THE SILVER VOLTAMETER—PART I

FIRST SERIES OF QUANTITATIVE EXPERIMENTS

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I. BRIEF HISTORY OF INVESTIGATIONS ON THE SILVER VOLTAMETER

The earliest employment of electrochemical decomposition as a means for the measurement of electricity appears to have been by Gay Lussac and Thénard [1] about 1811. They arranged a gas voltameter that gave them a qualitative idea of the conductivity of various solutions and the strength of their battery. It remained, however, for Faraday [2] to enunciate the conditions on which it may be used for the exact measurement of electric current. He, too, used a gas voltameter which he declared to be the "only actual measurer of voltaic electricity which we at present possess." Because of this he named it the volta-electrometer. He suggested the possibility of using a voltameter in which a metal should be deposited to measure the current, but he does not appear to have done it himself. The silver voltameter appears to have been first used by Poggendorff [3] and described by him in a footnote. He was attempting to find the minimum current that would cause a visible decomposition of water. His cell consisted of two platinum plates in a saturated solution of Ag_2O in HNO_3. After several hours a silver deposit was visible, without any of the water in his water voltameter having been decomposed. He raised the interesting question as to why the silver deposit is discontinuous, and whether any of the current passed through the platinum surface on which there was no silver deposited. An illustration of this voltameter appeared later.[4]

Sixty or more papers have been published dealing with the silver voltameter. In a part of these papers the authors have been primarily concerned with an investigation of the instrument as a means of measuring current; in other cases the investigators have used the voltameter merely to measure current, using the electrochemical equivalent determined by other observers; while a third class of papers is devoted to a study of various problems of electro-

[1] Recherches Physico-Chimique, **1**, p. 12; 1811.
[2] Experimental Researches, **1**, p. 217; 1834.
[3] Pogg. Ann., **70**, p. 181; 1847. (We are indebted to Prof. R. H. Weber of Rostock for this reference.)
[4] Wiedemann's Galvanismus, 1st ed., **1**, p. 314; 1861.

lysis. Of this last class one of the earliest is by Almeida.[5] He used the silver voltameter to study the decomposition of a simple salt and the effect of acid. He concluded that if both acid and salt are present they are both decomposed, but part of the metal deposited is due to a secondary reaction of the nascent hydrogen, and if acid is not present in excess before the electrolysis begins it will be formed to some extent as soon as the current starts, even with a soluble anode.

Kohlrausch[6] advised the use of silver in the voltameter. He used a silver crucible as cathode with a 15 per cent solution of $AgNO_3$ and the silver anode wrapped in cloth. A few years later Kirmis,[7] working at the University of Berlin under Helmholtz, employed the silver voltameter to measure electric current, and, becoming interested in the various forms of silver deposit, made a very careful study of them. We shall refer at length to his paper later on, in connection with the striations of silver deposits.

The first absolute measurement of the electrochemical equivalent of silver to be published was by Mascart,[8] who concluded that the silver and copper voltameters were more reliable than the gas voltameters. He used two plates for his electrodes and derived his values from the loss at the anode as well as the gain at the cathode. His value for the electrochemical equivalent, which was later corrected[9] to 1.1156 mg per coulomb, was obtained with the aid of a current balance. In 1884 Carhart[10] made use of the silver voltameter to measure the voltage of a Daniell cell, a principle which constitutes the chief use of the voltameter to-day, in connection with the cadmium cell.

The first thoroughly systematic study of the silver voltameter was by Lord Rayleigh and Mrs. Sedgwick.[11] They used platinum basins of considerable size for the cathodes and sheet silver anodes wrapped in filter-paper, a form which has been much used since, and named after Lord Rayleigh. The possibility of errors arising in this form has been a subject of lively discussion by many observers for the last 20 years. Most investigators have attributed the trouble to complications arising at the anode, which were sup-

[5] Ann. de Chim. et Phys. Series III, **51**, p. 257; 1857.
[6] Pogg. Ann., **140**, p. 170; 1873.
[7] Pogg. Ann., **158**, p. 121; 1876.
[8] J. de Phys. Series II, **1**, p. 109; 1882.
[9] J. de Phys. Series II, **3**, p. 283; 1884.
[10] Am. J. Sci., **28**, p. 374; 1884.
[11] Phil. Trans. A, **175**, p. 411; 1884.

posed to cause an excess of silver to be deposited on the cathode, if the latter is not suitably protected. A large part of our work has been devoted to a further investigation of this question, and we shall show that this effect is due not to the filter paper being an imperfect separator of the anode and cathode solutions, but to its not being chemically inert. Lord Rayleigh and Mrs. Sedgwick found an excess deposit when silver acetate was added to the solution and they at first attributed this to inclusions of the mother liquor, but later to the acetate itself.

They analyzed their deposits for inclusions, but without conclusive results. They, however, adopted the weighings after "strong heating" of the deposits for their final results. Their value for the absolute electrochemical equivalent in terms of their current balance was 1.11794 mg per coulomb. A very important fact in this work is that they obtained heavier deposits by about 2 in 10 000 in large bowls than in the smaller ones. Schuster and Crossley (see p. 155) attempted to explain this as due to the difference in size of the anodes used in the large and small bowls, but, as will be shown in the third paper of this series, it was due to the contamination of the electrolyte by the filter paper.

Shortly after this work another very important paper by F. and W. Kohlrausch [12] was published, although the work had been begun before that of Lord Rayleigh. It is largely taken up with a discussion of their tangent galvanometers for making an absolute determination of the current.

They used a platinum cup with silver anode protected by a small glass dish underneath as one form, a siphon voltameter as another, while a third form consisted of two parallel plates standing in a beaker, the cathode being protected from loss of silver particles by a small semicircular glass dish. The electrolyte was made from fused silver nitrate. They give as their final result 1.1183 mg per coulomb. All of their voltameters were very small.

Two papers quickly followed in which the voltameter was used as a measurer of current for the determination of electromagnetic rotation constants, basing the results on the work of Lord Rayleigh and F. and W. Kohlrausch. These were by Arons [13] and

[12] Wied. Ann., 27, p. 1; 1886. [13] Ann. d. Phys., 24, p. 161; 1885.

Koepsel.[14] The latter subsequently published[15] an absolute determination of the electrochemical equivalent, using a Helmholtz balance and obtaining 1.11740 mg per coulomb.

Thomas Gray[16] made an extended study of the silver and copper voltameters for the purpose of standardizing electrical measuring instruments. He preferred vertical plates in a beaker to the more usual forms and like Mascart used the loss at the anode to check the gain at the cathode. His conclusions were unlike those of his predecessors or successors in recommending very small current densities and weak solutions, and that the anodes should be larger than the cathodes to avoid slime. He made a few determinations of the electrochemical equivalent using a sine galvanometer obtaining 1.1183, but he does not consider this reliable owing to errors in the galvanometer.

Potier and Pellat[17] made an absolute measurement of the electrochemical equivalent in terms of an electrodynamometer using a Clark cell as an intermediary standard. Their attention was chiefly devoted to the measurement of current rather than the errors arising in the voltameter, which they used only twice, and hence little weight can be attached to their very high value of 1.1192 mg per coulomb.

Schuster and Crossley[18] attributed the excess weight of deposit in the large bowls over that in the smaller ones as found by Lord Rayleigh to the difference in size of the anodes, but it must be noted that in suspending the silver by platinum wire they had in reality a combination silver and platinum anode. Their observations showed that some of the current left the platinum wire, which was likely to produce marked changes in the acidity of the solution and vitiate the results. Their deposits made in vacuo were one part in two or three thousand heavier than in free air, which they attributed to the absence of oxygen. They apparently used the same solution repeatedly in the filter paper voltameter and thereby lessened to a considerable extent the value of their work.

Glazebrook and Skinner[19] in a determination of the emf of the Clark cell used the silver voltameter, following the procedure of

[14] Ann. d. Phys., 26, p. 476; 1885.
[15] Ann. d. Phys., 31, p. 250; 1887.
[16] Phil. Mag., 22, p. 389; 1886.
[17] J. de Phys., 9, p. 381; 1890.
[18] Proc. Roy. Soc., 50, p. 344; 1892.
[19] Phil. Trans., 183 A, p. 567; 1892.

Lord Rayleigh. Assuming the value 1.118, they found 1.434 as the value for the cell. The differences among the voltameter determinations, even in the same run were large, and they attribute them to the rate of deposition of the metal. Kahle [20] working on the same problem, however, made some study of the behavior of the voltameter, finding deposits heavier by 5 in 10 000 when the solutions were rendered basic by boiling a part of the $AgNO_3$ for a long time with Ag_2O. Deposits made in vacuo were 4 parts in 10 000 heavier than those made in air. In using the voltameter under such conditions to measure current, he increased the value for the electrochemical equivalent by these amounts.

Novak, [21] while not the first to ascribe the errors of the voltameter to effects at the anode, appears to have been the first to suggest the formation of the complex ion at the anode. The same idea was probably independently put forward by Rodger and Watson,[22] who found a continued increase in the deposit resulting from successive use of the same electrolyte.

A paper by Behn [23] on the striated arrangement of galvanic deposits is of especial interest, because of his many ingenious experiments to determine their cause. We shall refer at length to this paper later on.

A study of the effect of dissolved gases in the voltameter was made by Myers.[24] He reports a decrease in deposit in an atmosphere of CO_2, a result not since confirmed. His paper contains only the results of observations without any attempt at theoretical explanation.

Two interesting determinations of the emf of the Clark cell followed, the first by Kahle,[25] who found that the increased deposits due to the successive electrolysis of the same electrolyte were due (1) to the supposed fact that more silver is deposited upon a previous deposit of silver than upon a clean platinum surface and (2) to some change arising in the electrolyte. His results for the emf of the Clark cell at 15° were:

1.4327 from new electrolyte,
1.4341 from used electrolyte.

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[20] B. A. Report for 1892, p. 148.
[21] Proc. Roy. Bohem. Ac. Sci. Prague, **1**, p. 387; 1892.
[22] Phil. Trans., **186** A, p. 631; 1895.
[23] Wied. Ann., **51**, p. 105; 1894.
[24] Wied. Ann., **55**, p. 288; 1895.
[25] Zs. f. Instrk., **17**, p. 145; 1897.

The change occurring in the electrolyte in a filter paper voltameter due to repeated use we shall discuss later. The second paper on this same subject was a carefully executed piece of work by Perot and Fabry.[26] They followed closely the specifications of the Chicago congress and found 1.4341 volts for the Clark cell at 15°. They had previously determined the voltage in absolute units and from the ratio obtained a value for "v" in very close agreement with the determination made recently at the Bureau of Standards.[27]

Kahle [28] in 1899 published the results of an extended investigation of the silver voltameter, using as a reference standard several Clark cells. His voltameters were similar to the platinum cup voltameters of Kohlrausch, but considerably larger. He tabulated in all 115 deposits, noticing that many of them were striated, which he found to be characteristic when the same solution is used several times. In some cases he found a liberation of acid which he concluded accompanied the formation of oxidation products at the anode. He found the electrochemical equivalent to be 1.1183 mg per coulomb.

Patterson and Guthe [29] made an absolute determination of the electrochemical equivalent, using an absolute electrodynamometer. They used the filter paper form of voltameter and added Ag_2O to insure the neutrality of the electrolyte, which probably accounts, in part at least, for the high value, 1.1192 mg per coulomb, which they obtained.

This work was followed by papers by Richards, Collins, and Heimrod, and by Richards and Heimrod.[30] These papers had a marked effect on much of the work that followed. They undertook to find the cause of the difference between the atomic weight of copper as determined electrolytically and chemically. This led to an extended investigation of various forms of the voltameter, from which they derived corrections that brought the work of previous observers into closer agreement. From these corrected values they derived the electrochemical equivalent of silver,

[26] Ann. de fac. Sci. Marsaille, 8, p. 201; 1898.
[27] This Bulletin, 3, p. 433; 1907.
[28] Ann. d. Phys., 67, p. 1; 1899.
[29] Phys. Rev., 8; Dec., 1898.
[30] Proc. Am. Acad. Sci., 35, p. 123; 1899. Proc. Am. Acad. Sci., 37, p. 415; 1902.

obtaining 1.1175 mg per coulomb. In the first of these papers the authors definitely stated that the filter paper voltameter was in error because a complex ion was formed at the anode and passed through the filter paper and deposited an excess of silver on the cathode. To obviate this they substituted a porous cup of porcelain for the filter paper which was supposed to serve as a more perfect separator between anode and cathode. This form of voltameter has since been much used under the name of the Richards or porous pot voltameter.

We have found it to give excellent service, although our reason for using it has been very different from that given by Richards. The principal reason given by Richards and Heimrod for believing in the existence of the heavy anode ion is that under certain circumstances silver was found to be deposited on silver from an anode solution without an electric current. This observation was not confirmed by Smith, Mather, and Lowry, although still insisted upon by Richards [31] in 1908. Neither have we been able to confirm this observation of Richards, but we have found that a solution contaminated with filter paper will cause an increase [32] in the weight of silver immersed in it regardless of whether this solution had been in contact with the anode or not. We shall discuss the question of filter paper versus porous pot voltameter fully in a later paper. Richards determined the inclusions in his deposits of silver by heating them over an alcohol flame and found a loss in weight of 0.02 per cent, even in deposits from his purest electrolyte.

Merrill,[33] working at Johns Hopkins, carried out a series of measurements on the effect of pressures (above atmospheric), temperature, used solutions, size of anodes and comparison of the filter paper form with a voltameter without septum. His results were negative, except in the case of used solutions which gave a heavier deposit. This effect he attributed to a reduction in valence of the silver ion.

Leduc,[34] reporting to the International Congress of Physics, reviewed the voltameter situation and advocated the adoption of 1.119 instead of 1.118 for the electrochemical equivalent. In later

[31] Proc. Am. Ac. Sci., **44**, p. 91; 1908.
[32] Second Paper of this Series by Rosa, Vinal, and McDaniel.
[33] Phys. Rev., **10**, p. 167; 1900.
[34] Rapp. Cong. Int. de Phys., **2**, p. 440; 1900.

papers [35] he continued his discussion of the effect of impurities present in the electrolyte particularly with reference to HNO_3 and AgOH. His studies led him to the conclusion that the anode current density should be very small in order that only the simple reaction $Ag + NO_3 = AgNO_3$ may occur. With higher current densities the formation of acid occurs. The $AgNO_3$ and HNO_3 are then electrolyzed together, the H going to the cathode and reacting to form ammonia salts and the precipitation of silver. He believed that the presence of AgOH in solution is not objectionable *provided it is in solution.* In some of our latest experiments, to be described in the subsequent papers, we have found this so, but the AgOH is often present in a colloidal condition and may cause very serious errors. He advocated the use of Ag_2O to neutralize the acid of the electrolyte. In testing the acidity he notes the necessity of precipitating the silver before making the tests with methyl orange. This, we think, had not been mentioned before, and for this reason Leduc's acid determinations should have much greater weight than others previously made. Leduc thought that there is always an equilibrium value of the acid, and on this basis sought to reconcile the differences between Kahle and Patterson and Guthe. His experiments showed that the baser metals produce relatively little effect if present. With Pellat [36] he made an absolute determination of the electrochemical equivalent, using Pellat's electrodynamometer. The mean value was about 1.1195. These high values must be ascribed, in part at least, to the large amount of filter paper and muslin present for a long time in the voltameter. It may be in part due to an error in the measurement of current, which might also account for the high value obtained by Potier and Pellat (loc. cit.).

Watson,[37] in a paper dealing with the earth's magnetic field, gives much of importance concerning the previous work on the voltameter. He used both the porous cup and filter paper form, preferring the latter. He adopted the value 1.118 mg per coulomb, and expressed his results in terms of the cadmium cell at 20° and the filter paper voltameter.

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[35] J. de Phys., Series IV, 1, p. 561; 1902. Comptes Rendus, 135, pp. 23, 237, 395; 1902.
[36] Comptes Rendus, 136, p. 1649; 1903.
[37] Phil. Trans. Vol. A, 198, p. 431; 1902.

Two other papers appeared during 1902, the first being a short one by Mylius,[38] in which he dealt with the chemistry of the voltameter. Among other things he noted that the organic parts of the filter paper can act upon the $AgNO_3$ and produce a red silver precipitate, but this warning seems to have escaped general notice. The other paper is by Farrup,[39] who worked with cyanide solutions.

Guthe,[40] working at the Bureau of Standards, used (1) filter paper form, (2) the Ag_2O form, (3) the porous pot form, (4) the large anode form, (5) Leduc's form. He noted the agreement of (3) and (4), which is not surprising since they were practically the same voltameter. He regarded his work as furnishing further evidence that the complex ion was the source of trouble. In his later work he sought other means of eliminating the complex ion, believing the porous cup was not sufficient protection. In terms of his work on the Gray absolute electrodynamometer he gave the electrochemical equivalent of silver as

1.11773 mg per coulomb

as determined by the porous cup type.

Van Dijk and Kunst [41] attributed the differences among previous observers both to the measurement of current and to the handling of the voltameters. They employed two tangent galvanometers and made determinations using two filter paper voltameters. They relied on the reproducibility of the voltameters and the agreement of results of the two galvanometers to prove the accuracy of their measurements. Their mean value is 1.11823 mg per coulomb.

Snowden [42] investigated the possibility of getting a smooth deposit from $AgNO_3$. By adding glue to the $AgNO_3$ he obtained some purple colloidal deposits.

Van Dijk [43] made a careful comparison of the filter paper and porous cup form and found 0.023 per cent as the difference. A siphon voltameter gave a little heavier deposit than the porous pot

[38] Zs. f. Instrk., **22**, p. 155; 1902.
[39] Zs. f. Electro-Chem., **8**, 569; 1902.
[40] This Bulletin, **1**, p. 21; 1904. Phys. Rev., **19**, p. 138; 1904. Phys. Rev., **18**, p. 445; 1904. This Bulletin, **1**, p. 349, and **2**, p. 33; 1906.
[41] Ann. d. Phys., **14**, p. 569; 1904.
[42] J. Phys. Chem., **9**, p. 392; 1905.
[43] Ann. d. Phys., **19**, p. 249; 1906. Arch. Neerland. des Sci., Series II, **9**, p. 442.

form, for which fact he could not account, but he concluded that both gave lower values than the filter paper form, because in both the anode solution was kept away from the cathode. In discussing used solutions, he ascribed the excess of deposit as due in part to the complex ion and in part to the extracted dextrine products from the filter paper. He carried out tests [44] designed to expel the foreign matter included in the deposits by heating them to redness, but his results showed no appreciable change in weight. He gave as the value for the electrochemical equivalent of silver in absolute measure 1.1180 mg per coulomb.

Carhart, Willard and Henderson [45] published a preliminary paper on the use of silver perchlorate as an electrolyte for the silver voltameter, claiming as advantages in its use an adherent deposit and freedom from reduction products. They report, however, that the deposits were generally striated and heavier than the deposits from the nitrate, which is, of course, sufficient evidence to condemn its use.

Duschak and Hulett [46] published the results of a careful investigation of the voltameter in which they attained a high degree of reproducibility, using the porous pot form. In vacuo and in nitrogen they got slightly smaller deposits than in free air. In attempting to explain this they analyzed their silver deposits by heating a portion in a closed tube and examining for gas and liquid. They found the inclusions to be about 0.011 per cent in free air and slightly smaller in vacuo, which partly explains the observed difference in deposits.

The first of the recent series of determinations by the national laboratories was published by Smith, Mather and Lowry in 1907.[47] Their determination of the electrochemical equivalent of silver, 1.11827 mg per coulomb, is in terms of an absolute current balance and using several forms of voltameter. This elaborate and comprehensive paper is discussed on pages 167, 205 and also later in these papers.

In 1908 the careful work of Jaeger and von Steinwehr [48] of the Reichsanstalt was published. They give a detailed account of the precautions taken in their work, particularly in the matter of

[44] Arch. Neerland. des Sci., Series II, 10, p. 277.
[45] Trans. Am. El. Ch. Soc., 9, p. 375; 1906.
[46] Trans. Am. El. Ch. Soc., 12, p. 257; 1907.
[47] Col. Researches N. P. L., 4, p. 125.
[48] Zs. f. Instrk., 28, pp. 327, 353; 1908.

weighing the deposits. Using 1.118 mg as the electrochemical equivalent they determined the voltage of two sets of cadmium cells, old and new, using a porous cup voltameter and another without septum. They prefer the latter and give 1.01834 volts at 20° as the value of their new cells. The difference at first apparent between the two forms of voltameter vanished when experiments were made using them in series and they concluded that the forms are in good agreement.

Janet, Laporte, and de la Gorce [49] working at the Laboratoire Central d' Electricité, determined the voltage of the Weston cell by an absolute current balance and from the value thus found obtained 1.11821 as the electrochemical equivalent of silver using the filter paper form. An error was subsequently discovered [50] that lowered their value for the standard cell by about 3 in 10 000 which would considerably increase their value for the electrochemical equivalent. In a subsequent series of experiments [51] using the English values of their resistances and standard cells they obtained values very concordant with Smith, Mather, and Lowry.

Kohlrausch and Weber [52] pointed out that if a temperature coefficient for the voltameter such as was found by Lord Rayleigh and others really existed it would introduce great complications in theoretical chemistry. They tested the matter by examining for a deposition of ions at a surface bounding two widely different temperatures in a tube containing one of several salts in water thickened with arrow root. Their results showed that there was no change in the electrochemical equivalent as great as 1 in 10^7 per degree.

Since Richards had used his own work to assign corrections to other determinations, and among them that of F. and W. Kohlrausch based on the effect of anode liquid, F. Kohlrausch [53] undertook a recomparison of one of their original voltameters with forms in which the anode liquid was more confined. The difference found was only 2 in 100 000 and he therefore concluded that their earlier determination was correct.

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[49] Bul. Soc. Int. Electr., 8, p. 523; 1908.
[50] Comptes Rendus 153, p. 178; 1911.
[51] Bul. Soc. Int. Electr. 10, p. 157; 1910.
[52] Ann. d. Physik., 26, p. 409; 1908.
[53] Ann. d. Phys., 26, p. 580, 1908.

Bose and Conrat [54] published a brief paper on a silver microvoltameter, but this instrument is not suitable for the work we have in hand.

Eisenreich [55] published a paper supporting the complex ion theory of Richards. It does not appear from the data that he gives that the purity of his solutions was sufficiently high. We have observed many of the phenomena that he gives as establishing the existence of the complex ion and have found that they do not occur when solutions of a high degree of purity are used. Since 1909 we have used potassium permanganate [32] in testing $AgNO_3$ for reducing impurities and colloidal silver, and our results have been communicated to the various national laboratories and to the American Physical Society, but have not been hitherto published except in abstracts.

The work contained in the present paper was in a measure preliminary to the work of the International Technical Committee whose report has just been published. We shall not, therefore, attempt to review that work here. There still remain a few papers bearing on the voltameter indirectly, but it is impossible for us to deal with these.

Recent work in this and other laboratories has shown that impurities in the electrolyte produce such widely differing effects depending on the amount and size of the voltameter and the acidity or alkalinity of the electrolyte that we do not think it advisable to tabulate the preceding results and apply hypothetical corrections in order to obtain a value for the electrochemical equivalent. These papers contain many things of interest which it is impossible to discuss owing to lack of space. But the absolute values found and the differences between the various forms of voltameters were so much affected by impurities in the electrolyte used, that it is impossible to apply corrections or to attach much importance to the numerical results. We consider that the work of the International Technical Committee beginning in April, 1910, marks an epoch in the work on the voltameter, because electrolytes known definitely to conform to a sufficient standard of purity were used, and the close agreement of the porous pot and no-septum forms of voltameters was established.

[54] Zs. f. Electrochemie, 14, p. 86; 1908.

[55] Zs. Phys. Chem., 76, p. 643, 1911.

II. INTRODUCTION AND OUTLINE OF WORK

The silver voltameter was chosen as the official primary standard for the measurement of current by the International Electrical Congress at Chicago in 1893, the ohm being fixed by the resistance of a specified column of mercury and the volt by the emf of the Clark standard cell. At the International Electrical Conference of 1908, at London, two instead of three primary standards were chosen, namely, the ohm and the ampere. These were specified as before in terms of the resistance of a column of mercury and the current that will deposit a given mass of silver per second, respectively, the volt being defined in terms of the ohm and ampere by means of Ohm's law. But the numerical value to be assigned to the Weston Normal Cell, which was chosen at London in place of the Clark cell as the instrument for expressing concretely the value of the international volt, would depend upon the specifications adopted for the mercury ohm and the silver voltameter. It was therefore important that the specifications adopted for these two primary standards should be such as to give a very high degree of reproducibility, the more so since the accuracy obtained in absolute measurements has increased considerably in recent years, and the precision demanded in the standardization of instruments is also much higher than formerly.

Up to the time of the London Conference many papers had been published dealing with the silver voltameter (or coulometer), and of these several had given the results obtained using both the Rayleigh and the Richards voltameters.[56] In every case but one, the Rayleigh form, in which filter paper is used, had been found to yield a heavier deposit of silver than the Richards form. The difference was not uniform, varying generally from 4 to 5 parts in 10 000. The theory given by Richards to explain this difference was generally accepted. However, in an extended investigation of various forms of voltameters published in 1907, Smith, Mather, and Lowry reported agreement between these two forms, and believed the filter paper voltameter, as they used it, to be a reliable

[56] The name "coulometer" was suggested by Prof. T. W. Richards, as more appropriate than voltameter, since the instrument measures coulombs, and the word voltameter may be confused with voltmeter. "Coulometer" has been used by several authors, and is preferred at the Bureau of Standards. However, in deference to the decision of the London conference, which considered the question and decided to adhere to the old name, we use the name voltameter throughout these papers.

instrument, and the value given by it to be normal. It was at this point in the history of the voltameter that the work described in this paper was taken up (1908).

The investigation of the silver voltameter at this bureau was first begun, however, in January, 1904, by Dr. K. E. Guthe, and the results of his work were published in November of the same year. He found as the value of the electrochemical equivalent of silver using the porous cup or Richards form of voltameter 1.11683 mg per coulomb [57] and for the filter paper or Rayleigh form 1.11736, in terms of the Clark cell taken at 1.434 volts and the international ohm. The former of these values he subsequently changed to 1.11773 on the basis of his absolute measurements of the voltage of Clark and Weston standard cells by means of an electrodynamometer.[58] We have endeavored to connect our present work with these early values of Dr. Guthe and find that assigning the same numerical values to the standard cells that our values are about 2 parts in 10 000 larger than his, a closer agreement than could be expected when one considers the many sources of difference between that work and the present.

Nothing further was done with the silver voltameter at the Bureau of Standards until June, 1907, when Dr. N. E. Dorsey with the assistance of the present authors began what was intended to be a short series of determinations to accompany the absolute measurements of current with the Rayleigh balance which was then under construction, and to attempt to confirm the work recently done at the National Physical Laboratory. Some additional equipment was purchased and some refinements in the weighings of the platinum dishes were made. The differences between the individual determinations, however, were larger than was expected and larger than could be justified on the ground of accidental errors. Because of this and the fact that only the filter paper voltameter was used, the results obtained are of little value now, but it is interesting to observe that with new solutions of silver nitrate the mean value found was 1.11746 mg per coulomb (taking the Weston cell as 1.01890 at 25° C), which agrees closely with the mean obtained in the present work [59] with the same type of voltameter. With used solutions a mean value of 1.11761 was

[57] This Bulletin, 1, pp. 21 and 349. [58] This Bulletin, 2, p. 33. [59] This paper, p. 196.

found, being 14 parts in 100 000 higher than from the unused solutions. This increase had been noted by many investigators before, but we believe that no satisfactory explanation has as yet been offered for it. We have confirmed this result and in the later papers of this series a theory will be offered to explain it which we believe will be found adequate. Dr. Dorsey's work, which has not been published, was brought to a close in September, 1907.

In July of the following year more extensive preparations for voltameter work were begun by the present authors. Two new balances for weighing the deposit were bought and installed in a special constant temperature room in order to increase the precision of weighing. Selected standard cells maintained in an oil bath at uniform temperature, together with other additions of apparatus increased the facilities for accurate work. Some preliminary deposits without the measurement of current were made as manipulation tests.

On October 8, 1908, the first series of quantitative experiments was begun. We used at first only the filter paper voltameter, and obtained a fair degree of reproducibility, but the difference between it and the porous cup form of voltameter which developed on using the latter for the first time in December, 1908, led us into an investigation of the effect of filter paper.

In the extended investigation of the silver voltameter by Smith, Mather, and Lowry,[60] published in 1907, they compared the filter paper form with the porous cup form and found, contrary to the experience of many other observers, that the weight of silver deposited in the two forms agreed very closely. They had treated the porous cups differently in one important respect from what anyone else had done, namely, baking them in a furnace at a high temperature after washing with acid. They attributed the agreement between the two forms in part, at least, to this special treatment, which they believed freed the porous cups more perfectly from acid than had been done before. They believed therefore that, as they used them, both forms of voltameters gave normal deposits, which were determined with great care, and by means of which, together with an absolute current balance, the electro-

[60] Col. Researches N. P. L., 4, p. 123.

chemical equivalent of silver was ascertained to be 1.11827 mg per coulomb.

We found, however, that the filter paper form gave consistently heavier deposits than the porous cup voltameter, and that the deposits were imperfectly crystalline and distinctly striated. Using two or three sheets of filter paper increased the difference between the two forms to two or three times its value when a single sheet was used, and wrapping a sheet of filter paper around the porous cup gave the deposit the characteristic striated appearance and heavier weight of the ordinary filter paper voltameter.

It thus became evident that the filter paper employed in the voltameter was a source of serious disturbance, and that the usual explanation of the difference between the two forms of voltameter was incorrect. Instead of the porous cup serving to protect the cathode from secondary products formed at the anode, and the filter paper voltameter giving a heavier deposit because it was a less efficient septum than the porous cup, it became evident that the filter paper itself was the source of important chemical action in the electrolyte, while the porous cup on the other hand was neutral and did not so contaminate the electrolyte. At this point in the investigation Dr. A. S. McDaniel joined us to study the chemical questions that had arisen, and first of all to learn what the action of filter paper is whereby so considerable a change is made in the appearance and weight of the deposited silver. The work done subsequent to this time will be described in three papers following this, and in these papers Dr. McDaniel will appear as joint author. A long series of experiments was also made to find the effect of other organic substances, such as cotton, linen, and silk fabrics, various kinds of paper and wood fiber, etc. These were followed by chemical investigations to ascertain the nature and explanation of the various phenomena observed. This work will be fully discussed in the second paper of this series. Our explanation of the reason why Smith, Mather, and Lowry found the porous cup form of voltameter to give as heavy a deposit of silver as the filter paper form is given fully in the fourth paper. Briefly it is, that baking the porous cups to free them from acid renders them appreciably alkaline and this we have found increases the deposit. By chance, this increase of weight we suppose was

substantially the same as the increase in the Rayleigh form produced by the filter paper.

We also gave considerable attention to the explanation of striations. It has long been known that under certain circumstances the silver deposited in a voltameter is strongly striated. Sometimes it is slightly striated and sometimes it is altogether free from striations. This subject had been studied by several investigators, but no satisfactory explanation had been offered. In the second paper an account of studies of this subject and an explanation which appears satisfactory will be given.

Having discarded filter paper from the voltameter, we proceeded, in conjunction with Dr. McDaniel, to compare other forms with the porous cup form, especially the siphon and the Poggendorff, and to compare large and small voltameters of the same type. In nearly every case large voltameters gave larger deposits than small voltameters, and this phenomenon, which we called the volume effect, persisted even when the work was most carefully done with the purest silver nitrate available at that time. We noticed, however, that the volume effect was less with the purer salts, and we believed that with a solution strictly pure it would entirely disappear, as it should theoretically. Subsequent work has confirmed this belief, and we now regard the absence of the volume effect as one of the surest as well as one of the most rigorous tests of the purity of the electrolyte.

In the early part of our work we had used the purest silver nitrate which could be purchased, some from an American manufacturer and some from the Gold und Silber-Scheide-Anstalt, of Frankfurt, Germany. The latter salt gave a very beautiful crystalline deposit, and to chemical tests seemed to be of a high degree of purity and especially free from those impurities which we had found produced the most disturbing effects when added to the electrolyte. However, it gave a slight volume effect, and we believed it must contain some appreciable impurity. This led to an investigation of more delicate chemical tests for organic impurities in silver nitrate, which resulted in a new method which showed conclusively a small amount of reducing impurity in the silver nitrate, fully confirming the belief, based on the slight but undoubted volume effect, that the purest salt we had used was not quite pure enough for work of the highest precision.

This led to attempts to prepare still purer silver nitrate; that is, to get rid of the last traces of reducing impurity. Merely recrystallizing the salt repeatedly is not sufficient in all cases, unless certain special precautions are observed, but a method has been found (due in part to a suggestion from Mr. F. E. Smith) of obtaining silver nitrate so pure that it will show no volume effect and withstand the severe chemical test referred to above. This work is discussed in the third paper.

The work outlined above was carried out between October, 1908, and April 1, 1910. In the meantime an international investigation had been arranged to be carried out at the Bureau of Standards by representatives of four of the national standardizing laboratories, and we presented to the delegates selected, first in October, 1909, and again in April, 1910, on their assembling in Washington, a report of our work, and the conclusions we had reached on the subjects briefly indicated above. Work was carried on jointly during April and May of 1910 by the delegates, and the results obtained have been published in a separate report. We give in these papers mainly the results of our work up to the time the international delegates assembled in Washington, namely, April 1, 1910. We shall include results obtained since June 1, 1910, in the fourth paper of this series. On account of the salt employed in most of these earlier experiments not being quite pure we do not regard the numerical values obtained as final figures. They are, indeed, very nearly the same as we have found since, and as the international committee found, with very pure salt. But as this is an investigation of the silver voltameter as an instrument, and of the conditions necessary in order to secure normal results, we attach great weight to the numerical values given in the tables. The disturbances due to filter paper amount to from ten to a hundred parts in a hundred thousand. Avoiding filter paper and other organic septa and using an electrolyte so pure that there is no volume effect, the results are far more consistent, and the variations are reduced tenfold. There are still, however, some small uncertainties, due to slight impurities in the water employed, or to very slight acidity or alkalinity of the solution, or to gases absorbed by the electrolyte from the atmosphere, which we have investigated and upon which a report will be made

in our final paper. This work will, we hope, indicate what the complete specifications for the official silver voltameter ought to be. April, 1910, will mark an important epoch in the history of the silver voltameter, namely, the close of the period of individual effort, extending from 1880 to 1910, in which many papers have been published and much learned concerning the theory and use of the silver voltameter. Beginning with 1910 we enter the period in which the national standardizing laboratories attempt by cooperation to perfect the silver voltameter as an electrical instrument of precision, and to agree upon specifications so complete and so precise that it may become in fact, as it is nominally, an international electrical standard.

III. QUANTITATIVE EXPERIMENTS, FIRST SERIES

A. APPARATUS

1. PLATINUM DISHES

We have used 10 platinum dishes and 2 gold dishes for cathodes or counterpoises. Four of these have a capacity of 350 cc and we have designated them as the "large bowls," 4 have a capacity of 175 cc and we call them the "medium bowls;" the 4 smallest, capacity 125 cc, are called the "small bowls" or crucibles. All of the dishes of any one size were adjusted to the same weight, so that they could be interchanged on the balance without requiring any transfer of weights. In the course of a long series of experiments, however, the medium-sized bowls lost several milligrams in weight which has been made up by certain small weights prepared for the purpose. The losses in weight of the other bowls have been much less. The time necessary to adjust the weight of the bowls was amply repaid by the convenience and speed with which accurate weighings could be made.

Two bowls, one large and one medium, were reserved in the balances for counterpoises, and deposits were never made in them. The small bowls were counterpoised by a sheet of platinum.

Table I shows the size and weight of the 12 dishes together with 4 others purchased since the experiments recorded in the present paper were completed.

TABLE I

Weights and Dimensions of the Platinum Dishes Used in the Experiments

No.	Designation	Approximate size			Material	Approximate weight
		Depth	Diameter	Capacity		
		cm	cm	cc		g
95	Large bowl	7	10	350	Platinum	80.27
94	do	7	10	350	do	80.27
93	do	7	10	350	do	80.27
92	do	7	10	350	do	80.27
25	Medium bowl	4	9	175	do	55.09
26	do	4	9	175	do	55.09
127	do	5	8	175	do	55.09
128	do	5	8	175	do	55.09
27	Crucible	7	6	125	do	39.11
28	do	7	6	125	do	39.11
125	do	7	6	125	Gold	39.11
126	do	7	6	125	do	39.11
36	Small bowl	6	6.4	140	Platinum	38.30
37	do	6	6.4	140	do	38.30
38	do	6	6.4	140	do	38.50
39	do	6	6.4	140	do	38.50

No. 94 and No. 25 were reserved for tare.

2. WEIGHTS

For weighing the deposits three weights designated as $\dot{S}$, $\ddot{S}$, and Σ were used. The first two were of silver, gold plated, and were made to weigh about 4.098 grams, which is the approximate weight of silver deposited in one hour by a current numerically equal to the voltage of the Weston normal cell at 25°.0; that is a current, which, flowing through a 1-ohm standard, produces a difference of potential at the terminals equal to the electromotive force of the Weston cell. As the resistance of the 1-ohm standard varied slightly with the temperature at different times of the year and the Weston cells were kept at a slightly higher temperature in summer than in winter, the deposit was made as nearly as possible equal to the fixed weights by changes of a second or two in the length of the experiment. Later the current was reduced by one-half and the time of deposit made two hours, a 2-ohm standard being used. Σ was a collection of weights consisting of a 4-gram platinum piece, together with several weights from a fractional

gram set known as "μ", the whole weighing about 4.095 grams. This was used exclusively for weighing deposits in the medium-size cups, as the 3 mg difference between this and $\dot{S}$ and $\ddot{S}$ was made up by the small weights added to the dishes, as mentioned above when they were weighed empty. A buoyancy correction was always made when using this weight.

These three weights have been compared with the standards of the bureau and found to have the following values:

TABLE II

Calibration of the Special Weights

Date	$\dot{S}$	$\ddot{S}$	Σ
	mg	mg	mg
Oct., 1908			4095. 21
Jan., 1909	4098. 26	4098. 35	
Apr., 1910	4098. 26	4098. 36	4095. 23
Nov., 1911	4098. 27	4098. 37	4095. 23

3. THE VOLTAMETERS

(*a*) **Rayleigh Voltameter.**—This form of voltameter consists of an anode of silver in a solution of silver nitrate contained in a platinum dish serving as cathode, any particle becoming detached from the anode being prevented from reaching the cathode by a sheet of filter paper. In some few cases we have used various textiles as linen, cotton, or silk in place of filter paper, and for convenience have classed them all under this head. Figure 1 shows this form of voltameter as we have used it.

We have used different kinds of filter paper, such as Eimer & Amend's "best white," C. Schleicher & Schull's No. 595, No. 602, No. 598, No. 590, and some papers especially prepared from given materials. In a few experiments we have also used filter tubes, such as are employed in the Soxhlet extraction apparatus.

Large bell jars cover the voltameters and stands during the progress of the experiment.

(*b*) **Richards Type.**—The Richards voltameter differs from the Rayleigh in employing a porous cup of unglazed porcelain as the means of separating the anode and cathode. We have used

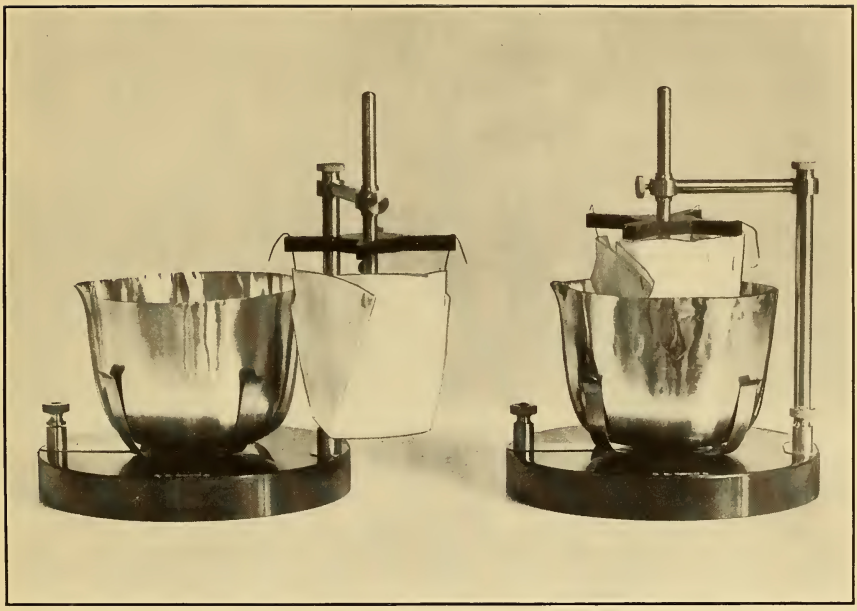

Fig. 1.—*The Rayleigh voltameter*

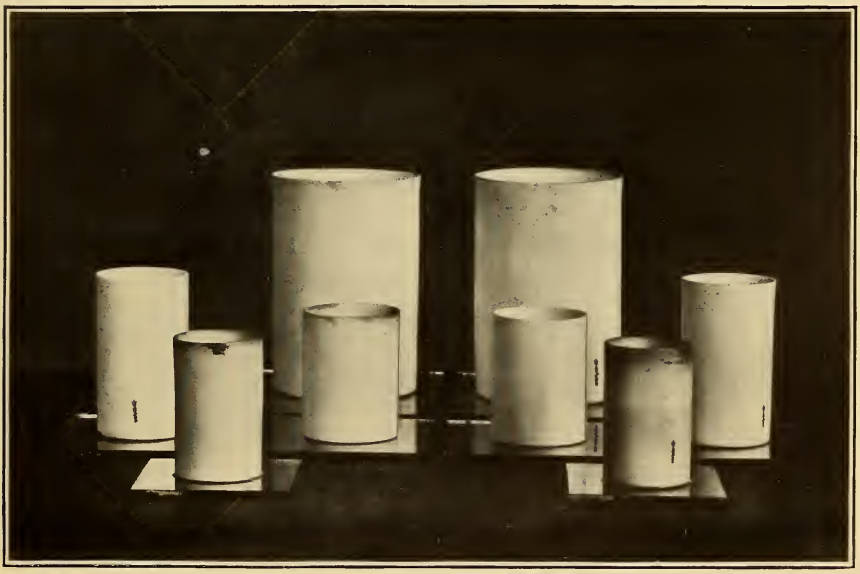

Fig. 2.—*The porous cups used in the Richards voltameter*

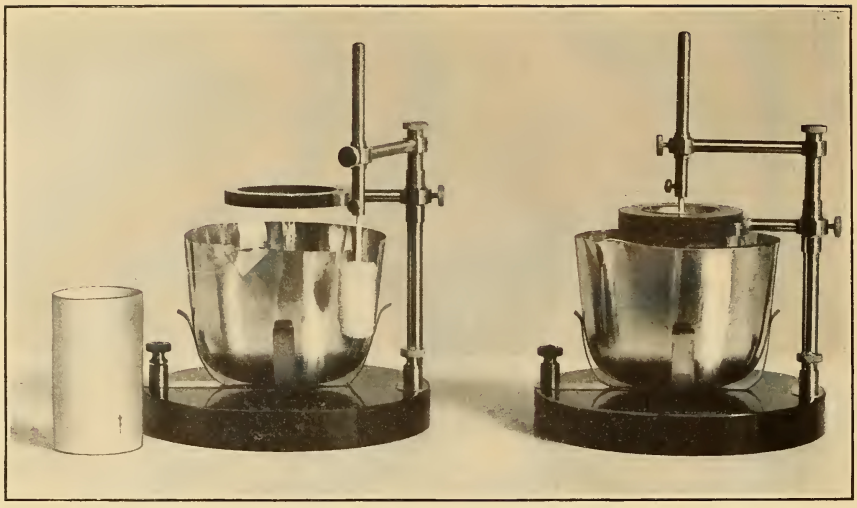

Fig. 3.—*The Richards voltameter, large size*

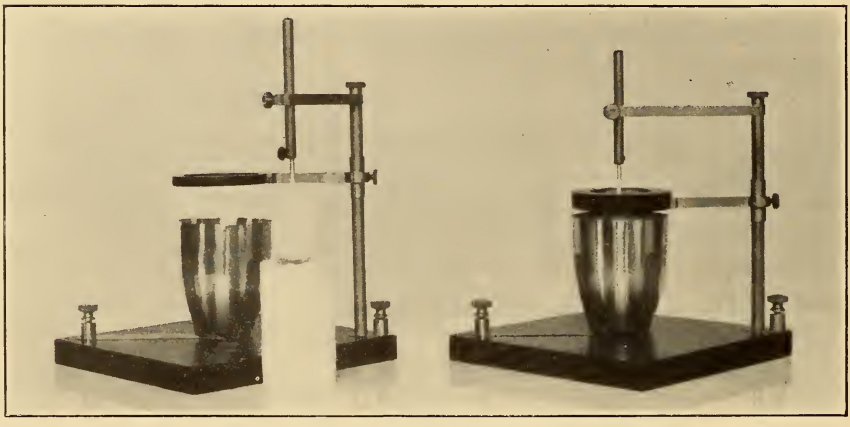

Fig. 4.—*The Richards voltameter, small size*

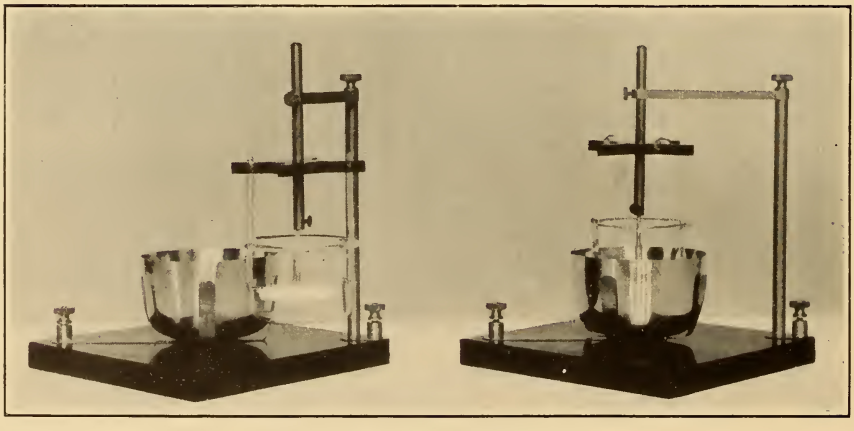

Fig. 5.—*The Poggendorff voltameter*

chiefly Pukal cups made by the Königlich Porzellan Manufaktur of Berlin. These are cylindrical, have thin walls, are of very fine grain, and of three sizes.

TABLE III

Dimensions of Porous Cups

Size	Diameter	Height
	cm	cm
Large	7	10.5
Medium	4	5
Small	3.5	5

The largest cups were used exclusively in the largest platinum bowls, but the smaller cups have been used in all the platinum dishes. They were white and without blemish before use.

The anode and cathode were mounted as in the Rayleigh form, but the porous cup was held in a split vulcanite ring made to fit closely around its top edge and supported from the same vertical rod as the anode. A large bell jar covers the voltameter when in use.

(*c*) **Poggendorff Type.**—The voltameter which we have designated as the Poggendorff type consists of silver anode and platinum bowl cathode, with electrolyte as above, but the only separation between the anode and cathode is a glass dish placed under the anode to catch any particles falling from it. We have in some few instances covered the top of the anode with a layer of silk, as we found that the glass dish was not always sufficient to confine the anode slime which is sometimes carried to the top of the electrolyte by bubbles of gas. Another way less open to objection of avoiding this difficulty was to support a ring of glass in the surface of the liquid. This prevented particles which came to the surface from floating out over the cathode space.

The mounting of the bowl and anode was the same as for the Rayleigh and Richards types, but the glass dish was supported by vertical rods of glass that hooked over ebonite arms projecting from the same support as the anode, so that at the end of the run all might be lifted out together. The ring of glass is sealed to the vertical glass rods at such a height as to be in the surface of the liquid when the voltameter is filled with electrolyte.

(*d*) **Siphon Type.**—The platinum dish serving as cathode and a ring of silver as anode are connected electrically by a column of electrolyte contained in a large glass siphon. The two sizes of siphons that we have used have been as follows:

Size	Axial length	Diameter	Capacity
	cm	cm	cc
Large	18	3.7	166
Small	10	2.2	44

These siphons were fitted with stopcocks to facilitate filling and emptying.

The siphon voltameter presents a serious difficulty in making absolute determinations by reason of the high resistance and consequent heating of the column of liquid, even in the larger siphons. This makes it very difficult to maintain the current at a fixed value. It may of course be used in comparison with other forms without keeping the current constant, but even then a very pure electrolyte must be used, since the large volume of liquid tends to give very high values if slight impurities are present. This will be discussed more fully in the third paper under the head of "volume effect."

In using the siphon voltameter we have mounted the platinum cup in one of the usual holders, while the anode (clamped in the usual way, but turned to one side) is placed in a glass dish mounted on a block of wood beside the cathode. The siphon is held in a wooden clamp stand. After all the parts were in place the platinum cup and glass dish were filled with electrolyte which was then drawn up into the siphon by means of the stopcock. For the large dishes and siphons about 500 to 600 cc of electrolyte were required.

As modifications of this form we have tried putting a porous cup over the anode or cathode ends of the siphon.

4. WEIGHING ROOM AND BALANCES

The weighings were made in a balance room built in the basement especially for the purpose. One-half of this room which has massive concrete walls was lined with hollow tile, an additional air

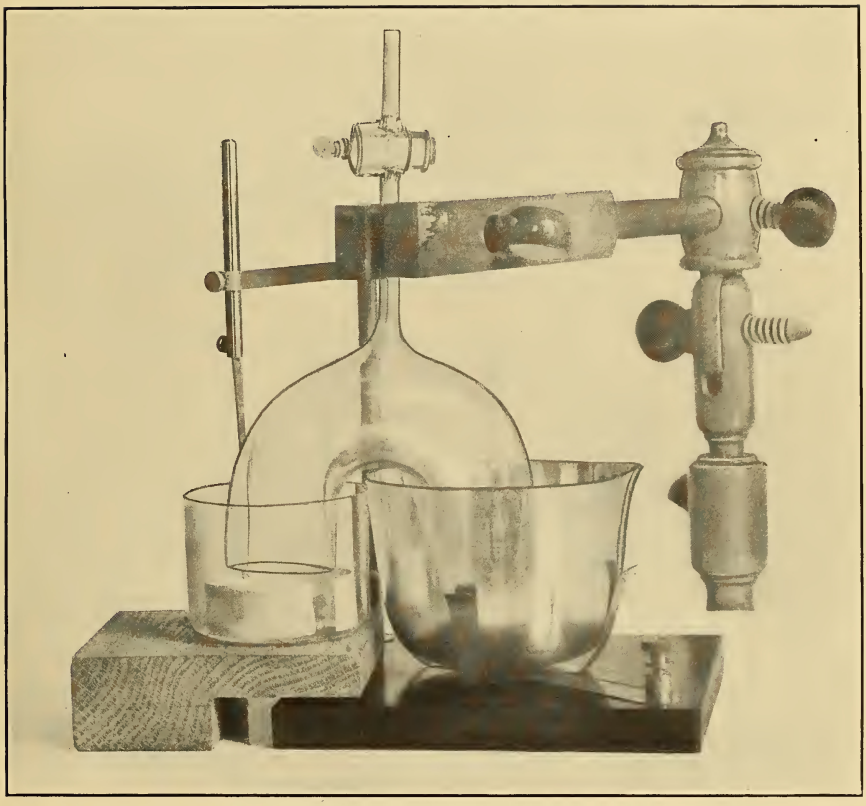

Fig. 6.—*The Siphon voltameter*

space being left between the tile and the concrete wall, and the tile plastered inside. A tile partition separates the balance room proper from the other end of the basement room, in the partition being double doors with vestibule between and two double windows.

Weighings were made from outside the balance room by observing the swings of the balances by means of telescopes extending through the windows. A plane mirror on the beam of the balance served to reflect a centimeter scale.

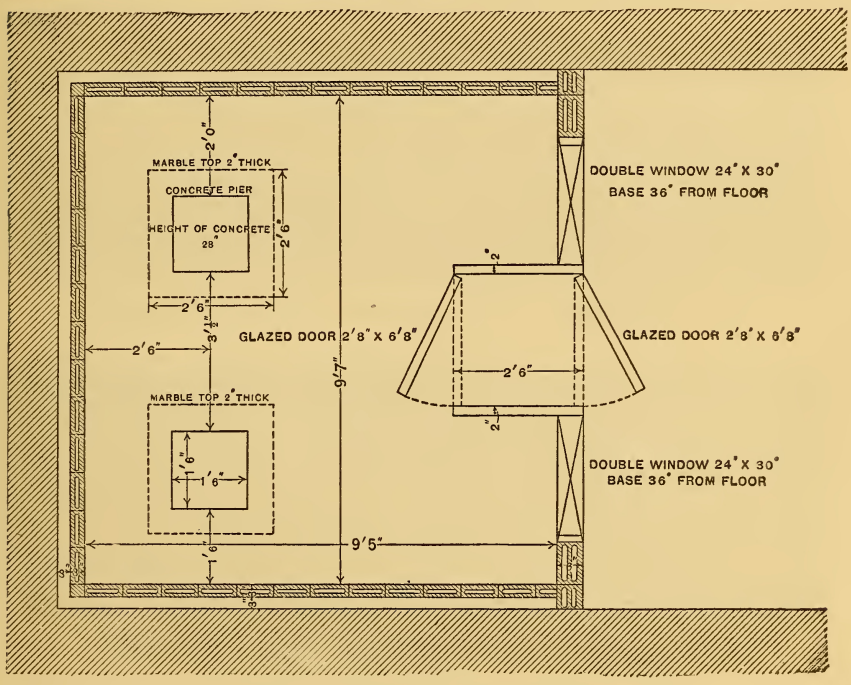

Fig. 7.—*Plan of the weighing room*

The temperature and humidity of the atmosphere inside the balance room were very constant, changing by only a few tenths of a degree and 1 or possibly 2 per cent, respectively, during 24 hours. They were recorded on a thermograph and hydrograph, of which sample records are shown.

If at any time the humidity became too high a drying apparatus holding about 50 pounds of calcium chloride was used to reduce it, but this was seldom required.

The balances were mounted on two marble-top piers independent of the foundations of the building. Three balances were used, each of 200 grams capacity. The first was by Oertling, the second by Rueprecht, and the third by Stückrath. Of these the Oertling has pans large enough to accommodate the largest platinum dishes used in the experiments and it was employed exclusively for weighing the four large bowls. All glass windows and doors on this balance are double to better protect the beam and platinum cups. The sensibility weight used on this balance was a 1-milli-

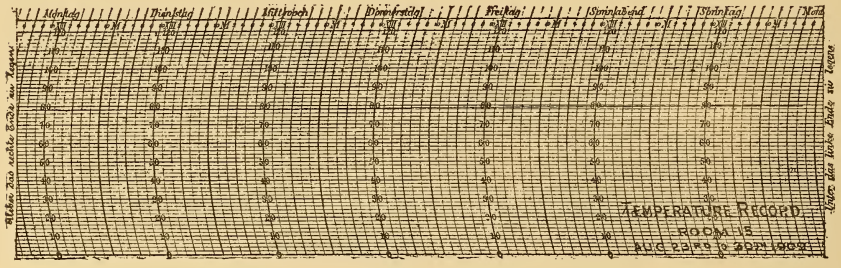

Fig. 8.—*Thermograph record of weighing room, August 23 to 30, 1909*

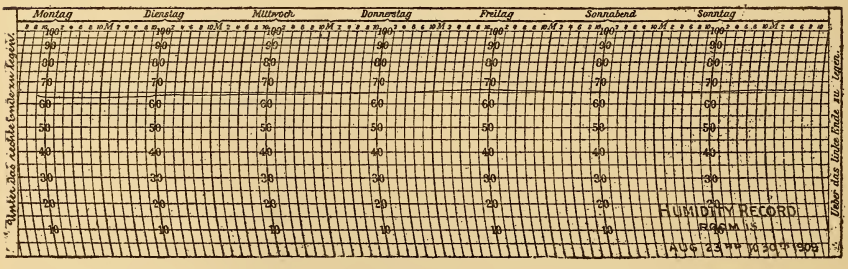

Fig. 9.—*Hydrograph record of weighing room, August 23 to 30, 1909*

gram rider always placed at division four and this four-tenths of a milligram produced a change in the equilibrium reading of 2.5 centimeters as read by telescope and scale.

The Rueprecht balance was best adapted to weigh the medium-sized bowls and was used for these alone. As the glass windows were single, the balance was further protected from radiations by heavy paper shields. A rider similar to that used on the Oertling was provided for this balance and its sensibility was about the same.

The Stückrath balance was used only for the crucibles, as its pans were small. It is arranged to be released and transpositions and changes of weights to be made from outside the room by means of rods and levers. All the glass windows and doors of the balance are double. The sensibility of the balance is about 16 scale divisions of 2 millimeters each for 1 milligram. Often all three balances were in use at the same time, one observer reading them and changing the loads in rotation. We described the method of making the weighings in the Report of the International Technical Committee, page 138.

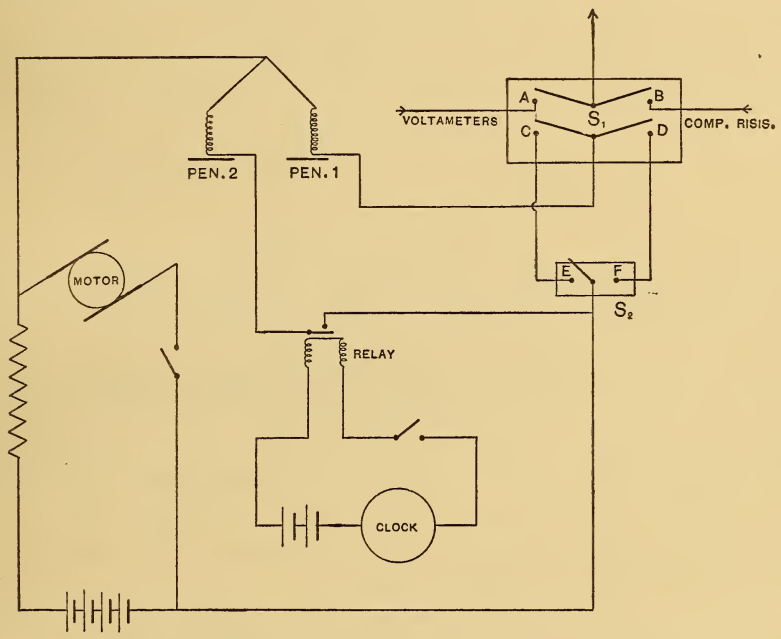

Fig. 10.—*Diagram of circuit for timing the duration of the experiments*

5. TIMING THE DEPOSITS

A quick, double-pole, double-throw switch serves to start the current through the voltameters and simultaneously to close another circuit which operates one of two pens on a chronograph. The two circuits were insulated from each other by the hard rubber yoke that united the blades of the switch. By reference to the diagram (Fig. 10) the operation of starting and stopping will be understood.

Before the beginning of the experiment the main switch S_1 is closed on the points B and D while the switch S_2 is on E. At the proper time the main switch is quickly thrown over to A and C. This starts the current through the voltameters and at the same time operates pen 1 of the chronograph. In order that the action of the chronograph pen may be the same at the start and at the end of the run the switch S_2 is then thrown from E to F. At the end of the experiment the main switch is thrown back to B and D. At the instant that the voltameter circuit is broken at A the pen circuit is made at D, and hence the first pen is again energized exactly as before. Thus any possible inequality in the working of the magnet on make and break circuit is avoided. The second pen records the ticks of the standard Riefler clock located in a constant

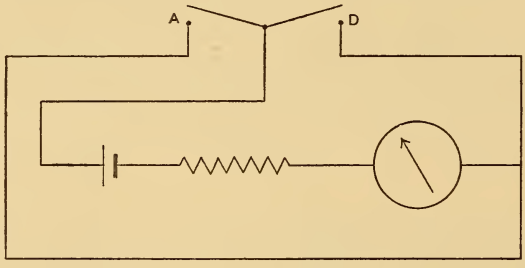

Fig. 11.—*Diagram of circuit for estimating the error of the timing device by ballistic method*

temperature room in the basement. The rate of this clock as determined by frequent signals from the Naval Observatory was rarely over a tenth second per day, and was usually less. Hence no corrections to the time record are necessary. The chronograph used was made by the Société Génèvoise.

Since we regarded the insulation of the timing device from the main voltameter circuit as necessary to avoid possible stray currents, the accuracy with which the duration of an experiment is recorded depends on the mechanical perfection of the main switch S_1. The possible errors introduced by the switch can be tested experimentally by the following method shown diagrammatically (Fig. 11).

The making of the current at D gives the time record for the breaking of the voltameter circuit at A, hence we must determine the interval between the breaking of the circuit at A and the making at D. A very small part of the divided voltage of a dry

cell was applied to a ballistic galvanometer with megohm box in series, the circuit being completed through A. This of course produced a steady deflection of the ballistic galvanometer which was also the case when the switch was closed on D. By operating the switch as is ordinarily done at the beginning and end of an experiment any throw of the ballistic galvanometer would measure the quantity of electricity that would have passed through the galvanometer if the current had not been interrupted. No throw of the galvanometer was observed except when the switch was operated more slowly than was done in practice in the voltameter circuit. The sensibility of the arrangement was such as to reveal an interval of time of 0.004 of a second. This shows that the error in time due to the switch could not be greater than this, which is less than a millionth part of the usual time of a deposit, namely, two hours. For determining the interval between the closing of A and C the same method with some necessary modifications was used. Here also the time interval was inappreciable.

6. THE VOLTAMETER CIRCUIT

The voltameter circuit consisted of a large ballast resistance, the voltameters with a parallel circuit of equal resistance for use before the run, two separate means of measuring the current, either of which could be used singly or both together, and suitable rheostats for quickly making large changes in the current or small changes, as occasion might require. Some modifications were made in the arrangement of the circuit during the progress of the work, but in the most essential features it remained the same throughout. Figure 12 shows the diagram of the circuit as it was used during the latter part of the work when currents of one-half ampere were used.

The standard resistance has usually been a Wolff open coil No. 2626 of 1 ohm for a current of 1 ampere or No. 2342 of 2 ohms for a current of one-half ampere. These were immersed in an oil bath, kept stirred by a small motor. They were frequently compared with the reference standards of this Bureau. The temperature of the oil bath was read several times during an experiment and from the computed average temperature the value of the resistance was obtained from the known coefficient of the coils.

The standard cells, four in number, were kept in an oil bath at the uniform temperature of 25° in winter and 28° in summer by a

thermostat regulating to 0°.01 C. They were frequently compared with the reference cells of this Bureau and showed a variation of only about 2 microvolts.

One pair of potential leads from the standard resistance passed to a Wolff potentiometer as described on page 128 of the Report of the International Technical Committee. The second means of measuring the current provided a higher sensibility (20 mm. for 1 part in 100 000) and avoided any errors introduced by the potentiometer such as may arise from the adjustment of the coils, thermoelectric forces, changes in battery current, etc. The standard cell was joined in series with a sensitive Siemens and Halske galvanometer, so that by depressing a key the voltage of the cell could be directly opposed to the drop in potential across the

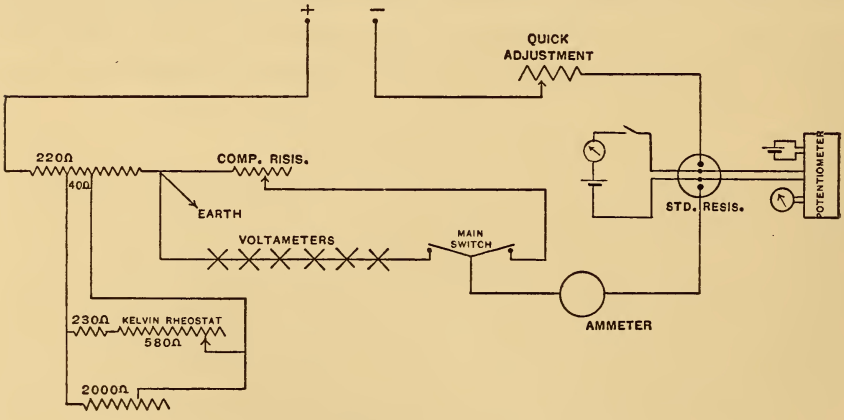

Fig. 12.—*Diagram of the voltameter circuit*

standard resistance. The telescopes of both galvanometers were near the apparatus for regulating the current, so that it could be held at the proper value by an observer at either telescope. On some occasions both were used together, the observer at the potentiometer holding the current and a second observer reading and recording the deflections of the direct balance. The mean deviation of the current from a constant value is only a few parts in a million, and the algebraic average of the deviations is not over one part in a million. Hence no correction is necessary to the value of the current computed from the mean value of the resistance standard and of the Weston Cell during the period of the experiment. The direct balance method is the more reliable, but no significant difference was ever found between them.

Insulation tests were made of all parts of the circuit at frequent intervals. The wiring was done especially with reference to high insulation. All wires passing from table to table or from one room to another were air insulated and supported only by vulcanite blocks fastened to wooden masts. All apparatus belonging to the circuit was mounted on vulcanite blocks. Further details as to the operation of the circuit are given in the Report of the International Technical Committee, page 126.

B. METHODS

1. METHOD OF WEIGHING

After drying the cups were allowed to come to equilibrium with the temperature and humidity of the balance case and room during several hours, because we believed that in the case of humidity it was better to weigh the cups in an undesiccated balance kept in a room of nearly constant humidity than to try to obtain weighings when the humidity in the balance case was changing every time it was opened, and the cup acquiring moisture during the process of weighing. Since, in every case, except for the smallest cups, the counterpoises were platinum dishes identical with those in use, and which always remained in the balance case, we believe the moisture deposited on counterpoise and cup to be the same when sufficient time for equilibrium to be established is allowed, and hence the humidity effect is eliminated. For the crucibles the counterpoise was sheet platinum, and hence this also approximated the best conditions.

The large surface of the cup makes it more difficult to weigh than the same mass of platinum in the form of a solid weight. Convection currents of air sufficient to introduce large errors in the result are set up by very slight differences in temperature. These may be caused either by the presence of the observer's body in making the necessary changes in the loads on the pans, or by light radiations falling on the surface of the cup. For this reason it was necessary to make the weighings in the constant temperature room which we have described. Even here it was necessary to allow the balance to swing from 10 to 20 minutes before reliable readings could be taken, as a drift of the equilibrium position was always apparent immediately after making changes in the loads on the pans.

The method of weighing adopted always involved an intercomparison of the weights of the several dishes, as well as a determination of their weights in terms of the counterpoise. The differ-

ences thus arising from experimental error were adjusted by least squares. If we designate three dishes, one of which (No. 94) is reserved for a counterpoise, by their numbers, No. 93, No. 95, and No. 94, we obtain the following equations:

$$\text{No. } 93 - \text{No. } 94 = a_1$$
$$\text{No. } 95 - \text{No. } 94 = a_2$$
$$\text{No. } 93 - \text{No. } 95 = a_3$$

If w_1 and w_2 represent the adjusted weight of No. 93 and No. 95 in terms of No. 94, we obtain the following equations for least square adjustment:

$$w_1 = \frac{1}{3}(2a_1 + a_2 + a_3)$$

$$w_2 = \frac{1}{3}(a_1 + 2a_2 - a_3)$$

Similarly for four dishes.[61]

The methods of making the observations are tabulated in the Report of the International Technical Committee, page 140.

2. METHOD OF RECORDING EXPERIMENTS

The form in which the records are preserved is as follows:

TABLE IV

Run of March 23, 1909

Holder	Cup	Anode	Septum	Electrolyte	Volume
					cc
A	92	Cup-shaped	Triple 598 f. p	Baker's 15%	335
B	93	do	Triple 595 f. p	do	335
C	95	do	Single 598 f. p	do	335
D	26	Disk	Single 595 f. p	do	175
E	28	Rod	Porous pot	do	95
F	27	do	do	do	95

Standard Cell No. 56 at 25°.04.
Standard Resistance No. 2342 at 21°.1 at start.
Standard Resistance No. 2342 at 22°.4 at end.
Time, 7199.74 seconds.
Current, 0.509426 ampere.
Room temperature, 20°.0.
Humidity, 34 per cent.
Appearance of deposit: No. 95, striated as usual, fuzzy like No. 26; No. 93, medium texture, very striated; No. 92, very striated; No. 26, fine texture, striations not marked, fuzzy; No. 27, very fine grain, no striations; No. 28, very fine grain, no striations.

[61] U. S. Coast and Geodetic Survey Report for 1892, Appendix 10.

The current, time, and mass of deposit being known, we obtain at once the electrochemical equivalent from the formula.

$$\text{Electrochemical equivalent} = \frac{\text{Mass of deposit}}{\text{Current} \times \text{time}}$$

or the value for the Weston normal cell emf $= \frac{\text{Mass} \times \text{resistance}}{1.11800 \times \text{time}}$

TABLE V

Platinum bowl	Electrochemical equivalent
No. 95	1.11762
No. 93	1.11786
No. 92	1.11807
No. 26	1.11744
No. 27	1.11708
No. 28	1.11708

Nos. 27 and 28 are standard cups.

These values for the electrochemical equivalent have been computed from the value of the standard cell in use in the United States prior to January 1, 1911; that is, the voltage at 25° C equals 1.01890. On the basis used since that time we obtain for the value of the standard cell, assuming the electrochemical equivalent 1.11800 mg per coulomb and adding in a correction [62] of 3 in 10^5 as determined by the International Committee,

No. 27.....1.01832 volts at 20°.

The deposits in the first four voltameters are obviously abnormal, due to the presence of filter paper, particularly in the case of No. 93 and No. 92, which had three times the quantity contained in No. 95 and No. 26. It is worthy of notice that filter paper No. 598, which gave larger values than No. 595, is a much heavier paper; that is, there is a greater mass of cellulose for the same size sheet of paper.

3. PREPARATION OF ANODES

The anodes were prepared for use in the quantitative experiments by depositing on them the silver from the bowls used in the preceding run. This provides an anode of great purity as well as affording a convenient and thorough method of cleaning the platinum dishes.

[62] Report of International Technical Committee, p. 26.

In order that the electrolytic silver should adhere closely to the anode it is necessary, (1) that all traces of anode slime from previous use be removed; (2) that the anode be made bright and clean by a scratch brush; and (3) that only a small current be employed in depositing silver upon the anode. It is convenient to start this process in the evening and allow it to continue until the following morning.

After receiving the deposit of electrolytic silver the anodes are rinsed in a few changes of distilled water to free them from silver nitrate and then baked in an electric furnace to free them from acid and to reduce any traces of silver salts that may remain on them. It is convenient to heat them to redness for a few moments for this purpose, although a much lower temperature would be sufficient to eliminate the acid.

Upon anodes prepared in this way very little anode slime is produced. This is not a matter of great importance in the porous cup voltameter, but is more important in any form of voltameter in which no septum is used between anode and cathode.

4. METHOD OF PREPARING CATHODES

The platinum dish, after being electrolyzed as is described under the method of preparing anodes, is emptied of solution and as much as possible of the black crystalline growth that forms upon it after the silver has disappeared is washed out. The cups are then filled with strong nitric acid (equal parts of concentrated HNO_3 and water) and allowed to stand for about half an hour. Following this they are thoroughly gone over inside and out with a new piece of cotton cloth, rubber gloves protecting the cups from the hands. They are then quickly immersed in a 10 per cent solution of NaOH to remove any possible traces of grease, and afterwards rinsed in dilute HNO_3 to remove the last traces of the alkali. After thorough rinsing with tap water they are immersed in three changes of distilled water, of which the last two are double distilled and then placed in the oven to dry for three-quarters of an hour. During the latter part of this process they are handled entirely with tongs.

5. METHOD OF WASHING THE DEPOSITS

After the removal of the anode and septum from the voltameter the electrolyte is drawn off by a siphon into a small beaker bearing

a letter to identify it with the particular voltameter. A few cc of electrolyte necessarily remain in the voltameter if floating silver is present, as this would otherwise be drawn over in the siphon. The dish is then filled with double distilled water. After all the voltameters have been thus dismantled the beakers containing the electrolyte are set on a sheet of black paper in a strong light and examined for loose silver particles. If any are found they are caught in a small pipette and put back into the platinum dish. The distilled water in the platinum bowls is then drawn off into large lettered beakers and then two or three more wash waters, according to the amount of electrolyte originally left in the voltameter, are used. The wash waters which have been collected are then examined for any particles of loose silver, as in the case of the electrolyte. After any such particles have been recovered and put back in the platinum bowl the process is repeated. Thus each voltameter is filled six or eight times with distilled water, of which the first and last two are double distilled. The last two or three never show any trace of $AgNO_3$ when tested with NaCl. After the last set of wash waters are examined the cups are removed to an electric oven for drying at 150°.

6. METHOD OF PREPARING THE POROUS POTS

The porous pots may be so thoroughly cleansed that they can stand for hours in distilled water without greatly increasing its conductivity. New porous pots of the best grade of unglazed porcelain will in general render the distilled water that they stand in alkaline. This is difficult to overcome by prolonged soaking in the best distilled water, but the process can be greatly shortened by letting dilute nitric acid filter through by gravity. This small amount of acid is easily washed out and a new pot, after such treatment for several days, is without effect on the conductivity of distilled water. As the porous pots are used from time to time they gradually become stained, particularly near the top. This, however, does not seem to affect the deposit of silver, as no certain difference has been detected between pots in constant use and others which were new and suitably treated. It is well, however, to clean and whiten them occasionally, and this may be safely done in two different ways, which require about the same time and are equally effective. By one method the porous pot is filled with

equal parts of pure nitric acid and water, which is allowed to filter through slowly by gravity. If the pot is not entirely whitened the process should be repeated. The pot is then to be soaked in distilled water, changed several times a day until the water that has slowly filtered through it is neutral to iodeosine.[63] Then after allowing several portions of the best silver nitrate to filter through, it is ready for use in the voltameter. (The above method was developed during the course of the work, but was not used at first.)

By the other method the pot is freed from the silver nitrate contained in its pores by soaking it for several days in repeated changes of distilled water. When the water that has slowly filtered through it shows no reaction with sodium chloride or hydrochloric acid the pot is to be placed in a clean electric furnace and heated to bright red for about half an hour and then allowed to cool slowly in the furnace to avoid cracking. It should now be white. The alkalinity of the pot produced by baking is removed by soaking it in dilute nitric acid for about a day. When all traces of this acid have been removed, as is easily done with several changes of distilled water, the pot is prepared for use in the voltameters by filtering several portions of best electrolyte through its pores.

Pots cleaned by these two methods and compared with those long in use revealed no difference in the weight of silver deposited by a given quantity of electricity. The method of using Aqua Regia, KCN, HNO_3, and boiling water as recommended by Guthe[64] and subsequently used by Smith[65] with the addition of baking the pots to eliminate the acid, was unsatisfactory and abandoned. It requires a much longer time, owing to the soaking necessary to remove the acids and especially the KCN. After use in the voltameter the pots treated in this way are often stained yellow.

A convenient method of keeping the porous pots in good condition between experiments is nearly to submerge those of the same size in pure $AgNO_3$ in a crystallizing dish covered with a clock glass. After the run the porous pots are rinsed free from all traces of anode slime by a strong jet of distilled water. They are then rinsed with double distilled water and put to soak in the electrolyte again.

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[63] This test will be given in the third paper of this series by Rosa, Vinal, and McDaniel.

[64] This Bulletin, 1, p. 23.

[65] Collected Researches of N. P. L., 4, p. 141.

C. MANIPULATION TESTS

1. ERRORS OF STARTING, STOPPING, AND TIMING THE DEPOSITS

The quantitative work which began in October, 1908, was preceded by certain manipulation tests designed to show what accuracy could be obtained in the measurement of current and time, and in washing, drying, and weighing the platinum dishes.

To magnify the errors incident to starting, stopping, and timing the deposits, nine short runs aggregating about 10 minutes in length were made and weighed as a whole. The mean value of the three voltameters gave 1.11818 for the electrochemical equivalent. This was 69 parts in 100 000 higher than the values found from the two subsequent experiments of 1 ampere for one hour. Since the time is one-sixth and the number of runs 9 the proportional error for a one-hour run would be $\frac{69}{54} = 1.3$ in 100 000. This error has probably been considerably reduced as the work has progressed.

2. COMPARISONS OF VACUUM DESICCATORS AND OVENS

Comparisons were made of drying the platinum dishes in vacuum desiccators over sulphuric acid and in an electric oven at 150° with results showing the superiority of the oven aside from the question of time saved. Three large platinum bowls prepared as if for a quantitative determination were allowed to dry in separate vacuum desiccators over night and then weighed against the usual counterpoise. They were then baked at 150° for 2¼ hours and weighed again with the following results:

TABLE VI

	No. 95—No. 94	No. 93—No. 94	No. 92—No. 94
	mg	mg	mg
Desiccator drying	−0.213	−0.134	0.000
After baking	− .316	− .214	− .089
Loss in weight	.103	.080	.089
After rebaking	− .321	− .218	− .093
Loss in weight	.005	.004	.004

Since 0.082 mg corresponds to 2 parts in 100 000 of the total deposit in a normal run the loss in weight found after the first

baking is too serious to neglect. The second baking, however, caused very little change.

Similar comparisons between vacuum desiccators and oven drying were tried with the bowls containing the deposit of a preliminary experiment. This showed better agreement between the two methods of drying. Immediately after finishing the washing of the deposit the cups were placed in separate vacuum desiccators and left over night. The following morning they were weighed and then baked at 150° for two hours and reweighed. The deposits were distinctly whiter after the baking. The results are as follows:

TABLE VII

Cup	After desiccation	After baking	Loss in weight
	mg	mg	mg
No. 95	4023.02	4022.99	0.03
No. 93	4023.23	4023.17	.06
No. 92	4022.86	4022.83	.03

Two reasons, however, led us to abandon the vacuum desiccator in favor of the oven. First, the oven was a much more expeditious method under our circumstances; second, we preferred to leave as much as 10 cc of double distilled water in the cups after washing the deposit, when, as often happened, there was loose silver floating on the surface of the water, rather than to drain the bowl and return the loose silver to the bowl.

3. WEIGHINGS

Throughout the course of the work the weighing of the cups was checked by observing the differences in weight of dishes that had been weighed singly against the counterpoise. Occasionally a whole new set of weighings was made and we present the following as typical. The first set is not as good as the average, but the second is perhaps a little better. The two sets are in satisfactory agreement since the maximum difference is equal to only 2.5 parts in a million of the deposit of silver.

TABLE VIII

Comparison Showing the Accuracy of Weighings

Nos. 127 and 128 were weighed against No. 25 on August 15, 1910.

	mg
(1) No. 127—No. 25	= −0.092
(2) No. 128—No. 25	= − .319
(3) No. 127—No. 128	= + .207

From the first and second weighings,

Nos. 127—128 = +0.227

The least square adjusted values are—

No. 127—No. 25 = −0.099
No. 128—No. 25 = − .312

These cups remained in the balance until August 19, when they were reweighed.

	mg
(1) No. 127—No. 25	= −0.092
(2) No. 128—No. 25	= − .312
(3) No. 127—No. 128	= + .228

From weighings (1) and (2)—

No. 127—No. 128 = +0.220

The least square of adjusted values are—

No. 127—No. 25 = −0.089
No. 128—No. 25 = − .315

Assuming that the tare No. 25 has remained constant during this time, we find the weights of the individual cups to be—

Date	No. 127	No. 128
	g	g
Aug. 15	55.089901	55.089583
Aug. 19	55.089911	55.089585

D. QUANTITATIVE RESULTS

1. LIST OF DEPOSITS.

Between October 8, 1908, and September 22, 1909, we have made 27 separate runs with various forms of voltameters, having from 3 to 10 cups in use in each case. There were made in all 122 deposits, one of which was spoiled by the breaking of an especially tender filter paper. All the other deposits made or attempted (excluding a large number of qualitative deposits not intended to be weighed) have been tabulated.

The first 21 deposits made were in Rayleigh voltameters, using large platinum cups (weight 80 g, volume 350 cc) with the same silver nitrate and filter paper used in 1907. The mean value found for the electrochemical equivalent from these 21 deposits was 1.11749, almost identical with the mean found in 1907. The average variation from the mean was 5 parts in 100 000, showing a good degree of reproducibility when the same procedure is followed.

The next 100 deposits were made between December 22, 1908, and September 22, 1909, in which we studied the effect of filter paper in varying quantities in the voltameter and compared the Rayleigh and Richards forms, also varying the electrolyte, and changing numerous working conditions.

Table IX consists of a complete tabulation of the deposits made during this period. The values for the electrochemical equivalent of silver are our original results based on the value of 1.01890 volts for the Weston normal cell at 25° C, as was the practice in the United States prior to January 1, 1911. The means of the various tables following are converted into values for the voltage of the Weston cell computed upon the assumption of the electrochemical equivalent of silver being 1.11800 mg per coulomb, in accordance with the decision of the London Conference of 1908.

Table X contains a list of 43 deposits in the Rayleigh voltameter taken from the preceding general table. Thirty-seven of them were made using one sheet of filter paper, four using two sheets, and two using three sheets. The average value for the first set was 1.11745, of the second 1.11768, and of the third 1.11796. This shows that the excess of the deposit above the correct value

is approximately proportional to the quantity of filter paper present.

Table XI gives a record of 53 deposits made in the porous cup form of voltameter, of which the first eight were contaminated with filter paper and three others were abnormal, Nos. 103, 109, and 117. The 42 normal deposits average 1.11704 for the electrochemical equivalent. This is a mean for large and small voltameters and different electrolytes. Most of it is 15 per cent new electrolyte, but a few deposits were made with used solutions. The large cups give a deposit which averages 2.5 in 100 000 greater than the small cups. This average is 40 parts in 100 000 lower than the value given by the filter paper voltameter.

TABLE IX

General Table of Quantitative Results for 1908 and 1909

Date	No.	Bowl	Form	Electrolyte	Time	Current	Deposit	El. Ch. Eq.	Remarks
1908					Seconds	Amperes	mg		
Oct. 8	1	95	Rayleigh	Baker 15%			4076.86	1.11755	Elmer & Amend's "Best white" filter paper used in first 22 deposits; all striated
	2	93	do	do	3578.94	1.01931	6.76	52	
	3	92	do	do			6.92	56	
12	4	95	do	do			4097.80	1.11742	
	5	93	do	do	3597.72	1.01931	7.92	46	
	6	92	do	do			7.82	43	
28	7	95	do	do			4103.72	1.11743	
	8	93	do	do	3602.88	1.01931	3.70	43	
	9	92	do	do			3.91	48	
Nov. 20	10	95	do	do			4101.25	1.11758	
	11	93	do	do	3601.69	1.01890	1.29	59	
	12	92	do	do			1.25	58	
Dec. 1	13	95	do	do			6503.66	1.11747	
	14	93	do	do	5712.01	1.01890	3.67	48	
	15	92	do	do			3.63	47	
8	16	95	do	do			8200.23	1.11745	
	17	93	do	do	7202.02	1.01893	0.01	42	
	18	92	do	do			0 39	47	
14	19	95	do	do			8198.66	1.11751	
	20	93	do	do	7200.28	1.01892	8.28	46	
	21	92	do	do			8.33	47	
22	22	95	do	do			4098.86	1.11743	
	23	93	Richards	do	3600.22	1.01886	8.29	27	
	24	92	do	do			8.11	22	
28	25	95	Rayleigh	do			4098.69	1.11735	S. & S. No. 595 filter paper
	26	93	do	do	3600.14	1.01891	8.55	31	S. & S. No. 602 filter paper
	27	92	do	do			8.55	31	E. & A. "Best white" filter paper

1909									
Feb. 2	28	95	.....do.....	.....do.....			4096.44	.....	S. & S. No. 602 filter paper
	29	93	Richards.....	.....do.....			5.54	.....	
	30	92	.....do.....	.....do.....			5.65	.....	
	31	26	Poggendorff.....	.....do.....	1 hour	1 amp.	9.96	.....	Anode slime on cathode
	32	27	Richards.....	.....do.....			5.26	.....	
	33	28	.....do.....	.....do.....			5.35	.....	
11	34	95	Rayleigh.....	.....do.....			4104.77	1.11751	S. & S. No. 602 filter paper
	35	93	.....do.....	.....do.....			5.54	72	S. & S. No. 602 filter paper, double
	36	92	Poggendorff.....	.....do.....			4.27	37	Striated
	37	26	.....do.....	.....do.....	7210.28	.509432	4.05	31	Do.
	38	27	Richards.....	.....do.....			3.49	16	Slightly striated
	39	28	.....do.....	.....do.....			3.50	16	Do.
27	40	95	Rayleigh.....	.....do.....			4098.60	1.11735	S. & S. 602 filter paper
	41	93	.....do.....	Kahlbaum 15%....			8.86	44	Do.
	42	92	Poggendorff.....	Baker 15%.....			7.57	09	
	43	26	.....do.....	Kahlbaum 15%....	7200.26	.509435	7.14	698	
	44	27	Richards.....	Baker 15%.....			7.49	707	
	45	28	.....do.....	Kahlbaum 15%....			7.84	17	
Mar. 11	46	95	Rayleigh.....	Baker 15%.....			4099.89	1.11775	S. & S. No. 595 filter paper, double
	47	93	.....do.....	.....do.....			9.75	71	S. & S. No. 602 filter paper, double
	48	92	.....do.....	.....do.....			8.53	38	S. & S. No. 602 filter paper, single
	49	26	.....do.....	.....do.....	7200.15	.509431	8.48	37	S. & S. No. 595 filter paper, single
	50	27	Richards.....	.....do.....			8.60	40	Probably contaminated
	51	28	.....do.....	.....do.....			8.61	40	Do.
23	52	95	Rayleigh.....	.....do			4099.12	1.11762	S. & S. No. 598 filter paper, single
	53	93	.....do.....	.....do.....			4100.00	786	S. & S. No. 595 filter paper, triple
	54	92	.....do.....	.....do.....			0.77	807	S. & S. No. 598 filter paper, triple
	55	26	.....do.....	.....do.....	7199.74	.509426	4098.49	744	S. & S. No. 595 filter paper, single
	56	27	Richards.....	.....do.....			7.17	708	Electrolyte not filtered through filter paper
	57	28	.....do.....	.....do.....			7.14	708	
Apr. 5	58	95	.....do.....	.....do.....			4097.39	1.11710	Electrolyte free from filter paper contamination
	59	93	.....do.....	.....do.....			7.30	08	Do.
	60	27	.....do.....	.....do.....	7199.99	.509428	7.29	07	Do.
	61	28	.....do.....	.....do.....			7.15	04	Do.

TABLE IX—Continued

General Table of Quantitative Results for 1908 and 1909—Continued

Date	No.	Bowl	Form	Electrolyte	Time	Current	Deposit	El. Ch. Eq.	Remarks
1909									
Apr. 9	62	95	Richards	Baker 15%			4098.61	1.11741	Filter paper outside cup, striated
	63	93	do	do	7200.10	.509430	7.70	17	
	64	27	do	do			7.62	15	
	65	28	do	do			7.59	14	
16	66	95	do	do			4097.33	1.11705	Filter paper inside porous cup
	67	93	do	do	7200.07	.509439	7.28	04	
	68	27	do	do			7.26	03	
	69	28	do	do			7.21	02	
24	70	95	do	Used solution			4097.56	1.11707	No striations
	71	93	do	Baker 15%	7200.40	.509436	7.97	18	Do.
	72	27	do	do			7.75	12	Do.
	73	28	do	Used solution			7.54	06	Do.
May 6	74	95	do	do			4096.85	1.11697	Electrolyte filtered through porous pot
	75	93	do	do			7.01	702	Do.
	76	92	do	do	7199.98	.509420	7.56	16	Electrolyte not filtered, not clear
	77	26	do	do			8.65	46	Electrolyte from Rayleigh voltameter
	78	27	do	do			7.07	03	Electrolyte from Richards, not filtered
	79	28	do	do			6.94	00	Electrolyte from Richards, filtered
18	80	95	do	Baker 15%			4097.07	1.11709	Unused electrolyte
	81	93	do	Used electrolyte			6.65	698	Electrolyte from Richards, filtered
	82	92	do	do	7199.99	.509392	6.59	697	Do.
	83	26	Rayleigh	Baker 15%			8.49	748	5 sheets No. 590 filter paper, very thin
	84	27	Richards	Used electrolyte			7.54	722	Filter paper outside porous cup
	85	28	do	do			7.99	735	Electrolyte from Rayleigh voltameter
June 3	86	95	do	Baker 15%			4100.24	1.11802	Filter paper soaked in electrolyte
	87	93	Leduc	do	7200.24	.509345	0.80	817	Linen bag around anode
	88	92	do	do			4098.59	757	Silk bag around anode

	89	26	Rayleigh	do	7200.24	.509345	8.45	753	2 sheets No. 595 filtered paper
	90	27	Richards	do			6.44	698	Standard cup
	91	28	do	Used electrolyte			6.44	698	Not striated, fine grain
10	92	93	do	Baker 15%	7199.98	.509329	4096.57	1.11710	Standard cup, large
	93	27	do	Used electrolyte			6.27	702	Anode liquid from Richards
	94	28	do	Baker 15%			7.92	746	Silk soaked in electrolyte
Aug. 18	95	95	do	Frankfurt 15%	7199.97	.509361	4096.45	1.11700	Special distilled water
	96	93	do	Baker 15%			6.28	695	
	97	92	do	do			6.39	698	
	98	128	do	Frankfurt 15%			5.82	683	
	99	27	do	Baker 15%			6.23	694	
	100	28	do	Frankfurt 15%			6.11	689	
26	101	93	Rayleigh	do	7201.68	.509361	4098.38	1.11726	Linen paper, especially made
	102	92	do	do			7.96	14	Cotton paper, especially made
	103	128	Richards	do			7.99	15	Electrolyte contaminated
	104	27	do	do			7.39	699	Normal voltameter
	105	28	do	do			7.21	694	Do.
Sept. 9	106	95	do	do	7202.05	.509366	4098.32	1.11717	Normal voltameter, large
	107	93	Rayleigh	do			9.01	36	Little filter paper as possible
	108	92	do	do			9.72	55	Ordinary amount of filter paper
	109	128	Richards	do			8.57	24	Electrolyte contaminated
	110	27	do	do			8.21	14	Normal voltameter
	111	126	do	do			7.99	08	Do.
17	112	95	do	Baker 15%	7200.29	.509367	4096.89	1.11707	Do.
	113	93	do	do			7.23	17	Electrolyte filtered hot through filter paper
	114	92	Poggendorff	do			5.17	.....	Lost silver
	115	26	do	do			7.87	.....	Slime on cathode
	116	27	do	do			7.13	14	Very small anode
	117	28	Richards	do			6.82	05	Normal voltameter
22	118	127	do	Frankfurt 15%	2 hours	½ amp.	4100.26	.....	
	119	128	Poggendorff	do			0.81	.....	
	120	125	Richards	do			0.05	.....	
	121	126	Poggendorff	do			0.61	.....	

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TABLE X

Rayleigh Voltameter

Date	No.	El. Ch. Eq.	Kind of filter paper
1908			
Oct. 8	1	1.11755	E. & A. "Best white"
	2	752	Do.
	3	756	Do.
12	4	742	Do.
	5	746	Do.
	6	743	Do.
28	7	743	Do.
	8	743	Do.
	9	748	Do.
Nov. 20	10	758	Do.
	11	759	Do.
	12	758	Do.
Dec. 1	13	747	Do.
	14	748	Do.
	15	747	Do.
8	16	745	Do.
	17	742	Do.
	18	747	Do.
14	19	751	Do.
	20	746	Do.
	21	747	Do.
22	22	743	Do.
28	25	735	S. & S. No. 595
	26	731	S. & S. No. 602, hard
	27	731	E. & A. "Best white"
Feb. 11	34	751	S. & S. No. 602, hard
	35	772	2 sheets No. 602, hard
27	40	735	S. & S. No. 602, hard
	41	744	Do.
Mar. 11	46	775	2 sheets No. 595
	47	771	2 sheets No. 602, hard
	48	738	1 sheet No. 602, hard
	49	737	1 sheet No. 595
23	52	762	1 sheet No. 598, very heavy paper
	53	786	3 sheets No. 595
	54	807	3 sheets No. 598
	55	744	1 sheet No. 595
May 18	83	748	5 sheets No. 590, very thin; equivalent to 2 sheets No. 595
June 3	89	753	2 sheets No. 595
Aug. 26	101	726	Unsized linen paper
	102	714	Unsized cotton paper
Sept. 9	107	736	Less than ordinary No. 595
	108	755	1 sheet No. 595

Mean of 43=1.11749.
Mean of 37=1.11745, with 1 sheet of filter paper.
Mean of 4=1.11768, with 2 sheets of filter paper.
Mean of 2=1.11796, with 3 sheets of filter paper.

Taking the value obtained for the normal Rayleigh voltameter (e. g., with 1 sheet of filter paper) we find the voltage of the Weston normal cell at 20°, assuming the electrochemical equivalent of silver to be 1.11800 mg per coulomb, is 1.01866 volts.

TABLE XI

Richards Voltameter

(The electrolyte for the first eight deposits was filtered through filter paper. For the others no filter paper was used, except as noted, and in most cases the electrolyte was not filtered. The large, medium, and small voltameters are denoted by l, m, s, respectively.)

Date	No.	Size	El. Ch. Eq.	Remarks
Dec. 22	23	l.	1.11727	Porous cups soaked in used electrolyte from Rayleigh voltameter
	24	l.	722	
Feb. 11	38	s.	716	
	39	s.	716	
27	44	s.	707	
	45	s.	717	Kahlbaum $AgNO_3$
Mar. 11	50	s.	740	Electrolyte probably contaminated
	51	s.	740	Do.
23	56	s.	708	Discontinued use of filter paper for filtering electrolyte
	57	s.	708	
Apr. 5	58	l.	710	
	59	l.	708	
	60	s.	707	
	61	s.	704	
9	63	l.	717	
	64	s.	715	
	65	s.	714	
16	66	l.	705	(Filter paper inside of porous cup)
	67	l.	704	
	68	s.	703	
	69	s.	702	
24	70	l.	707	Used solution
	71	l.	718	New solution
	72	s.	712	Do.
	73	s.	706	Used solution
May 6	74	l.	697	Used electrolyte, filtered through porous cup
	75	l.	702	
	76	l.	716	Used electrolyte, not filtered, not clear
	78	s.	703	Used electrolyte, not filtered, clear
	79	s.	700	Used electrolyte, filtered
18	80	l.	709	New electrolyte
	81	l.	698	Used electrolyte filtered through porous cup
	82	l.	697	Used electrolyte, filtered
June 3	90	s.	698	New electrolyte
	91	s.	698	Used electrolyte
10	92	l.	710	New electrolyte
	93	s.	702	Used anode electrolyte

TABLE XI—Continued

Richards Voltameter—Continued

Date	No.	Size	El. Ch. Eq.	Remarks
Aug. 18	95	l.	1.11700	Frankfurt salt
	96	l.	695	Baker salt
	97	l.	698	Do.
	98	m.	683	Frankfurt salt
	99	s.	694	Baker salt
	100	s.	689	Frankfurt salt
26	103	m.	715	Electrolyte contaminated
	104	s.	699	Frankfurt salt
	105	s.	694	Do.
Sept. 9	106	l.	717	
	109	m.	724	Electrolyte contaminated
	110	s.	714	
	111	s.	708	
17	112	l.	707	
	113	l.	717	Electrolyte filtered hot through filter paper
	117	s.	705	
Mean of 42.....			1.11704_3	

Average difference=2½ in 100 000 between large and small in same runs.

The mean of these 42 determinations gives for the value of the Weston normal cell at 20° 1.01828_7 volts. The first eight and Nos. 76, 103, and 109 have been omitted in taking the mean.

TABLE XII

Summary of Miscellaneous Deposits

Date	No.	El. Ch. Eq.	Remarks
1909			
Apr. 9	62	1.11741	Baker salt, small voltameter with porous cup, having strip of filter paper 50 by 6½ cm wrapped around outside of latter
May 6	77	1.11746	Porous cup used electrolyte from Rayleigh voltameter
18	84	1.11722	Used electrolyte, with filter paper 30 by 5 cm wrapped around porous cup
	85	1.11735	Used electrolyte from No. 62
	86	1.11802	New Baker electrolyte, 2 sheets of filter paper soaked over night in electrolyte
	87	1.11817	Linen bag around anode, as used by Leduc
	88	1.11757	Silk bag around anode
June 10	94	1.11746	New Baker electrolyte 15 per cent raw silk soaked in it over night
Mean of 8.		1.11758	

Weston cell at 20°=1.01878.

Table XII gives a list of eight deposits, in some of which filter paper was placed in the electrolyte outside the porous cup, or a filter paper solution was used in a porous cup form, or a silk or linen bag was used instead of filter paper or a porous cup. In every case the deposit is too heavy; in two cases by nearly one-tenth per cent.

Table XIII gives the results of 10 deposits in the Poggendorff form of voltameter, 3 of which were failures. The value of the equivalent as given by a porous cup voltameter is also given (in one comparative run the latter is assumed as 1.11703). The mean value is somewhat higher than the porous cup form has given.

TABLE XIII

Summary of Poggendorff Form, Without Silk Septum

Date	No.	El. Ch. Eq.		Remarks
		Poggendorff	Porous pot	
1909				
Feb. 2	31	.....	.....	Deposit 4 mg too heavy, anode slime on cathode
11	36	1.11737	716	Deposit striated Baker salt 15 per cent
	37	731	716	Deposit striated
27	42	709	707	Baker salt 15 per cent
	43	698	717	Kahlbaum salt 15 per cent
Sept. 17	114	.....	.....	Deposit 1.7 mg too light, silver lost
	115	.....	.....	Deposit 1 mg too heavy, anode slime
	116	714	705	Good deposit
22	119	721	703	Do.
	121	716	703	Do.
Mean of 7.		1.11718	709	

Weston cell at 20°=1.01841 volts.

The electrolyte was not quite pure, so that the deposit should have been a little too heavy. The small porous cup voltameters in use at the same time for comparison gave 1.11709, or 8 parts in 100000 less.

2. NARRATIVE OF THE TRIALS OF FILTER PAPER, ETC.

Between October 8 and December 14, 1908, seven experiments were made using three large Rayleigh voltameters, all assembled under as nearly identical conditions as possible. The current and time were accurately measured and were 1 ampere and one hour,

respectively, thus depositing about 4.098 grams of silver. The result of these experiments was to show a very fair degree of reproducibility, but the value obtained for the electrochemical equivalent of silver was considerably in excess of that found by Smith, Mather, and Lowry.[66] On December 22 two porous pots made by Königlich Porzellan Manufaktur of Berlin were used for the first time.

The values obtained with the porous pots were almost 2 in 10 000 smaller than with the filter paper. This suggested that the "Best white" filter paper which we had been using up to this time might not be sufficiently good. In the next run of December 28, 1908, we therefore compared it with No. 595 S. & S. and No. 602 S. & S. and found all in substantial agreement. A further comparison of filter paper and porous cups on February 2, 1909, confirmed the conclusions of the preceeding runs that the Rayleigh voltameter gives a higher deposit than the porous cup type. We supposed at this time that this was due to the filter paper not acting as a perfect separator of the anode and cathode solutions as has been suggested by Richards.[67] In the hope of rendering the filter paper more efficient in this regard we tried in succeeding experiments the effect of doubling or even trebling the thickness. But instead of agreeing better with the result obtained with the porous cup, the deposits were still heavier, two sheets of filter paper giving an excess of about double, and three an excess about treble that due to one sheet. That is, the excess in weight was proportional to the quantity of filter paper, and was therefore not due to the filter paper being an imperfect filtering medium. This result also followed when the finest grades of filter paper were used, the excess weight above the normal weight in a Richards voltameter being practically the same for all filter paper tried, if the weight of filter paper submerged in the electrolyte was the same. The excess weight of silver, with a relatively large amount of filter paper, may be as much as 0.1 per cent. Striations are more marked as the quantity of filter paper is greater, so that one can predict a heavy deposit by its appearance.

This evidence, which seemed to indicate that the filter paper voltameter was giving abnormally high values for the electro-

[66] Collected Researches, N. P. L., 4, p. 157. [67] Proc. Am. Academy, 35, p. 123. 37, p. 415.

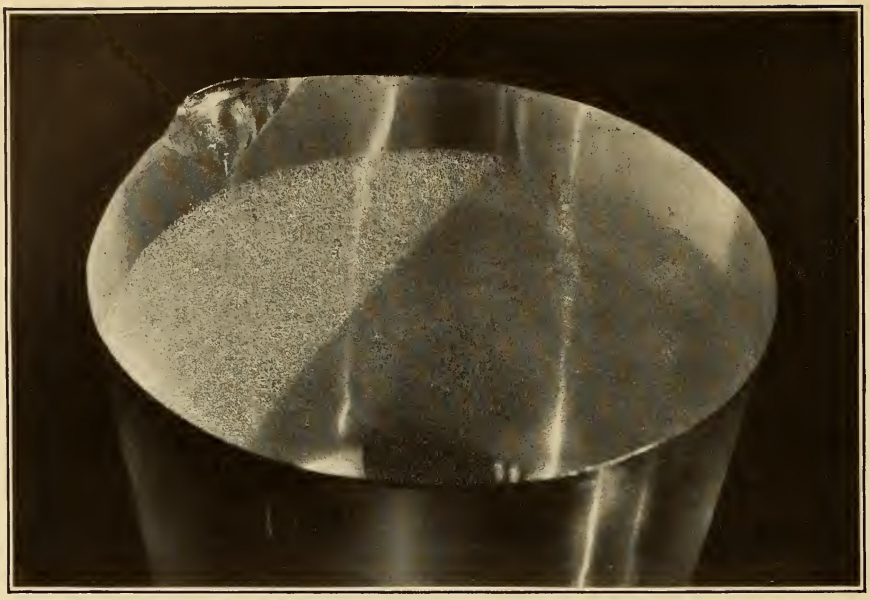

Fig. 13.—*Characteristic deposit in Richards voltameter. The electrolyte had been previously used in a voltameter free from filter-paper contamination*

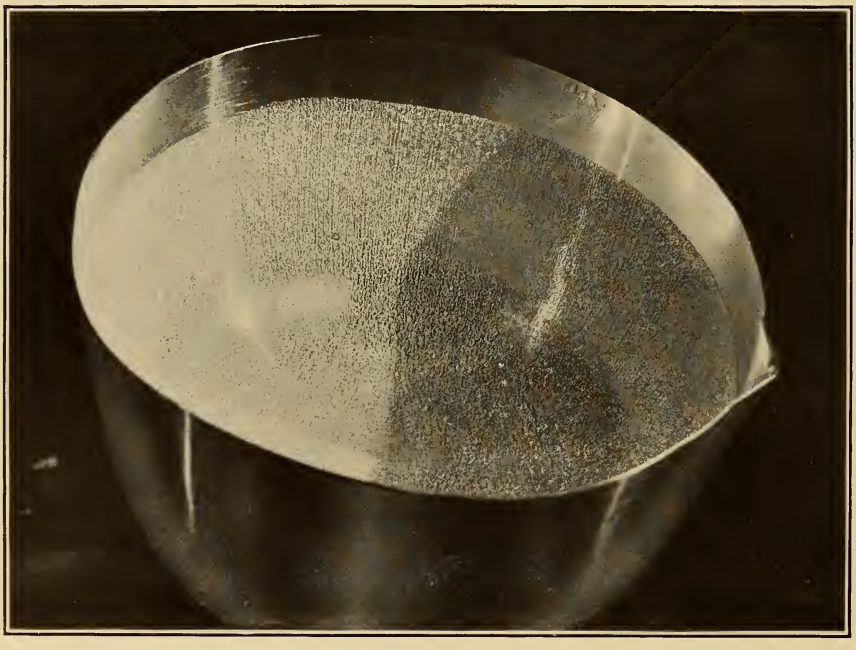

Fig. 14.—*Striated deposit made in a Richards voltameter from an electrolyte previously used with filter paper*

chemical equivalent, was confirmed on April 9 and 16, when we compared voltameters having both the porous cup and filter paper with the ordinary porous cup type. In the former experiment a strip 50 by 6.5 cm of No. 602 S. & S. filter paper was wrapped around the outside of the porous cup. The deposit in this voltameter was strongly striated and 26 parts in 100 000 heavier than the mean of the three normal Richards, which agreed closely among themselves and were free from striations. On April 16 a similar experiment was performed, differing only in the fact that the strip of filter paper was placed inside of one of the porous cups. The four deposits of this run were all fine grain and free from striation and the maximum difference in weight between any two is only 3 parts in 100 000. These results were confirmed by a subsequent experiment on May 18.

Having thus satisfied ourselves that filter paper is capable of exercising a profound effect on the appearance and weight of the deposit, we were naturally led to inquire whether it was necessary to have the paper present at the time the electrolysis was actually in progress. We obtained the first definite knowledge that such was not the case on May 6, when we electrolyzed for the second time the cathode solution that had been used in the combined porous cup-filter paper voltameter of April 9. This time the electrolysis was made in a normal Richards voltameter and was compared with solutions that had been used previously with porous cups only. The results of this experiment were very conclusive. The deposit from the electrolyte contaminated with filter paper was again strongly striated and gave a value for the electrochemical equivalent that was characteristic of the Rayleigh voltameter, while the others gave nonstriated deposits of what we believed to be about the normal weight. Two contrasted deposits of this run are shown in photographs, figures 13 and 14. The results of this experiment justified the conclusion which we had previously reached, that it was unwise to filter the electrolyte through filter paper before use. This practice had been discontinued beginning with the run of March 23, 1909, and since that time we had been obtaining lower values for the electrochemical equivalent with the Richards voltameter.

On June 3 and June 10 we began to try other substitutes for filter paper, particularly linen and silk textiles. In the former of

these two runs we inclosed the anodes in silk and linen bags as was done by Leduc and compared them with a Richards voltameter taken as standard. We also electrolyzed at this time 340 cc of the same electrolyte in which two sheets of 19 cm No. 595 S. & S. filter paper had been allowed to soak over night. This was done in a Richards voltameter. The deposits from the silk and the linen were both abnormally high, the latter being more than 0.1 per cent higher than the standard voltameter, but this may have been due in part to some anode slime passing through the meshes of the cloth.

The deposit from the electrolyte contaminated with filter paper was also 0.1 per cent heavy. The sides of this cup were more heavily striated than any we had seen up to this time and the bottom was covered with stiff vertical rods of silver several millimeters long. (See Fig. 15.)

On June 10 we compared the deposits from an electrolyte in which some of the same sample of silk as used in the previous run had been soaked over night, with a normal voltameter, and also with a voltameter in which the electrolyte was anode solutions saved from previous runs and free from filter paper contamination. This last was tried because we believed that if a complex ion were really present in the anode liquid we should get an abnormally heavy deposit. This, however, we did not find, but in fact it gave a lower deposit than the standard cup. In appearance, weight, etc., it behaved like the used cathode liquid reelectrolyzed in some previous experiments. (See Fig. 16.) The result of the silk test was a deposit very abnormal in weight and appearance. (See Fig. 17.)

3. USED SOLUTIONS

Further evidence of the action of filter paper and similar substances in increasing the weight of the deposit was obtained by reelectrolyzing certain of our old solutions saved from previous experiments. Many observers [68] have recorded an increased deposit from solutions electrolyzed two or more times. This we believe to have been due to contamination of the solution with filter paper, because in our earliest work done during the summer

[68] Novak, Proc. Roy. Bohemian Ac. Sci. Prague, **1**, p. 387; 1892. Rodger and Watson, Phil. Trans. A, **186**; 1895. Kahle, Zeitschr. f. Inst. **18**, p. 229; 1898. van Dijk, Ann. d. Phys. **19**, p. 249; 1906. Guthe, Phys. Rev. **19**, p. 138; 1904. This Bulletin, **I**, p. 355; 1904.

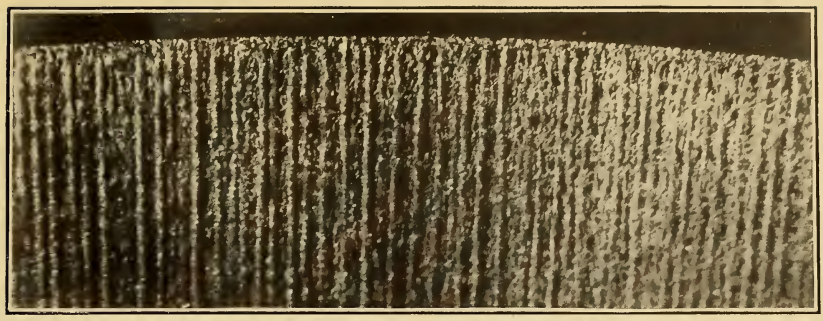

Fig. 15.—*Heavy striations due to excess of filter paper*

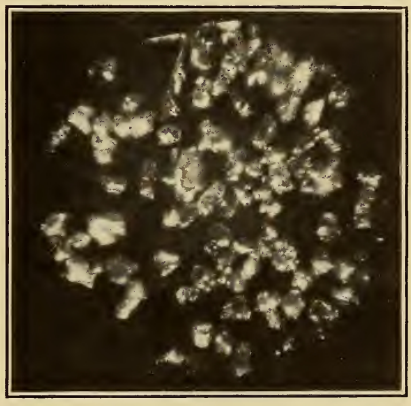

Fig. 16.—*Showing a normal crystalline deposit from an electrolysis of anode solution.* × *16*

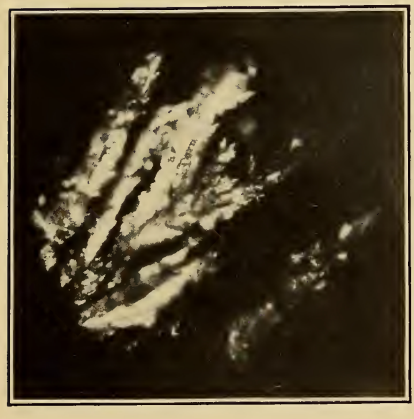

Fig. 17.—*Showing the effect of silk in changing the crystalline character of the deposit.* × *16*

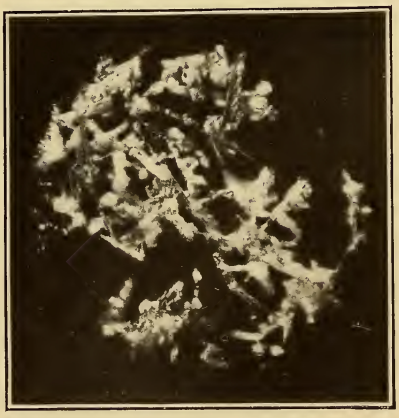

Fig. 18.—*Showing the modification of crystalline structure due to filtering the electrolyte hot through filter paper.* × *16*

of 1907 we observed this increase many times while we were using the Rayleigh type of voltameter. We found for the means of new and used solutions

34 deposits unused solutions..... 1.11746
21 deposits used solutions..... 1.11761

But on the other hand we have repeatedly used solutions saved from the Richards voltameters of previous runs and have found the deposit to be substantially normal in weight and appearance, tending rather to be lighter in weight than heavier. Since in this latter case we were dealing with solutions that had not been in contact with filter paper we believed this to be an added proof that filter paper is an active agent in the voltameter. Smith [69] found that long continued electrolysis is without effect upon the deposits made subsequently with the same electrolyte, but it is to be noted that in performing this experiment he omitted the use of filter paper in the major part of the experiment.

During the quantitative work of 1909 we made eight determinations of the electrochemical equivalent with used solutions saved from the Richards voltameter and which were therefore free from filter paper contamination, and at the same time five determinations with new solutions with results as follows:

TABLE XIV

Date	Size	New electrolyte	Used electrolyte	Remarks
1909				
Apr. 24	l.	1.11718	.....	Baker $AgNO_3$
	s.	712	.....	Do.
	l.	.....	1.11707	Cathode liquid
	s.	.....	706	Do.
May 6	l.	.....	716	Electrolyte not clear, omitted
	s.	.....	703	Cathode liquid
18	l.	709	.....	Baker $AgNO_3$
	l.	.....	698	Cathode liquid
	l.	.....	697	Do.
June 3	s.	698	.....	Baker $AgNO_3$
	s.	.....	698	Cathode liquid
10	l.	710	.....	Baker $AgNO_3$
	s.	.....	702	Anode liquid
	Mean	1.11709	1.11702	

[69] Collected Researches, Nat. Phys. Lab. Vol. IV, p. 164.

In the column headed "size" the letters l and s are used to denote the large bowls and small bowls, respectively. The crystals from used electrolyte are well formed but usually finer; that is, there are more to the square centimeter of area than in the other case.

Repeated electrolysis makes the deposit still finer in grain. On November 3, 1909, we assembled a voltameter with 100 cc of pure unused electrolyte as if for a quantitative run. We made four runs at 1 ampere for one hour each with this electrolyte, examining and removing the deposit between each run. As the 100 cc of 15 per cent solution contained at the start 11.2 grams of silver and during the four experiments we removed 16 grams, this served as a test of complete exhaustion. The deposit from each successive run was finer than that of the preceding. At the end of the fourth experiment the electrolyte was neutral to methyl orange after precipitating the silver with neutral KCl solution and filtering. Apparently the acid plays an important rôle in diminishing the size of the crystals, as only very small amounts are required, but it also seems possible that this decrease in size of the silver crystals is due in part to the decrease in concentration of the electrolyte outside the porous pot. We have found that concentration, like current density, exercises a marked influence upon the size of the crystals. This may not, however, be the whole explanation of the phenomena, since the deposit seems to be slightly lighter in weight as well as of finer grain. We have made quantitative comparisons of deposits from different concentrations without being able to detect any certain difference in weight.

Aside from the small changes in weight and appearance continued electrolysis is an effective method for purifying a badly contaminated solution. In a series of experiments [70] on a solution contaminated with filter paper, electrolyzing the solution repeatedly, we were able to observe this purifying effect, as the deposit gradually changed from the strongly striated molten appearance at first to a somewhat crystalline and slightly striated stage, and finally to a state of complete freedom from striations and well-defined crystalline deposit. Using solutions that we knew to be slightly impure we have made them give values for the electro-

[70] Described in the second paper of this series by Rosa, Vinal, and McDaniel.

chemical equivalent more nearly consistent with what we believe the correct figure by this preliminary electrolyzing process. Two such samples of $AgNO_3$ were put in Richards voltameters and 8 grams of silver deposited. The cathode liquid was then drawn off and used in several voltameters in a quantitative experiment. Omitting one voltameter, which was obviously abnormal, we have:

TABLE XV

Effect of Electrolysis on Impure Solutions

Original Baker	1.11711	Original Frankfurt	1.11706
Electrolyzed Baker	1.11708	Do	1.11706
Do	1.11708	Electrolyzed Frankfurt	1.11700

4. USE OF FILTER PAPER IN FILTERING

Smith[71] in his description of a standard method of preparing silver nitrate makes the following statement:

> For filtering the hot solution we prefer to use a Hirsh porcelain funnel, the perforated plate of which is covered by two disks of filter paper.

We believed that the electrolyte might be sufficiently contaminated in this way to render the results unreliable, and accordingly tried the following experiment: The electrolyte for one cup of the run of September 17, 1909, was mixed hot and concentrated and then filtered, as described by Smith. Afterwards it was cooled and diluted to 15 per cent and electrolyzed in a Richards voltameter. The excess weight of 1 in 10 000 over the normal Richards, as well as the appearance, shows that the deposit has been affected by the filter paper. To the unaided eye the deposit looks woolly and striated. A magnified sample of it is shown in figure 18.

The conclusions of our work with the Rayleigh voltameter have made it evident, we believe, that for work of high accuracy any voltameter containing filter paper or similar substance is to be avoided, and that in the preparation of silver nitrate care must be exercised to keep it free from contamination by filter paper.

[71] Collected Researches, N. P. L., 4, p. 163.

IV. CONCLUSIONS

In this first paper we have briefly reviewed the work of preceding investigators and have described our own methods of work. We have recorded all of the quantitative measurements up to and including September 22, 1909. This first series of experiments definitely established the following facts:

1. That the filter paper voltameter as ordinarily used, gives a relatively large excess of deposit over the porous pot form.

2. That this excess is due directly to the chemical activity of the filter paper and not to its failure to confine the anode products.

3. That in using two or three thicknesses of the paper the effect is approximately doubled or trebled.

4. That the deposits from relatively pure solutions are crystalline and not striated, while deposits from solutions contaminated with filter paper, linen, or silk are noncrystalline and striated.

5. That it is not necessary that the filter paper should be present in the voltameter at the time of electrolysis to produce its effects, if the solution has been previously in contact with it.

6. That repeated use of the same solution in the filter paper voltameter yields an increasing excess of deposit owing to the increasing contamination of the electrolyte.

7. That a contaminated solution may on the other hand be rendered less impure by electrolysis in the absence of organic material.

8. That anode solutions saved from the porous cup voltameters may be used as the electrolyte in a voltameter without yielding any excess of weight or making the deposit striated.

9. That the appearance of the deposit is a valuable criterion of the purity of the electrolyte.

The next paper of this series will deal at length with the chemical questions involved in the filter paper voltameter and a theory will be given as to why a contaminated electrolyte yields a deposit differing in appearance from the normal crystalline one. Following this will be given the second series of experiments leading up to the work of the International Technical Committee, April 1, 1910. This work was chiefly a comparison of different types of voltameters and a study of the purity of the electrolyte for which some rigid criteria will be given. Finally the observations made

since the committee adjourned will be given. In this the effect of acid and alkali in the electrolyte have been studied and a number of deposits made using the approved types of voltameter with electrolytes of the highest purity for the determination of the electromotive force of the Weston normal cell and the absolute electrochemical equivalent of silver.

WASHINGTON, August 1, 1912.