mr. Laird, as described in another communication.

Materials Used.

In previous work we learned that filter paper was to be avoided, and in the present investigation we soon found that not only filter paper, but dust, organic matter of every kind and even dissolved glass so affected a silver nitrate solution that it gave abnormally heavy deposits. This research is therefore largely devoted to the question of the purity of the materials used in coulometer work.

In order to have a reliable and reproducible basis of comparison it was found necessary to work with a silver nitrate solution made in a definite way, which was essentially the same as that used by Richards in preparing the silver nitrate from which he determined the atomic weight of silver. This must give us a solution in which the equivalence between Ag and NO_3 is exactly equal, provided we rigorously exclude organic matter in all subsequent operations. We therefore paid particular attention to the elimination of all organic matter from our water, and

used only quartz, gold and platinum vessels, so that there could be no possible reduction of the silver nitrate by dissolved glass or by any other reducing agent. This is our "normal" coulometer electrolyte.

Preparation of Silver.

The first step in purifying silver is to obtain it in the form of silver chloride. Richards[5] digested silver chloride in a solution of potassium hydroxide and sugar, in order to obtain metallic silver. If, however, the silver chloride is dissolved in ammonium hydroxide and filtered, certain substances are eliminated, and there is an advantage in reducing silver directly from a solution rather than from the solid. We encountered a difficulty in reducing the silver from an ammoniacal solution with hydroxide and sugar in a desirable crystalline form, but found that this could be done as follows: Silver was obtained from the U. S. Mint, dissolved in nitric acid and precipitated as silver chloride. It was then digested in aqua regia for several hours on the water bath, filtered and washed. The silver chloride was dissolved nearly to saturation in a closed container in ammonium hydroxide of specific gravity 0.93. Five hundred c.c. of this silver-ammonium chloride solution was then decanted and filtered into a liter flask which contained 25 g. of cane sugar dissolved in 50 c.c. of water. Silver did not appear at first, but when the solution was heated to incipient boiling the silver began to separate in a very finely crystalline form. The ammonia which distilled was led into pure water for future use. As the reduction proceeded a solution containing 100 g. of sugar and 25 g. of potassium hydrate in 150 c.c. of water was added through a dropping funnel, rapidly at first and more slowly as the evolution of ammonia becomes less. After the sugar solution had been added and the evolution of ammonia had ceased, the liquid was vigorously boiled for fifteen minutes. Under these conditions we were able to reduce silver from an ammoniacal solution in a crystalline form which could be readily washed. It was found to be finely granular, and contained only exceptionally the slightest traces of silver chloride, which were entirely removed by shaking thoroughly with ammonium hydroxide. The small-grained silver possessed the virtue of lessening the possibility of

[5] Richards and Wells; Jour. Chem. Soc., **27**, 475 (1905).

silver chloride and other impurities being occluded, it was easily soluble in nitric acid, and the solution gave no cloudiness on dilution. The silver was now placed in a Jena flask, dissolved in nitric acid, the solution evaporated, and the residue fused in an electric furnace. The fused silver nitrate was dissolved in "conductivity" water, and the metal precipitated with ammonium formate according to the directions of Richards and Wells. This silver was composed of large crystals, and was as pure as "atomic-weight" silver. It was melted and cast into molds, as has been already described. This silver was used in the preparation of our "normal" electrolyte.

Purification of Water.

Since dust, organic matter or dissolved glass in the water would partially reduce our purest silver nitrate, particular care was exercised in purifying the water employed in our work. The apparatus consisted of a 15-liter Jena retort, the neck of which was drawn down and cut off so as to just fit a quartz condenser tube ground into and *extending into the retort*. The arrangement was such that only vapor could enter the condenser, the water separating on the glass simply flowing back into the boiling liquid. Air filtered through absorbent cotton and deprived of all organic matter by passage over a glowing platinum spiral, wound evenly on a porcelain tube, was bubbled slowly through the gently boiling water. This water contained a small amount of $KMnO_4$ and $Ba(OH)_2$ and was freshly prepared conductivity water. The whole apparatus was drained for fifteen minutes before any water was condensed, only the second third being caught and retained in a quartz flask. Since this water had been in contact with quartz only, it must have been free from all traces of dust and organic matter.

Preparation of Silver Nitrate and Nitric Acid.

The nitric acid was purified according to a method identical in the main to the one employed in obtaining pure water. No air, however, was bubbled through the acid during its distillation. The purest silver was dissolved in this nitric acid and water prepared by the foregoing method. The quartz flask was placed in an electric furnace where the temperature was accurately con-

trolled, the solution was evaporated, and the residue fused according to Richards' directions until the last trace of nitric acid had been expelled. Extending down into the quartz flask which contained the silver nitrate was a porcelain tube through which passed air purified as previously described. The silver nitrate was kept covered, in a dark place, until used the day following, and the water was prepared and the solution made just before the experiment was started. A 15 percent solution was used in all experiments. We regarded this as the purest obtainable silver nitrate solution on a reproducible basis.

Manipulation.

After obtaining the accurate weights of the cathode cups they were placed on the circular glasses and filter papers with a strip of platinum foil under each cup, which served as a conductor for the electric current. The glass jackets were placed over them, and the silver nitrate solution, prepared as above, was added. The porous cups were now rinsed with silver nitrate solution and placed in position; thus the catholyte began immediately to diffuse into them. The anodes were fixed in place, and then the anolyte was added, but only to such a level that the catholyte was always passing into the anode chamber. After a current of about 0.3 ampere had passed through the coulometers for about four hours, depositing approximately 5 grams of silver in each cup, the current was broken and the anodes were removed. The anolyte was drawn off with a pipette, and following this the catholyte was removed by the same method. Finally the porous cups were removed and examined for small particles of loose silver which might have adhered to them. The anolyte and catholyte were reserved in separate flasks, and, although all solutions were tested for acidity, they were always found to be neutral.

The cathode cups were allowed to drain into small crystallizing dishes, each inclined against a glass support. The cups were next filled with distilled water, which was removed with a freshly-blown bulb pipette, run into a marked flask, and the cathode cups were drained again into the same crystallizing dishes. This was repeated three times, until the water which had stood over night in the cups gave no test for silver with KI. It was quite

impossible for any loose silver to escape us in this way, for previously it was shown that as little as 0.002 mg.[2] of silver could be detected in a flask and recovered. The cathode cups were always handled with tongs, wound with linen thread, so that no dust or liquids came in contact with the outside of the cups, which were always bright and polished. The loose silver was placed in the proper cathode cups, and these were dried in vacuum desiccators and weighed. We also satisfied ourselves that there was no appreciable change in weight when the cathode cups with the deposits were subsequently heated to 160° for thirty minutes. In the experiments made using the two platinum and two gold cathode cups a "Rayleigh" form was also run in the series. The results are as follows (Table I):

TABLE I.

Run No.	On Pt.		Differences mg.	On Au		Differences mg.
	1	2		3	4	
7	5.83369	5.83383	0.14	5.83449	5.83444	.05
8	5.47605	5.47586	0.19	lost	5.47637	. . . .
9	5.59653	5.59663	0.10	5.59756	5.59746	.10
10	4.98000	4.97953	0.47	4.98036	4.98038	.02
11	6.26536	6.26540	0.04	6.26589	6.26603	.14

Run No.	Average Pt. deposit	Average Au deposit	'Rayleigh' deposit	Deposit on Gold heavier than on Pt. mg.	Rayleigh deposit heavier than on Pt. mg.
7	5.83376	5.83446	5.83525	+0.70	+1.49
8	5.47595	5.47637	5.47749	+0.42	+1.54
9	5.59658	5.59751	5.59848	+0.93	+1.90
10	4.97976	4.98037	4.98184	+0.61	+2.08
11	6.26538	6.26596	6.26661	+0.58	+1.23

If we calculate the percentage difference in the weight of silver deposited on platinum and on gold by the same current, we find that the deposits on the gold are 0.012 ± 0.0012 percent heavier than the deposits on platinum, while in the Rayleigh coulometer, where Kahlbaum's C. P. silver nitrate and the filter paper enclosed anode were used, we found the deposits to be 0.030 ± 0.0033 percent heavier than the deposits made on the normal platinum cathode cup. In every case it was found that the silver

deposited on gold was heavier than that deposited on platinum by the same current, the average excess being 12 parts in 100,000. This could be explained by assuming that part of the current in the platinum coulometers passed from the catholyte to the platinum cathode by removing oxygen from the platinum.

The silver samples reserved from these runs were investigated by Mr. Laird, but before the method of determining the conclusions was in its final state, the deposits from the gold cups showed in all cases slightly more inclusions and those from the Rayleigh form very much more than did the deposits from the platinum cups. The difference in the amounts of inclusions in the silver from the platinum and gold may be due to the fact that the silver crystals deposited on the gold were close together and nearly covered with gold, whereas those on the platinum were isolated.

These deposits on the platinum also contained impurities, so in our judgment it matters little which metal we use as cathode when the exact electrochemical equivalent of silver is to be determined, for the impurities in the silver deposit must be determined in any case if an accuracy greater than 1 in 5,000 is desired.

In examining the deposits we found that the silver crystals deposited on the platinum cathode were rather large and well defined, being placed irregularly on the sides of the cathode cups, with only a few on the bottom. Only in very few cases was there a tendency towards a striated arrangement of the crystals on the platinum, and in all cases the silver was easily detached by a platinum spatula without appreciably changing the weight of the cups. One of the difficulties encountered in using a platinum cathode was the fact that there was always a small amount of loose silver present which had to be recovered.

It seemed to us that gold might be a more desirable metal for the cathode cups than platinum, and when the surface of the gold cups was slightly rough there was generally no loose silver, but sometimes there was, for the adhesion of the silver crystals to the gold cups was not sufficient invariably to retain all of the silver during the manipulations. However, the adhesion was sufficient to make it a very difficult matter to remove the silver for examination as to inclusions. Gold is a soft metal, and the thin-walled cups were difficult to handle. Since the silver crystals

completely covered certain parts of the gold cathodes, and there may have been more chance for inclusions between the silver and gold than between the silver and platinum in the platinum cathodes, the platinum cups appear on the whole to be superior to those of gold, and if the dissolved oxygen plays any rôle it is only a few parts in 100,000.

The deposits in the "Rayleigh" form were feathery and striated at all times. The comparative character of the deposits in the platinum and gold cups can be seen in Fig. 2.
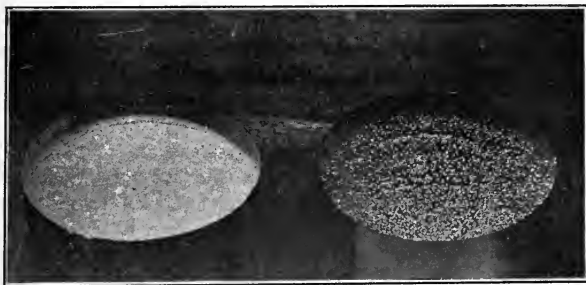

FIG. 2. The gold cup on the right shows the small Ag crystals as compared with those deposited on a platinum cup as shown on the left.

The Effect of Solutions of Known Purity.

Since the impurities in the deposits caused the abnormal weights, we decided to try some experiments in which the silver nitrate solutions in the cathode cups were of different but of known sources. In platinum cup No. *1* we used our "normal" solutions, in No. *2* a solution of Kahlbaum's C. P. silver nitrate which had been recrystallized after adding 1 c.c. of our purest nitric acid to the solution, decanting, evaporating and fusing the salt as directed above. The manipulation was carried out in detail as in the previous experiment. In the last four experiments we also ran a "Rayleigh" type which contained the same recrystallized silver nitrate solution contained in cup No. *2*. The results were as follows:

TABLE II.

Run No.	1 "Normal"	△ mg.	2 Kahlbaum's	mg. Heavier thau Normal	Rayleigh Kahlbaum's
12	7.12175	0.58	7.12233	....	......
13	4.96636	0.76	4.96560	....	......
14	5.97746	0.82	5.97828	....	......
15	5.86213	0.86	5.86299	....	......
16	6.66193	0.29	6.66222	2.99	6.66492
17	5.72269	1.61	5.72430	3.19	5.72588
18	6.04101	0.41	6.04142	1.53	6.04254
19	5.04073	0.30	5.04103	3.18	5.04391
20	5.77169	—1.09	5.77060	2.09	5.77378

In experiment *20* the silver deposit in coulometer No. *2* was partially discolored, and, while the cause is unknown, it was obviously to be rejected, although we proceeded with the weighing as a matter of form. Referring to table No. *2*, coulometer No. *1* always contained our "normal" silver nitrate solution, while in No. *2*, which was like No. *1* in all other respects, was placed the solution made from our best water and Kahlbaum's silver nitrate, which had been treated with a little nitric acid, recrystallized and fused as previously described. This same solution was also used in the Rayleigh form. We expected to find that the Kahlbaum's C. P. silver nitrate when treated in this way would give the same results as our "normal" solution, but we found that coulometer No. *2* in every case gave a heavier deposit, the average excess being 0.009 percent. We noticed also that the Rayleigh form with the same solution as that in coulometer No. *2* gave a deposit which was always much heavier than that obtained from our normal electrolyte, the average excess being 0.036 percent. Furthermore, the deposits from coulometer No. *2* show distinctly more inclusions than those from coulometer No. *1*, while the deposits from the Rayleigh show still greater amounts of inclusions than from No. *2*.

It would follow, therefore, that the source and previous history of the silver nitrate solution always plays a measurable rôle in the weight of silver deposited by a given number of coulombs. We are therefore forced to the conclusion that it is necessary to determine and allow for the inclusions in the deposited silver when any attempt at great accuracy is made, and, although

reasonably pure materials for the electrolytes will suffice, the purer the solutions used the less the error due to inclusions, which is as small as one part in 10,000 for our "normal" electrolyte in a porous cup platinum coulometer, where the anolyte has no access to the catholyte during the electrolysis.

Effect Due to the Anolyte.

It has been maintained by Richards and others that the solution formed at the silver anode in a silver nitrate solution is abnormal in that it will yield an abnormally heavy deposit when used as catholyte. Table II clearly shows that the Rayleigh form gives a markedly heavier deposit than does the porous cup coulometer with the same solution. Filter paper has the property of so changing a silver nitrate solution that it gives a heavier deposit, a fact which in part or wholly would account for the difference between the results obtained with coulometer No. 2 and the Rayleigh form, as shown in Table II. There is another possible factor. In the Rayleigh coulometer the silver nitrate formed at the anode increases the density of the solution at the bowl, and it flows down through the filter paper and comes in contact with the cathode. In order to get some evidence on the possible effect of the anolyte we carried out the following experiments :

In our porous cup coulometers *1*, *2*, *3* and *4*, filter paper and all organic matter were excluded; furthermore, the anolytes in the porous cups were always maintained at a lower level than the catholytes, so that the flow of liquid was from the catholyte to the anolyte. Now, by keeping the electrolyte at a higher level in the anode than in the cathode cups, we can cause the anolyte to flow through the porous cups into the catholyte.

We ran two coulometers in series. From No. *1* we removed the anolyte by a constant level syphon which extended to the bottom of the porcelain cup, thereby removing the heaviest liquid as it collected at the bottom. In No. *2* the catholyte was removed by a quartz syphon which only extended below the top of the catholyte, thereby removing only the lighter and allowing the heavy liquid to flow through the porous cup and collect at the bottom of the cathode cup. The electrolytes were our "normal" silver nitrate solutions, and all details of the two coulometers

were identical except the direction of the flow of the electrolyte. The results were as follows:

TABLE III.

Run No.	Catholyte removed	Anolyte removed	Difference mg.
32	4.66181	4.66079	+1.02
33	4.13056	4.12998	+0.58
34	3.75443	3.75361	+0.82
35	5.12350	5.12286	+0.64
36	4.64026	4.63926	+1.00

These results show that the heavy anolyte does play some rôle in the formation of the heavier deposits obtained. These five results indicate an increase in weight of the silver deposited of 0.019 percent, due to the presence of the anolyte during electrolysis. This is approximately half of the increase in weight (0.036 percent) observed in the Rayleigh form, where the anolyte not only flows into the catholyte, but filter paper also is present.

Porous Cups of Different Material.

The porous cups with vitreous upper portion, which we used, were entirely satisfactory. They offered, however, more resistance to the current than was desired, and it took a considerable length of time to wash them absolutely free of acids. For other reasons it seemed desirable also to test porous cups made of some other material than porcelain, and we selected "alundum," which can be made into excellent filtering tubes. It did not seem conceivable that crystalline alumina could affect a silver nitrate solution. These tubes were of the same dimensions as the porous cups, only thin walled (1.5 mm.), allowed the liquid to filter through much more readily, and could be washed thoroughly in a short time. Four alundum cups having the above dimensions were obtained and thoroughly cleaned with nitric acid and water. Experiments 21, 22, 23 and 24 of Table IV were made with these substitutes for the porous porcelain cups, the normal electrolyte being used. The catholyte and anolyte were maintained at the same level. Here the agreement of the results obtained with the platinum cups No. 1 and 2 is particularly good, and a comparison

of the results obtained with the gold cups *3* and *4* is also good; but here again we find the heavier deposits in the gold cups. In run 23 there was a very fine scum floating on the catholyte in the platinum cups which could not be accounted for. The run, however, was completed as in all cases. These alundum cups retained the anode slime perfectly, but are quite porous, and no doubt some of the anolyte diffused through them to the catholyte. We therefore made six experiments with the two platinum cups. Coulometer No. *1* was provided with an alundum porous cup in which the anolyte was at the same level as that in the cathode chamber, while No. *2* contained the original porcelain cup where the anolyte was at a lower level and there was no diffusion in to the catholyte. In every case except in 27 the coulometer with the alundum cup showed a heavier deposit. The average is 0.026 percent. The results are as follows:

TABLE IV.

Run No.	1 Alundum	Difference mg.	2 Alundum	Gold heavier than Plat. mg.	3 Alundum	Difference mg.	4 Alundum
21	5.88568	0.31	5.88537	+2.06	5.88766	0.16	5.88750
22	5.33804	.05	5.33809	+0.59	5 33874	0.16	5.33858
23	5.71143	.05	5.71138	—0.49	5.71104	0.22	5.71082
24	4.42802	.03	4.42799	+0.26	4.42820	0.06	4.42826
			Porcel'n				
25	4.71515	+0.03	4.71518	....	....	....	......
26	4.92720	+0.19	4.92706	....	......	....	......
27	4.36494	—0.14	4.36508	....	......	....	......
28	4.52397	+0.28	4.52369	....	......	....	......
29	5.11922	+0.31	5.11891	....	......	....	......
30	3.83131	+0.11	3.83120	....	......	....	......

The effect here is, no doubt, due to the anolyte diffusing through the porous alundum cup, and, while we could arrange syphons to keep it slightly lower and cause the flow to be into the anolyte, the use of syphons makes the apparatus complicated and causes the failure of a larger percent of the experiments than occurs when the denser, less porous porcelain cups are employed, where it sufficed to remove a little of the anolyte with a small bulb pipette from time to time, which is a simple operation, and, besides, there was no diffusion through the cup. Alundum cups could be made of the same texture as the porcelain

cups, but then they would lose the advantage of being easily washed. Our porcelain cups with vitreous upper portions were distinctly superior to the "alundum" cups, and the coulometers as used were made for simplicity and exactness in manipulation, and were quite free from sources of accidental error.

General Summary.

1.   It was found that the slightest traces of impurities, such as dust and organic matter, so affected a silver nitrate solution that it gave abnormally heavy deposits. Particular attention was paid to preparing a reproducible "normal electrolyte." It was necessary to take unusual precaution in preparing all materials, and we used only quartz, gold and platinum utensils.

2.   In preparing "atomic-weight" silver the usual method was modified. We found the conditions under which silver could be precipitated from an ammoniacal solution of silver chloride in a crystalline condition, which is a distinct advantage over reducing solid silver chloride with sugar and caustic potash.

3.   In preparing pure water, particular attention was paid to the exclusion of dust and organic matter of all kinds, even to the burning of volatile organic matter which might be present in the air that came in contact with the solutions used. Since the solubility of glass suffices to affect measurably a silver nitrate solution, the water employed in our work was only permitted to come in contact with quartz.

4.   Silver nitrate was obtained from "atomic-weight" silver and pure nitric acid, the excess of acid being driven off at a definite temperature in an electric furnace, and with the exclusion of all organic matter. With this silver nitrate a solution was prepared which contained exact equivalents of Ag and NO_3. Kahlbaum's C. P. silver nitrate, recrystallized and fused, gave a deposit 0.009 percent heavier than that obtained with our normal electrolyte, and other solutions yielded distinctly heavier deposits.

5.   Four porous-cup coulometers were run in series. The cathode cups in *1* and *2* were of platinum, while *3* and *4* were gold. They contained the same solutions and were treated in exactly the same manner. In every case we found the deposits on gold to be heavier than those on platinum, the average excess being 12 parts in 100,000.

6. In experiments with a "Rayleigh" form which contained Kahlbaum's C. P. silver nitrate solution, when run in series with our normal coulometer, the Rayleigh gave a deposit 0.036 percent heavy. The anode of the coulometer was wrapped in filter paper, and the anolyte diffused through to the cathode during electrolysis.

7. In our porous-cup coulometers the anolyte was always lower than the catholyte, and the former did not flow through except in special experiments, which showed that when the anolyte is allowed to pass through the porous cup and come into contact with the cathode a deposit heavier by 0.019 percent was obtained. This is nearly one-half of the abnormal effect caused by the heavy anode liquid and filter paper as shown in the Rayleigh form.

8. Experiments were made with thin-walled porous alumina cups substituted for the porcelain cups. The silver deposits made using the alundum cups show a heavier deposit in every case, due to the anolyte passing through to the catholyte during electrolysis.

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