The Electrochemical Equivalent of Pure Silver—A Value of the Faraday

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January 30, 1980

Oxygen-free high-purity samples were used in a precise determination of the electrochemical equivalent of silver. A comprehensive mass spectrometric analysis for impurities was performed. Our value agrees well with prior measurements of the same quantity at the National Bureau of Standards (NBS) by Craig and coworkers. We find the electrochemical equivalent of pure silver to be 1.1179648 mg C_{nns}^{-1} . Attached to this figure is an uncertainty whose random component (standard deviation of the mean of 8 determinations) is 9.5×10^{-7} mg C^{-1} (0.85 ppm). The root-sum-square of systematic uncertainties of known origin is 1.07×10^{-6} mg C^{-1} (0.96 ppm). The above value for the electrochemical equivalent of silver leads us to calculate the Faraday to be:

 $F = 96486.33 (24) A_{NBS} \cdot s \cdot mol^{-1} (2.5 \text{ ppm}).$

Key words: Coulometry; electrochemical equivalent; electrochemistry; Faraday; fundamental constants; silver.

I. Introduction

The Faraday constant, which has units of coulombs per mole of univalent substance, is the charge, q, in the expression $q = N_A e$, N_A being the Avogadro constant, and e being the elementary charge. The Faraday constant can be found in different ways. Historically, the Faraday constant has been found electrochemically by reacting a substance electrolytically with an assumed 100 percent efficiency. Then, if the equivalent weight of the substance is known, the Faraday constant can be found by measuring the mass of substance reacted and the charge passed during electrolysis:

$$F = \frac{(\text{equivalent weight}) \times (\text{charge})}{(\text{mass})}.$$

Alternatively, the Faraday constant can be found by combining other fundamental physical constants, for example,

$$F = \frac{\gamma'_{p(low)} \cdot M_p}{\mu'_p / \mu_N \cdot K^2}, \qquad (1)$$

where M_p is the proton rest mass in atomic mass units, $\gamma'_p(low)$ is the proton gyromagnetic ratio measured by the

so-called low field method, μ'_p/μ_N is the proton magnetic moment in units of the nuclear magneton, and K is the ratio of the as-maintained ampere in terms of which $\gamma'_p(\text{low})$ is determined to the SI ampere.

Both methods of arriving at the Faraday constant should, of course, agree. In fact, however, the modern electrochemical measurements of the Faraday constant are self-consistent but fail to agree with the constant calculated from eq (1). The situation is summarized by Cohen and Taylor in their 1973 least squares adjustment of the fundamental constants [1].¹ These authors view the statistical evidence as providing an indictment of the electrochemical measurements. Since 1973, a new and novel electrochemical Faraday determination has been made [2]. A recent recomputation [3] of this latest measurement now places it in good agreement with the value recommended in [1] but the estimated errors in the measurement are too large to allow the results to be definitive.

We have undertaken an electrochemical determination of the Faraday constant using the silver dissolution coulometer. This method was pioneered by Craig, et. al. some twenty years ago. It was our hope that, with a few innovations in the method, the statistical scatter in the measurements could be reduced to something approaching 1 ppm. At this

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¹ Figures in brackets indicate literature references at the end of this paper.

level, it was hoped, systematic errors which may be present in electrochemical Faraday determinations would yield to more precise analysis than has hitherto been possible.²

2. Chemical principles

In this study, the method used is the anodic dissolution of silver into a solution of perchloric acid, 20 percent $HClO_4$, which contains silver perchlorate (0.5% by weight). The electrochemical reaction is:

$$Ag(s) \rightarrow Ag^+ + e^-$$
 (2)

where e⁻ represents an electron and s indicates the silver is metallic. The silver perchlorate is present in the solution to reduce to insignificant proportions the already meager spontaneous dissolution of silver into perchloric acid. The work establishing these desirable conditions was done at the National Bureau of Standards (NBS), by Craig et al [4] in preparation for his determination [5] of the Faraday.

In his paper [5], Craig postulated a set of possible reactions which involved the chemical entities Ag⁺, ClO₄, OH⁻, H^+ , H_2O , O_2 , and so forth, which are known to be present in the solutions where the reaction of eq (2) takes place. From thermodynamic arguments he shows that the reactions of the constituents of the solutions either follow eq (2) namely at a potential of -0.799 V with respect to a normal hydrogen electrode, or have reduction potentials of at least 0.4 V lower. Hence, unless the overpotential of the dissolution of silver is high, the contribution from reactions other than the desired reaction is negligible, i.e. less than 0.1 ppm. The arguments, which our experiment demonstrates to be correct, are presented in Craig's paper and need not be repeated here. We shall take the view that if the overpotential of dissolution has measurable effect, the values of the electrochemical equivalent of the samples should vary with current density or dissolution rate. No such variation is found, as will be seen.

The formation of Ag_2O and water from silver and aqueous hydroxyl ion during the reaction:

$$Ag(s) + OH^{-}(aq) \rightarrow 1/2 Ag_2 O + 1/2 H_2 O(1) + e^{-1}$$

is equivalent to the desired reaction, eq 2, since the reaction

$$1/2 \operatorname{Ag}_2 O + \operatorname{HClO}_4 \rightarrow \operatorname{AgClO}_4 + 1/2 \operatorname{H}_2 O$$

occurs spontaneously.

It is quite a different matter for silver oxide which is on, or in, the silver sample. Since the oxide dissolves spontaneously, as it comes to the surface of the silver anode it reacts with perchloric acid. Sixteen parts by weight of oxygen would carry into solution 216 parts of silver, bypassing the reaction of eq (2). Methods for eliminating oxide are described in another section.

The reverse of eq (2) governs the cathodic recovery of that silver which falls away from the anode during dissolution. Details of the recovery are given below.

3. Materials

Perchloric Acid. The perchloric acid used in the coulometer was commercially available "70 percent" reagent grade, which the manufacturer labeled as "distilled in Vycor" and "99.9999 percent pure." The material received no further treatment. It exhibited no detectable attack on silver over the period of an experiment, provided a small amount of silver perchlorate was present.

Silver Oxide: The solution used as supporting electrolyte, in which silver (within experimental error) is insoluble, is a mixture of perchloric acid and silver perchlorate, prepared by adding silver oxide, Ag_2O , to 20 percent by weight perchloric acid solution. The silver oxide was of reagent grade, purchased from a commercial chemical supply house, and was subjected to no further purification. Any solid silver from this material remaining in the perchloric acid-silver perchlorate solution was removed by filtration through solid silver powder on a fine fritted glass funnel before the solution was introduced in the coulometer.

Water: The water used in making up the solutions was what is commonly called "conductivity" grade. The water was distilled in a stainless steel boiler from water which had been passed through an ion-exchange resin for prior removal of ionic impurities. In the boiler water was a small amount of pyrophosphoric acid to hold back ammonia. The steam so generated was passed through a scrubber to remove CO_2 although no effort was made to guard the water against reentry of CO_2 after cooling. The water was condensed, kept in tin-lined storage tanks and fed to a spigot in tin-lined pipe. The result was a water which exhibited a resistivity of $1.2 M \Omega$ -cm at air equilibrium. No attempt was made to remove equilibrium carbon dioxide.

Silver powder: As mentioned above, the perchloric-acid silver perchorate solution was filtered through silver powder on fritted glass. During the eight runs of the final experiment we used a silver powder, advertised as "five nines" pure, which was obtained from a manufacturer of high-purity metals. This was a precaution. However, during most of the preliminary practice runs we used a silver powder obtained from a chemical supply house. No significant differences could be ascribed to this substitution of the high purity material.

² Throughout this paper, random errors quoted refer to one standard deviation of the calculated mean of a set of data. Systematic errors are estimated at the same level of confidence as random errors.

Silver sample: The silver samples were part of a large lot purchased by the National Bureau of Standards for certification and issue as a Standard Reference Material. From this lot, most of which was issued as a high temperature vapor-pressure standard, were selected a few rods which were characterized by residual resistivity ratio, and set aside for research purposes at NBS. The samples furnished to us by the Office of Standard Reference Materials of NBS were from Rod 55 of the lot used for Standard Reference Material 748 Silver Vapor Pressure Standard. Rod 55 was divided into 45 cm lengths labeled by letter sequentially in the direction of the draw. These lengths were cut into segments 50 mm long numbered again in the direction of the draw. The pieces furnished to us were labeled thus 55: A-7, B-7, D-7, E-7, F-7, G-Y2, G-Y3. The last two pieces were near the end of section G.

The preparation of the silver sample by the manufacturer is proprietary, but NBS was informed by the manufacturer that high purity silver was subjected to dissolution and electrolysis, and was then melted in vacuum and formed. The resulting rod is polycrystalline. No further purification was attempted other than an effort to remove oxygen by heating in a high vacuum, a process described elsewhere in the paper.

4. Apparatus

When one electrolyzes pure silver anodically into a solution of perchloric acid, small quantities of finely divided solid silver fall away from the anode. In the experiments of Craig [4] this finely divided material was recovered, filtered and weighed. It was counted as part of the final weight of the anode. The weighing inevitably required the collection and the transfer of this anodic residue to a filter before the final weighing. There exists the possibility of loss of material during transfer. Furthermore the large scatter induced by the taring of a sintered-glass filter crucible would greatly add to the random experimental error.

To secure an accurate value for the mass of the residue, it was decided that the residue must never leave the anode compartment of the coulometer and must be treated and analyzed in the compartment itself. The method fixed upon was the filtration of all anodic electrolyte solution through a sintered glass filter embedded in the anode compartment wall, the dissolution of the finely divided solid silver into nitric acid, the evaporation of the nitric acid to dryness leaving silver nitrate and finally the analysis for silver by controlled potential coulometry. The charge consumed in the last operation was added to the total anodic charge in the constant-current part of the experiment in calculating the electrochemical equivalent of the silver sample. A detailed account of this procedure is presented in reference [6].

To effect the retention of the residue in the anode compartment for direct potentiostatic analysis within the compartment, the coulometer was fashioned as shown in figure 1. The weighed silver sample was attached to an adjustable fixture which set the immersion depth of the sample in the solution of perchloric acid-silver perchlorate. The anode compartment consisted of a beaker in the side of which was a fine fritted glass disc leading to a side-arm which curved upward to one part of a spherical joint. The spherical joint was set at about the same height over the bottom of the beaker as the beaker lip, as shown in figure 1, to ensure no loss of liquid from a full beaker. The second part of the spherical joint was attached to a siphon with stopcock-not shown-on top for filling which had, at the far end, a medium-fritted glass disk. The glass frit was placed at this point to prevent solid silver, which might bear an electrical charge, from migrating from the cathode compartment. The first siphon led to a large beaker which was connected to another large beaker, the cathode compartment, by a second siphon. The cathode compartment contained a large platinum mesh electrode, with an area of about 90 cm². The resistance of this cell, cathode to anode, was about 20Ω .

Several precautions were taken to minimize leakage resistance and to protect the coulometer from contamination by air-borne pollutants. The whole assembly reposed upon a sheet of 6 mm-thick teflon which in turn rested on a 12 mm sheet of polymethyl methacrylate. Passing through the teflon and anchored into the methacrylate were rods (12 mm diameter), also of polymethyl methacrylate. One rod of aluminum was also passed through the teflon sheet and was anchored into the methacrylate. The plastic rods were posts for attachments of metal claw clamps which supported the siphons. Metal was substituted for plastic in the case of the post which supported the silver anode and its mechanism of adjustment of immersion. This last measure was required to lend rigidity to the anode holder and anode. Vibration of these parts affected the current control. The resistance of the supporting parts, from the metal rod to any other part of the teflon or methacrylate sheet or rods, with acid solution wiped onto the teflon was of the order $10^{13} \Omega$.

To the metal post was attached a new metal clamp of the adjustable claw type with plastic covered fingers. The clamp held the anode immersion assembly, figure 2. The assembly consisted of a glass tube, 5 mm diameter, through the length of which passed a brass rod, 3 mm in diameter, threaded at one end. The tube was held upright by the claw clamp, and a nylon nut on the end of the adjustable brass rod served to set the height of the rod. Soldered to the lower unthreaded end of the rod was a piece of brass 20 by 75 mm. The brass rod was soldered about 25 mm from the end of this last piece. This 20×75 mm piece was large enough to receive the clamps from the positive lead and from the sample. The motion of this brass assembly was kept linear (ver-



FIGURE 1 The cell of the coulometer. As the sample dissovles into the anolyte, fragments of the sample fall to the floor of the anode compartment. The fragments never leave the anode compartment during completion of the experiment. D₂ is a high-impedance voltmeter, normally open, used to monitor the difference in voltage between the anode and a silver wire in equilibrium with the electrolyte.

tically) by two guides of copper wire attached to a teflon block which was in turn attached to the glass tube.

The silver sample had a tightly twisted silver wire on one end which in turn was held by small battery clips. Between the battery clip and the silver sample was a small piece of high-purity sheet silver. The purpose of the sheet silver was to protect the silver sample from the gripping force and contamination of the cadmium-plated jaws of the clip. The silver sheet was weighed in every experiment in order to observe whatever extraneous electrolyte reactions might occur at the contact of the silver sample and the jaws of the clip. The average change in weight of the silver sheet after a Faraday run was $+1.5 \mu g$ with a standard deviation of 2.4 μ g. The cadmium-plated clip was attached back-to-back to another such clip which hung directly from the 20 imes 70 mm brass piece. The positive lead from the current control was attached through a similar clip to the 20×70 mm plate of the immersion adjuster. It was anticipated that the silver anode would be lowered further into the electrolyte during the course of a measurement. This procedure proved to be unnecessary and was never attempted.

Also suspended in the anode compartment was a curved glass tube filled with anolyte in which a high purity silver wire was immersed. This wire was connected to the silver anode holder in series through a high impedance $(10^{12} \Omega)$ digital voltmeter, D₂, figure 1, and a switch, normally open. The meter reading permitted the monitoring of the overvoltage of the anode above its quiescent condition during the course of the experiment.



FIGURE 2 Device for controlling depth of immersion of the silver anode in the analyte solution.



FIGURE 3 General schematic diagram of the electrical and timing circuit. As current is switched from a dummy load, R_d , whose resistance matched that of the coulometer, the timer is switched on simultaneously.

The whole glass assembly, the supporting rods, teflon, and methacrylate sheets were housed in a methacrylate box with hinged doors to allow loading of the coulometer and adjustment of the parts during the determination.

The electrical connections required for the dissolution of the silver anode at constant current are shown in figure 3. The current controller, a Tinsley type 5390,³ provided lownoise, low-drift, direct current. The current was ripple-free. Before beginning the experiment, constant current of the desired level was maintained in a substitute load, R_d , whose impedance was matched closely to the impedance of the silver coulometer. The precise value of the current was known by comparing the voltage drop across a standard resistor (R_s) with the voltage of a standard unsaturated cell (S.C.). Slight adjustments in the controller settings were made until the difference in voltage as read on D₁ was zero $(\pm 0.1 \ \mu\text{V})$. D₁ is a Leeds and Northrup 9829-D high-impedance (10 M Ω) linear amplifier which was used as a nulldetector. A reversing switch was used to eliminate the effect of thermal emf's.

At the beginning of the experiment, mecury-wetted relays simultaneously transferred current from the substitute resistor to the coulometer and started an electronic timer. The relays were de-activated to end the dissolution.

During the experiment, the current was continuously monitored by D_1 . The high impedance and small voltage

difference across the inputs of D_1 allowed continuous monitoring with negligible (<0.1 ppm) uncertainty.

Since gassing at the platinum cathode of the coulometer causes fluctuations in the current, this condition must be avoided. Gassing occurs when the concentration of Ag^+ at the cathode becomes so depleted that H^+ must undergo reduction in order to maintain a constant current. As a remedy, a small amount of Ag_2O was added to the cathode compartment at intervals of about $\frac{1}{2}$ h. The oxide dissolved, keeping the catholyte sufficiently rich in silver ion.

The current, I, maintained in the coulometer, is simply the voltage, V, of the standard cell divided by the resistance, R_s , of the standard resistor. If current flows in the coulometer for an interval of time, t, then the total charge (Q) passed during silver dissolution is

$$Q = (V/R_s)t. \tag{3}$$

Equation (3) only holds provided transient effects may be neglected. The following examination shows that this neglect is justified.

An oscilloscope was used to demonstrate that the timer and coulometer are activated and deactivated simultaneously. The minimum duration of any of the dissolution experiments reported in this paper is 13×10^3 s. Hence to achieve an accuracy of 0.1 ppm in Q, the switching must be simultaneous to 1 ms. This rather modest criterion was easily met.

Switching transients in the current controller must also be negligible. Experiment has shown that matching the

³ Brand names are used throughout this paper only for purposes of identification. Such use implies neither endorsement by the National Bureau of Standards nor assurance that the equipment is the best available.

impedance of the substitute resistor to that of the coulometer will insure a negligible transient when the current is switched to the coulometer. As the impedance mismatch is made worse, the transient increases. Switching the current back to the substitute resistor does not produce any measurable transient in the coulometer. In the worst case encountered in these experiments, the effect of transients as determined by oscilloscope measurements is approximately 0.1 ppm in Q.

There is one last transient effect which deserves mention. It is assumed in eq (3) that all current which flows is "Faradaic" although in reality a small portion is not. A small fraction of the total current goes into charging a double layer capacitance at the surface of the anode. The rest of the current is due to transport of ions across that capacitance. The capacity of the double layer is thought to be 100 μ F/cm² and is charged within the first millisecond of current flow [7]. The surface area of our anodes was 10 cm². Oscilloscope measurements show that our anode voltage jumped by 8 mV within the first millisecond as compared to the voltage of the quiescent silver electrode. Although most of this voltage rise is probably ohmic and not due to charging of the double layer, we will assume a worst case. Hence the amount of current which goes to charging the double layer is 10 μ C. In the experiments we have performed, this amounts to less than 0.01 ppm in Q.

With transient corrections to eq (3) negligible, it only remains to explain how V, R and t were measured.

A standard unsaturated cell (S.C. mentioned above) was used to monitor current constancy during the course of silver dissolution. This unsaturated cell was maintained in a thermostated enclosure with four standard saturated cells. A cable was installed from the standard cells to the NBS standard cell laboratory. By means of this cable, our saturated cells were compared at weekly intervals with standard cells whose emfs were known in terms of the NBS as-maintained unit of voltage (defined in terms of the ac Josephson effect) to 0.1 ppm. It was, therefore, never necessary to move the cell enclosure in order to calibrate the standard cells.

We determined the emf of our unsaturated cell by means of the following procedure. A voltage divider was constructed in such a way that an adjustable emf of approximately $\sim 900 \ \mu$ V would be produced. This is the approximate difference in emf between saturated and unsaturated standard cells. The divider consisted of precision resistors, known to ± 0.01 percent, and a mercury cell. The resistors were calibrated before and after the series of Faraday measurements reported herein. Prior to a measurement, the emf of the mercury cell was measured to better than 0.01 percent, using a calibrated Leeds and Northrup type K-5 potentiometer.

By means of appropriate switches, the emf of the unsaturated cell could be compared to that of a saturated cell plus the divider output voltage. The variable resistor was adjusted until the emfs were equal as determined by the high-impedance null detector previously described. Knowledge of the divider output voltage and saturated cell emf permitted calibration of the unsaturated cell. Thermal emfs in the divider were measured under typical operating conditions and found to be negligible, i.e. less than 0.1 μ V.

Immediately preceding the start of a Faraday determination, the unsaturated standard cell was compared with each saturated cell using the procedure outlined above. The measurements were repeated immediately after the dissolution of the silver anode was stopped. In this way, the unsaturated cell emf was known to within 0.1 ppm during the experiment. No significant change in unsaturated cell emf from beginning to end of a Faraday determination was ever detected (fig. 4).



FIGURE 4 Diagram showing drift of working cells with time. The open circles indicate cell calibration immediately prior to a Faraday run while the companion crosses show the calibration just after the run.

The standard resistor, the IR drop of which is matched to the emf of the working standard cell, was constructed in this laboratory following suggestions of R. D. Cutkosky. The resistor itself was made from two 10-ohm Rosa coils of manganin wire wound on brass cylinders closed at one end (see fig. 5). The closure at one end of each cylinder provided the support for the coils on threaded steel rods which ran axially through the resistor. The upper end of the rod went into a teflon sheet 1 cm in thickness. The coils thus hung



FIGURE 5 Resistance apparatus used in experiment. No electrical leads or terminals are shown. The apparatus is suspended from two robust current terminals mounted on the upper teflon sheet.

from the teflon sheet. The teflon sheet was attached by another steel rod through its center to an upper teflon sheet 1 cm in thickness, and connections from the coils were brought up through both sheets of teflon with ample looping. The upper piece of teflon bore all the contacts and suspensions. The purpose of this type of construction was to avoid all mechanical stress on the lower teflon sheet, thereby avoiding strains in connnecting wires and resistors.

The two 10 Ω coils could be used singly or connected in series or in parallel. Of the three nominal values thus afforded, the 5- and 10- Ω configurations were used in this experiment (fig. 6). The resistor was maintained and calibrated in its own thermostated oil bath. The calibrations were made at the power levels actually used in the experiment and in terms of the NBS as-maintained unit of resistance.

The time, t of an experiment was measured by switching the NBS 10 kHz ac mains into a General Radio 1192B counter simultaneously with the switching of current to the coulometer.



FIGURE (6a). Schematic of resistor apparatus showing electrical connections to the Rosa resistors. The circles represent copper pads. The three pads connected directly to the Rosa resistors are mounted on the bottom of the lower teflon sheet (fig. 5). The remaining pads as well as the terminals to which the current leads are connected are all attached to the top of the upper teflon sheet.

(6b). 5- Ω configuration. The added resistance network is rigidly mounted on a teflon sheet. The 50- Ω resistors are stable and matched to ±0.01 percent. The dashed lines indicate copper links. The links make contact with the copper pads through a mercury amalgam, indicated by a dot in the drawings.

(6c). 10- Ω configuration.

(6d). 20- Ω configuration (not used in this work).

5. Procedure

5.1 General

With the description of the coulometer as background it becomes possible to give a general description of the whole experiment or, rather, the history of a sample of silver through a whole determination. Every step in the process will be mentioned in this description, but details of each step will be treated more searchingly in later sections of this paper.

The sample, a rod of high purity silver, about 50 mm long and 6 mm in diameter, is bored along a diameter near one end with a new 2 mm steel drill bit to accommodate the suspending silver wire. After the hole is drilled, the sample is given a strong etch with nitric acid, treated with ammonium hydroxide, and then rinsed with conductivity water. It is handled during these operations with teflon-covered forceps. A temporary silver loop of high purity wire, also etched with nitric acid, is passed through the hole and the sample is hung by the wire from a small pyrex stand and placed in an oven to dry for about 300 s at 100 °C.

Thus dried, the sample is placed in a crystalline quartz tube which had been carefully cleaned with nitric acid. The tube is then connected to a pumping station and is pumped overnight to a good vacuum (10⁻⁵Pa). The next day, the pumps still going, the quartz tube is inserted into a thermally controlled muffle furnace. The temperature is raised gradually (through several hours) to 955 °C for about $\frac{1}{2}$ h and then is gradually lowered to room temperature, the pumps still on. The sample is then furnished with a hook twisted from high purity silver wire, the manipulations being carried out with teflon covered forceps. The sample is hung on a glass hook stand inside the microbalance case to be weighed. The weighing is performed by the method of double substitution against a set of single-piece, stainless steel, standard weights. Corrections for the buoyancy of the air are applied. The sample is still held in the forceps and with another forceps a weighed piece of high purity silver foil is folded over the hook. The battery clamps of the coulometer are applied to the silver foil, holding the sample securely. The silver sample is now mounted in the anode compartment of the coulometer and constant current is passed through the coulometer with the sample as anode. A timer is switched on and off simultaneously with the constant current. At the end of a determined time the current and the timer are switched off. The inevitable small quantity of finely divided silver residue is in the anode compartment. The sample clip is carefully disconnected and the sample is washed down, the washings falling into the anode compartment. The tube which houses the "quiescent electrode" is similarly washed down into the anode compartment. The sample is then carefully disconnected from the foil covering the clips and is hung on its glass stand to dry in an oven at 100 °C for about 600 s. It is then removed to the balance case for weighing. The silver foil is also washed in distilled water and readied for weighing.

In the meantime, the anode compartment and first siphon are carefully lifted out and an appliance leading to a water aspirator is fitted against the frit at the end of the first siphon. The anode solution is drawn from the anode compartment through the frit, through the first siphon and exhausted with the waste water. Once the anode compartment is merely moist, it becomes an easy matter to empty the first siphon and the sidearm of perchloric acid solution. The anode compartment is then separated at the spherical joint.

The anode compartment now contains the finely divided silver and a small residue of perchloric acid solution. The perchloric acid solution must be removed because it contains traces of silver ion. It is essential at this point that the walls of the anode compartment be washed most carefully with conductivity water many times, the wash being drawn off through the frit. Special care is also applied to washing of the frit and side arm, because any silver ion anywhere in the vessel will be detected in the ensuing analysis for silver.

Once the anode compartment is cleared of perchloric acid and silver ion, the next step is the conversion of the finely divided silver into ionic form so that the amount of silver residue may be determined by electrolysis. The silver residue is dissolved in hot dilute nitric acid. Acid is added both to the anode compartment and to the side-arm. The acid is evaporated off by heating the compartment gently in a water bath. If the evaporation and drying have been gentle, the residue in the compartment is silver nitrate. After addition of supporting electrolyte the amount of charge required to remove cathodically at constant potential all the silver is then determined. The charge at constant potential is added to that at constant current. A second weighing of the silver anode yields total loss of mass of the anode. From the total charge passed and the weight loss, the electrochemical equivalent of the anode silver sample can then be computed immediately.

5.2 Methods of Weighing

The mass of the silver anodes used in the Faraday experiment was determined using a single-pan microbalance. The mass of the anode was adjusted prior to each experiment so that it was nearly equal to an integral number of grams. The total electrical charge passed during an experiment was chosen so that an integral number of grams was dissolved. As a result, when the anode mass was compared with an appropriate selection of single-piece weights, the discrepancies were always small (<500 μ g). Our single-piece weights were calibrated in terms of the national standards by the NBS calibration service before and after the series of experiments reported here. We also had the opportunity to check our weights against platinum weights which had been calibrated by the Bureau International des Poids et Mesures (BIPM) and we found no detectable difference in the two methods of assigning our mass.

With these considerations in mind, it is useful to derive the formula used to determine the mass loss from a silver anode during dissolution.

Let

 $M_{A_{g,i(f)}}$ = initial (final) mass of silver.

- $M_{M,i(f)}$ = initial (final) mass of single-piece weights.
- $M_{A_{g,i(f)}}^{\star}$ = initial (final) weight in air (divided by g, the acceleration of gravity at the balance) of silver as determined from the microbalance.
- $M_{M,i(f)}^{\star}$ = initial (final) weight in air (divided by g) of single-piece weights as determined from the microbalance.
 - D_M = density of single-piece weights at room temperature = 7.89 g/cm³
 - D_{A_B} = density of silver at room temperature = 10.50 g/cm^3 .
 - $\varrho_{i(f)}$ =initial (final) density of air at the time of the weighings. ($\sim 10^{-3}$ g/cm³).

Because the difference in mass between the silver anode and the appropriate selection of single-piece weights is always small, the following relations hold to better than 0.1 ppm.

$$M_{A_{g,i(f)}}^{\star} - M_{M,i(f)}^{\star} = M_{A_{g,i(f)}} \left(1 - \frac{\rho_{i(f)}}{D_{A_g}}\right) - M_{M,i(f)} \left(1 - \frac{\rho_{i(f)}}{D_M}\right)$$
$$m_s \equiv M_{A_{g,i}} - M_{A_{g,f}}$$

$$= [M_{A_{g,i}}^{*} - M_{M,i}^{*} + M_{M,i} (1 - \frac{\rho_{i}}{D_{M}})](1 - \frac{\rho_{i}}{D_{A_{g}}})^{-1} - [M_{A_{g,f}}^{*} - M_{M,f}^{*} + M_{M,f} (1 - \frac{\rho_{f}}{D_{M}})](1 - \frac{\rho_{f}}{D_{A_{g}}})^{-1}.$$

The measured quantity $M^*_{A_{R,i}(f)} - M^*_{M,i(f)}$ was always small enough (<500 μ g) to permit the following expansion without introduction of significant error:

$$m_{s} = (M_{M,i} - M_{M,j}) + (M^{\bullet}_{A_{g,i}} - M^{\bullet}_{M,i}) -$$
(4)

$$(M^{\bullet}_{A_{\mathcal{B},f}} - M^{\bullet}_{\mathcal{M},f})$$

$$+ (\rho_{i}M_{M,i} - \rho_{f}M_{M,j}) (1/D_{A_{R}} - 1/D_{M}) + (M^{*}_{A_{R,i}} - M^{*}_{M,i}) \frac{\rho_{i}}{D_{A_{R}}} - (M^{*}_{A_{R,f}} - M^{*}_{M,f}) \frac{\rho_{f}}{D_{A_{R}}} - (\rho_{i}^{2}M_{M,i} - \rho_{f}^{2}M_{M,f}) (\frac{1}{D_{A_{R}}D_{M}} + \frac{1}{D^{2}_{A_{R}}})$$

Equation (4) was used to arrive at the loss in anode mass. The term $(M_{M,i} - M_{M,f})$ is simply the difference in mass of the selection of single-piece weights used in the initial and final weighings. For example, suppose the silver anode originally weighed 18 g. Then $M_{M,i}$ would be the sum of the 10 g, 5 g and 3 g single-piece weights. If 5 g of silver were dissolved from the anode then $M_{M,f}$ would be the sum of only the 10 g and 3 g weights. Hence $M_{M,i} - M_{M,f}$ would be the mass of our 5 g weight. This number and its uncertainty were supplied to us by the Mass and Volume Section of the National Bureau of Standards. In all the Faraday measurements reported here, either 5 g or 3 g were dissolved.

The terms $(M^*_{A_{g,i}} - M^*_{M,i})$ and $(M^*_{A_{g,f}} - M^*_{M,f})$ are the differences in mass between the silver anode and standard weights as determined from reading the microbalance. To measure $(M^*_{A_{g,i(f)}} - M^*_{M,i(f)})$, the procedure known as "single-pan substitution" was employed [8]. By this method, a single measurement of $(M^*_{A_{g,i}(f)} - M^*_{M,i(f)})$ requires four weighings. We repeated each such series four times and averaged the results in order to arrive at each measurement of $(M^*_{A_{g,i}(f)} - M^*_{M,i(f)})$. The significant figures of this difference are read on the optical scale of the microbalance, which is calibrated by means of a known sensitivity weight, the nominal mass of which is 5 mg. The remaining terms of eq (4) include the necessary correction for the buoyancy of air. The density of air was calculated using an algorithm [9] which requires temperature, relative humidity and barometric pressure as measured parameters.

Temperature was read with a calibrated mercury thermometer housed in the case of the microbalance.

Barometric pressure was determined using a calibrated Fortin-type mercury barometer with temperature corrections made according to the Smithsonian Tables [10]. The density of mercury at 0 °C was taken as 13.5951 g/cm³ [10]. The acceleration of gravity at our laboratory is known to be 980.102 cm/s² based on a survey of the NBS, Gaithersburg campus [11]. The barometer was located in the same room as the balance.

Relative humidity was measured using a wet and dry bulb psychrometer located in the same room as the balance. Published tables [10] were used to convert to relative humidity.

The standard algorithm used to compute the density of air has been confirmed experimentally to the required accuracy in a separate study [12].

5.3. Recovery of residue

In the course of the Faraday experiment, some of the silver anode is lost not thorugh electrolytic dissolution but rather by mechanical separation. The silver residue, referred to as "anode sludge" by Criag et. al, appears at the bottom of the anode beaker as a finely-divided powder. This metallic silver—up to 2 mg typically—must be accounted for in order to arrive at an accurate value of the Faraday.

Craig's procedure for recovering the residue was to collect it on a previously tared sintered-glass filter. The filter was then reweighed and the difference in weights was taken to be the weight of the ''anode sludge.'' The weaknesses in this method of recovery of the residue are: (1) two precise weighings of a sintered glass filter are required and (2) silver powder must be efficiently transferred from one vessel, the anode beaker, to another vessel, the filter. It is a tribute to Craig's deftness as an experimenter that despite the pitfalls of this recovery procedure his experimental scatter due to all causes was only 19 ppm [5]. With the hope of decreasing the experimental scatter we sought an improved residue-recovery procedure which would avoid the two difficulties raised above.

Our solution was to convert the silver residue into silver ions dissolved in electrolyte. The ionic silver was then plated on a platinum cathode held at constant voltage with respect to a reference electrode. The amount of *charge* passed during this electrolysis rather than the *mass* of the residue, becomes the correction to the determination of the electrochemical equivalent of the silver sample (E_{A_S} , see eq (6) below).

Our method thus answers the first objection raised above. By performing all the residue recovery manipulations in the same beaker which serves as the anode compartment during silver dissolution, the second objection is also overcome. The reader is directed to reference [6] for further details of this method.

A difficulty of our method of silver analysis is that one never recovers the silver with perfect current efficiency. It is common, for instance, for too much charge to be measured in plating a known amount of silver. The difference between the measured charge and the charge one would measure at perfect current efficiency is referred to as the "background." The background charge corresponds to a mass of silver of the order of 10 μ g and may be influenced by such things as impurities in the supporting electrolyte, size of the silver sample and other experimental details [6].

In our experiments, the background was determined experimentally by means of a "dummy" anode beaker subjected to all the manipulations of the actual beaker used. At the end of the silver dissolution phase of the Faraday experiment, both anode beakers were emptied through their side arms and rinsed. Nitric acid was added to the residue-containing beaker. At the same time, a measured aliquot of silver ion in nitric acid was added to the dummy and both beakers were placed in the same water bath. The result of the aliquot titration, when combined with that of the residue titration and the results from the preceding silver dissolution experiment, determines the electrochemical equivalent of the silver sample, E'_{Ag} . That this is so can be shown as follows.

Let

- $m_s = \text{mass}$ loss of silver anode during dissolution (eq (4))
- Q =total charge passed during anode dissolution (eq (3))
- $M'_{A_{B}} =$ mass of anode residue
 - Q' = total measured charge during titration of residue (i.e. includes any background errors)
 - B = Background charge error inherent in coulometric titration method
- $M_D =$ Mass of silver in dummy aliquot
- Q'' = total measured charge during aliquot titration (including background)

(The quantity *B* was found to be slightly dependent on residue size [6]. For this reason, M_D was made approximately equal to M'_{A_B} during analyses).

The three different measurements provide us with the following three relations:

$$E'_{A_{R}} = \frac{m_{s} - M}{Q} A_{R}$$
$$M'_{A_{R}} = (Q' - B) E'_{A_{R}}$$
$$M_{D} = (Q'' - B) E'_{A_{R}}$$

These can be combined to yield the resulting important equation:

$$E'_{A_{g}} = \frac{m_{s} - M_{D}}{Q + Q' - Q''} \tag{6}$$

This equation gives E'_{A_R} in terms of precisely measurable quantities. In table 1 are listed E'_{A_R} for the eight determinations on seven samples. The table also shows the sample masses, the current used the duration of each experiment, M_D , B, Q', Q'' and the maximum voltage the anode reached with respect to a quiescent silver wire in the same electrolyte. The large negative value of B for the last sample is due to a change in the details of the coulometric titration.

We should point out that a score of preliminary measurements were carried out over a period of months in order to perfect the techniques reported above. The reported experiments were the final eight, made with anodes identified prior to the preliminary measurements as the best available.

6. Impurities in the silver sample

Of all elemental impurities which may be present in silver anodes, oxygen is the most worrisome to the Faraday experiment. The reasons are not difficult to comprehend. Silver readily oxidizes in air, and oxygen is known to diffuse through a silver matrix. Furthermore, the reaction of silver oxide dissolved by perchloric acid $(Ag_2O + HClO_4 \rightarrow$ $AgClO_4 + 1/2 H_2)$, if mistaken for the expected reaction Ag $\rightarrow Ag^+ + e^-$, could cause a serious error in the Faraday experiment. An inpurity of only 1 ppm of oxygen, if in the form of Ag_2O , would produce an error of -14.6 ppm in the Faraday.⁴ To achieve an accuracy of 1 ppm in the Faraday therefore requires analysis of oxygen to better than 0.1 ppm by weight. This level is too small for direct measurement but, fortunately, indirect methods exist for insuring that silver is oxygen free.

Over a decade ago, work by Eichenauer and Muller [13] (confirmed by Verfurth and Rapp [14]) established the following relations for the solubility and diffusion rate of oxygen in silver: in oxygen at atmospheric pressure, the solubility, L, is

$$L = 6.69 \times 10^{-2} \exp(-11860/RT) \frac{\text{atoms of oxygen.}}{\text{total atoms}}$$

The solubility was found to obey the Sieverts square-root law [15]. The diffusion coefficient, $D = 3.66 \times 10^{-3} \exp (-11000/RT) \operatorname{cm}^2/\mathrm{s}$.

Our silver anodes were annealed in a quartz tube at a pressure of 10^{-5} Pa. The tube was inserted in a muffle furnace and was evacuated by a liquid-nitrogen-trapped oil

⁴ The presence of oxygen in the silver samples can only *lower* the value of the measured Faraday constant from its actual value.

diffusion pump. The temperature in the furnace was initially raised to 955 °C, slightly below the melting temperature of silver. At this temperature oxygen diffuses rapidly in silver and its solubility is extremely high. At the lowest pumping pressures available to us, however, the equilibrium solubility of oxygen in the silver was 7.5×10^{-9} moles of O_2 /mole of silver. This was sufficiently low to have a negligible effect on our Faraday measurement. Still under vacuum, the temperature was lowered over a period of hours to room temperature after which the anode was prepared for use.

As a check of our assumptions, we decided to test the Eichenauer and Muller data. We therefore annealed a silver anode exposed to ambient air at a temperature of 490 °C. This temperature was maintained for two days. Under these conditions, the Eichenauer and Muller data imply that, using the above-treated silver, a correction of 25 ppm to a Faraday measurement would be necessary. When the Faraday experiment was performed using this silver anode, the result was found to differ by 15 ppm from the mean of the values obtained using oxygen free anodes. Because the experiment was performed only once, it is prudent only to conclude that agreement with a prediction based on the data of Eichenauer and Muller is satisfactory.

7. Results— Corrections to electrochemical equivalent. Calculation of the Faraday constant.

The electrochemical equivalent, $E_{A_{g}}$, of the sample was calculated from eqs (6) and (3). The results of the calculation are listed in table 1 along with the respective experimentally observed quantities. The low random scatter of these results reveals a high uniformity among the samples.

Sample ^e	m,(g)	<i>I(A</i>)	<i>t(s)</i>	<i>М_D(µg)</i>	<i>B</i> (mC)	Q' (mC)	<i>Q</i> ″(mC)	$E'_{Ag}(\mathrm{mg}\mathrm{C}^{-1})$	Max. Overvoltage (mV)
A -7	4.9998304	0.20383818	21,939.2099	269.2	+5.2	232.2	245.8	1.1179611	121
B-7	2.9997288	.20383813	13,162.11876	260.9	+13.2	258.6	246.6	1.1179667	143
B-7	3.0002905	.10192240	26,326.1190	273.2	+6.4	498.4	250.8	1.1179624	97
D-7	4.9999965	.10192237	43,873.0350	996.9	-3.3	786.4	888.4	1.1179588	93
E-7	3.0001070	.20383782	13,164.3419	241.3	+10.2	169.2	226.0	1.1179621	116
F-7	2.9998111	.10192226	26,325.1964	264.9	+ 7.9	166.1	244.8	1.1179635	138
G-Y2	4.9995848	.20385086	21,935.2051	505.9	+9.3	534.5	461.8	1.1179662	145
G-Y3	5.0006969	.10192882	43,874.0443	1132.0	-7.8	1029.9	1020.3	1.1179609	107
							Avg.:	1.1179627	
							S.D.:	0.00000268	(2.40 ppm)
							SDM:	0.0000095	(0.85 ppm)

TABLE 1. Electrochemical Equivalent of Silver Sample and Experimental Parameters.

* The constant current phase of the measurements here reported took place on the following days of March, 1975: 4th, 6th, 11th, 13th, 18th, 20th, 24th, and 25th.

The electrochemical equivalent of silver, E_{Ag} , is m_{Ag}/q_{Ag} , where m_{Ag} is the amount of pure silver dissolved with the passage of q_{Ag} coulombs. If m_s is the mass of sample dissolved with the passage of q_s coulombs (where $q_s = Q + Q' - B$) in electrolyzing the sample, and if m_i is the mass of the impurity, *i*, in the sample and q_i is the charge required to electrolyze the impurity, *i*, we have

$$E_{A_g} = \frac{m_{A_g}}{q_{A_g}} = \frac{m_s - \Sigma m_i}{q_s - \Sigma q_i} \,. \tag{7}$$

 $E'_{A_B} = m_s/q_s$ is the electrochemical equivalent of the sample. If we allow v_i to be the oxidation number of the impurity, *i*, and assume that the product of the Faraday constant and the electrochemical equivalent of the silver sample approximates the atomic weight of silver, A_r (Ag), we may then expand the right hand side of eq (7) and obtain

$$E_{A_g} = E'_{A_g} \left[1 + \Sigma \frac{m_i}{m_s} \left(\frac{A_r(Ag)}{A_r(i)} \nu_i - 1\right) \dots\right]$$
(8)

to first order. Here $A_{i}(i)$ is the atomic weight of the impurity *i*. Use of higher order terms in eq (8) is unjustified because the impurities are known to occur only at trace levels.

The acid in the coulometer was so concentrated and the concentration of ions formed from any metallic impurities was so tenuous (10^{-6} molar) that in the calculation of the electrochemical equivalent of pure silver the electrochemical oxidation was assumed to be the maximum permissible

under conditions imposed by the oxidation-reduction potentials of the ions [16] and by the actual potential of the silver electrode.

Modern techniques of mass spectrometric analysis allowed us to assess, with detail unprecedented for an electrochemical determination of the Faraday, the correction for the impurities in the sample. The analysis for impurities, except for the oxygen test described above, was performed entirely by mass spectrometry. Several distinct classes of measurement were undertaken. The varying methods of determination dictate special handling of the statistical interpretation of the experiments.

1. A broad survey of all elements by spark-source methods was performed on our samples. The results appear in table 2. This survey was compared to a similar more detailed analysis of silver samples from the same standardsample lot. The report of analysis stated that no significant differences were found between our sample and the general samples of the lot. In the spark-source method the values are not based upon an internal standard. An assessment of the accuracy of such surveys performed in the mass spectrometric laboratories of the Center for Analytical Chemistry, NBS, is provided by an unpublished report by Paulsen [17].

In a study designed to test the validity of a number of assumptions and theories claimed to predict the mass-spectrometric sensitivity factors for various elements, Paulsen

Spark-source n	nass spectrometric analysis	Isotope-dilution Mass Spectrometry			
Element	Wt. fraction of Sample × 10 ⁶	Element	Wt. Fraction of Sample $\times 10^6$	Element	Wt. fraction of Sample $\times 10^6$
Li	0.0005	Pb	0.05	Fe	0.164 ^c
В	.002	Tl	.03		
С	.05	Nd	.007		
Ν	.01	Ba	.007		
F	.04	Te	.009		
Si	.4 (0.85) ^a	Sn	.02		
S	.1	Cd	.015		
Cl	.1	Pd	.01		
Sc	.04	Sr	.005		
V	.08	Se	.004		
As	.08	Ga	.01		
Rb	.05	Zn	.18		
Pt	.3	Cu	.08		
		Ni	.04		
Au	.3 ^b	Cr	.02		
		Ti	.02		
Al	.08°	Cu	.07		
Na	.2°	K	.18		
		Mg	.02		
orrection to $E'_{A_8} 3.4 \times 10^{-7} \text{ mg C}^{-1}$ (0.29 ppm)			$1.0 \times 10^{-6} \text{ mg C}^{-1} (0.89 \text{ ppm})$	8.8	$3 \times 10^{-7} \text{ mg C}^{-1}$ (0.79 ppm)

TABLE 2. Results of Analysis for Impurities in Silver Samples.

 $^{\circ}\,$ Figure in parentheses represents Si content as ${\rm SiO}_2,$ the value and form assumed in these calculations

^b Spark source at Ames Laboratory

° Separate analysis

accumulated data on 33 elements in 12 NBS Standard Reference Material matrices, all metals, and he determined 110 independent relative sensitivity factors. He assumed all elements to have the same atomic sensitivity as the host matrix, and he corrected for linewidth variation, and for variation of photoplate sensitivity with the mass of the element. Paulsen finds that 70 percent of his results so determined fall within a factor of 3 of results for the same elements certified by independent analytical methods and all results fall within a factor of 10 of the certified values.

A histogram of the 110 results plotting the frequency against the ratio (determined value to certified) was kindly made available by Paulsen. The skew population of this set was normalized [18] by plotting, on log-probability paper, the sensitivity factor against the cumulative percentage of the measurements. The resulting linear relationship permitted the evaluation of the average and standard deviation of the logarithmic distribution, from which the average and standard deviation of the original set could be calculated [19], with due consideration given to the finite population correction [20].

These results may be fairly said to reflect, statistically, the output of the spark-source analysis capability of the Center for Analytical Chemistry and we view the 16 measurements of our silver samples as belonging to the same parent population as Paulsen's measurements. The estimated standard deviation of Paulsen's set is 2.4 in the sensitivity factor, and the estimated mean is 2.3. Paulsen's spark-source results can therefore be expected to be slightly more than twice the values certified by other methods. One may normalize Paulsen's ratio of 2.3 to 1; the correction for the spark-source results to the electrochemical equivalent then becomes 3.4×10^{-7} mg C⁻¹ (or 0.29 ppm) (table 2) with an estimated standard deviation of the mean of 3.5×10^{-7} mg C^{-1} (0.30 ppm) which is carried forward as a systematic uncertainty (table 3). Included in this first group is a value for gold which was determined by spark-source methods similar to those of the Center for Analytical Chemistry, NBS. The value was determined at the Ames Laboratory, U.S. Department of Energy. The general scan from this laboratory yielded results that were almost all higher, often by orders of magnitude, than the values from the Center for Analytical Chemistry. However, the latter values are well confirmed by isotope-dilution analysis. On the other hand, the report from the Ames Laboratory is our only source for a value for gold, the spectrometer at Ames not using gold sample holders. Despite our suspicion that the reported value for gold, like that for many elements, may be high, we shall use the value from the report of the Ames Laboratory [21]. The report assigns an uncertainty of only 15 percent. We assign Paulsen's broader, and in our view, more realistic uncertainty. The magnitude of the correction for gold is 0.3 ppm.

TABLE 3.

A. Estimate of u	ncertainties in E_{A_8} from	n known sources.
Source	Systematic Uncertainty (ppm)	Random Uncertainty (ppm)
Voltage	0.2	
Resistance	.2	
Time	.2	
Weighing	.5	
Silver residue analysis	.6	
Spark source general		
analysis	.3	
Iron analysis by isotopic		
dilution	.08	
19-element analysis by		
isotopic dilution	.05	
Spark source undetected		
elements	.3	
Experimental scatter		0.85
RSS	0.96	0.85
Combined uncertainty	1.28	ppm

B. Estimate of uncertainties in F from known sources				
Source	Uncertainty (ppm)			
$E_{A_{\mathcal{B}}}$	1.28			
Atomic mass of anode				
silver	2.1ª			
Combined uncertainty	2.5 ppm			

Work underway at NBS is expected to reduce this number five-fold.

2. The value for iron in the sample (sixth column table 2) rests on the report of a set of three determinations performed by members of the Center for Analytical Chemistry, NBS. The analysis was performed by isotope-dilution mass spectrometry. The value for iron represents the mean of three measurements which impose a correction of 8.1×10^{-7} mg C⁻¹ (0.72 ppm). An uncertainty of 0.08 ppm is associated with this quantity.

3. Also in table 2 appear the mass spectrometric analyses, for the elements shown, by isotope-dilution techniques. These determinations, like those for iron, have an internal standard for each element. No blank measurements are available for these measurements. The values are therefore upper limits; any blank would decrease the values. The absence of blanks requires us to handle the results in a special way.

From the data in table 2, we can compute a correction to the electrochemical equivalent of silver resulting from each of the 19 impurities. Some of these corrections will increase E_{A_8} and some will have the opposite effect. The only information we possess is an upper limit on impurity levels. From this, however, we can compute the range of possible corrections to E_{A_8} , which calculation yields $+2.03 \times 10^{-6}$ mg C⁻¹ to $-.02 \times 10^{-6}$ mg C⁻¹ (+1.82 ppm to -.02 ppm). We shall assume that the most probable correction lies midway between these values, i.e. 1.0×10^{-6} mg C⁻¹ (0.89 ppm). It is useful to estimate an uncertainty for this number in order to calculate an estimated uncertainty for the experiment. In the absence of guidance concerning the statistical distribution governing this correction, we shall assume that all values within the range are equally probable (uniform distribution). In this case, the standard deviation of the estimated correction can be approximated by dividing the range by 3.5 [22, 23]. Thus the standard deviation is expected to be approximately 0.5 ppm.

4. For the sake of completeness, the elements undetected by spark-source methods, with known limit of detection in grams of contaminant per gram of sample, were reviewed. If the detection limits are used as upper limits on the presence of the elements in the sample, we may use the statistical techniques given above to estimate a correction. Our estimate of the correction is about 0.9×10^{-7} mg C⁻¹ (0.08 ppm) with an estimated standard deviation of 2.3×10^{-7} mg C⁻¹ (0.2 ppm). The calculation was done to assure the meagerness of the contribution of these contaminants. They are not known to be present, the correction was not made, and the uncertainty has been listed among the known systematic uncertainties.

These computations permit us to advance for the electrochemical equivalent of pure silver the value, 1.1179648 mg C_{wBS}^{-1} . Attached to this figure is an uncertainty whose random component (standard deviation of the mean of 8 determinations) is 9.5×10^{-7} mg C⁻¹ (0.85 ppm) and whose root-sum-square of systematic components of known origin (at an estimated level of one standard deviation) in this experiment is 1.07×10^{-6} mg C⁻¹ (0.96 ppm). The separate components of systematic uncertainty are listed in table 3A. The combined random scatter in the first five items of table 3A gives rise to the observed experimental scatter in E'_{Ag} .

From the electrochemical equivalent of pure silver and the atomic mass of the silver sample one may calculate the Faraday constant:

$$F = \frac{A_r(Ag)}{E_{A_k}}$$

Since the atomic mass of the silver in our samples is required for this calculation, the samples used in this measurement were submitted to the Center for Analytical Chemistry, NBS, for determination of the isotopic abundance ratio. The isotopic composition of five samples, 55 A, B, D, E, F, was determined by the Center using thermalionization mass spectrometry. The methods used are described elsewhere [24]. The average value for the ratio, 10^{7} Ag/ 10^{9} Ag, was determined by comparison of the ratio of the two isotopes in our sample with the ratio of a silver sample whose isotopic abundance was determined by Shields et al. [24,25] at NBS. The ratio found for our sample was 1.07599. We consider this value to be within the extensive population of determinations on silver made at NBS which has the value r = 1.07597. The authors have not been able to reconcile the uncertainties contained in the original internal NBS report and those stated in [25]. Taylor et al. [26] make what appears to be a reasonable estimate of these uncertainties. We shall therefore follow these authors and accept for the purpose of this paper a combined one standard deviation uncertainty of 0.00049 in r. The above ratio ¹⁰⁷Ag/¹⁰⁹Ag (1.07597) and uncertainty when combined with the atomic masses of the individual isotopes [27], yield an atomic mass for silver of 107.86833(23) (2.1 ppm). The uncertainty in the atomic mass of silver thus imposes on the Faraday constant a systematic uncertainty of 2.1 ppm. The uncertainty on the individual atomic masses of silver is two orders of magnitude lower [27].

Using eq. (9) we calculate the Faraday constant from the electrochemical equivalent of silver and the atomic mass of our samples:

$$F = 96,486.33(24)A_{NBS} \text{ s mol}^{-1}$$
 (2.5 ppm),

in terms of the electrical units as maintained at the National Bureau of Standards in the spring of 1975.

With this number is associated an uncertainty with a systematic component of 0.22 Cmol^{-1} (2.3 ppm) and random component of 0.08 Cmol^{-1} (0.85 ppm). Combination of these uncertainties by the root-sum-square rule [1] yields the uncertainty given in parentheses.

8. Discussion

In order to compare the value of the Faraday obtained by our work with values obtained in other laboratories, all numbers must be expressed in the same electrical units. The electrical unit involved is the coulomb, or ampere-second. Laboratory time is measured in terms of the SI second, but current is measured in terms of a ratio of voltage to resistance—both units being defined in terms of laboratory standards and thus differing from the SI definition at the part per million level. It is convenient to convert all values of the Faraday constant to so-called "BI69" electrical units, defined in reference [1]. In terms of these units, our value for the Faraday constant becomes

$$F = 96486.21(24) \,\mathrm{A}_{BI69} \,\mathrm{s} \,\mathrm{mol}^{-1}.$$

Figure 7 shows the value of the Faraday reported here (point F) as well as Faraday constants measured by other workers [3, 5, 28] (points A, B, C, and E). It will be observed that the present results are in agreement with most of the previous electrochemical measurements of the Faraday.

 $\langle 0 \rangle$



FIGURE 7. Comparison of recent determinations of the value of the Faraday. Uncertainty assignments (one standard deviation) are indicated by extended bars:

- A. Craig's silver determination, 1960[5];
- B. Marinenko and Taylor, benzoic acid 1968[28];
- C. Same authors oxalic acid 1968 [28];
- D. Recommended value based on physical constants, Cohen and Taylor 1973 [1].
- E. Koch and Diehl, 4-aminopyridine 1976 [2, 3];
- F. This experiment;
- G. Kibble and Hunt, proton gyromagnetic ratio [31];
- H. Deslattes et. al., Avogadro constant [29];

The results, when converted to BI69 electrical units, yield the following values for the Faraday constant:

A.	96486.72(66)A _{BI69} · s · mol ⁻¹	(6.8 ppm)
B.	96487.30(1.12)	(11.6 ppm)
C.	96486.25(1.57)	(16.3 ppm)
D.	96484.49(50)	(5.2 ppm)
E.	96484.40(1.08)	(11.2 ppm)
F.	96486.21(24)	(2.5 ppm)
G.	96486.00(10)	(1.1 ppm)
H.	96485.40(10)	(1.1 ppm)

However, the present determination has a significantly reduced estimate of uncertainty compared to the others. Furthermore, our list of systematic uncertainties is more comprehensive and searching than those of prior determinations. Figure 7 also shows the CODATA recommended value of Cohen and Taylor [1] (point D), which is calculated from other physical constants via least squares. The difference may be seen from the figure. Evidently, a significant systematic error has been overlooked or underestimated. Since this discrepancy exists between the physical and chemical experiments which are of approximately the same high precision, we must examine our experiment for possible sources of the observed difference.

The Faraday constant calculated from physical quantities (i.e., the least-squares adjustment value, 96,484.49(50) A_{BI69} \cdot s \cdot mol⁻¹ (5.2 ppm) [1]) is about 18 parts per million lower than the value found in our experiment.

If a significant systematic error exists in our experiment rather than elsewhere it must have the effect of dissolving too little silver for the passage of a given charge. One possible cause of such an occurrence might be parasitic leakage currents in the circuitry external to the electrolysis cell. However, we made every effort to measure all leakage resistances with care. Another possible cause of too little delivery of silver into solution might be less than perfect efficiency of the electrode in generating silver at the anode. Electrode efficiency to the required precision cannot be directly measured (the most precise measurements have established the reversibility of the silver coulometer to only 60 ppm [4]). Indirectly we can seek correlations of E_{Ag} with the current or the maximum overvoltage of the anode during dissolution. Linear regression analysis of E_{A_B} as a function first of the current and then of the maximum overvoltage gives correlation coefficients of $r^2 = 0.27$ and $r^2 =$ 0.74, respectively. The second coefficient may be significant but both correlations, when extrapolated, increase the discrepancy of our result with respect to the non-electrochemical Faraday constant.

Still another possible cause for the discrepancy might be that the capacitive charging effects have been underestimated. These transient charges should have a smaller relative effect the more total charge is passed. Again, no effect is observed with variation of the duration of the experiment.

The determination described here does agree well with several previous electrochemical measurements. The mean value for the Faraday calculated from the 11 silver samples prepared in vacuum by Craig [5] agrees to within 6 ppm with the present value, and agrees also with the values advanced by Marinenko and Taylor [28] for benzoic acid and oxalic acid. However, the uncertainties attributed to these studies are large compared to the uncertainty attributable to the present experiment. Our value for the Faraday constant does not agree well with the most recent (but again, relatively uncertain) value advanced by Koch [3] for the Faraday constant determined via 4-aminopyridine [2].

Since the 1973 least-squares adjustment [1], two additional, high precision measurements have been made which have a bearing on the present discussion. These are the measurement of the Avogadro constant, N_A , by Deslattes et al. [29, 30] and the measurement of the proton gyromagnetic ratio in a high magnetic field, γ'_{p} (high), by Kibble and Hunt [31]. Some implications of the new results have been discussed by Taylor [32]. In particular, we may use eq (7), (8) and (9) of ref. [32] to compute the Faraday constant in BI69 electrical units by two different ways: (1) equating the right hand sides of equation (8) and (9) of ref. [32], F_{BI69} may be computed from constants the combined uncertainty of which is dominated by the uncertainty of γ'_{p} (high); (2) equating the right hand sides of eq (7) and (9) of ref. [32] allows one to compute F_{BI69} from constants whose combined uncertainty is dominated by the uncertainty of N_A . The two methods produce results which are labeled "G" and "H" respectively in figure 7. Our value for F_{BI69} is in remarkably good agreement with F_{BI69} calculated via γ'_{p} (high) but is some three standard deviations distant from that calculated via N_A . (In performing these calculations, use was made of the most recent data available [30, 31, 33].) Clearly, further work in a number of areas will be necessary before the present discrepancies are understood.

A large number of workers, all at NBS, cooperated and provided assistance to the authors in the course of this long experiment. We are grateful to R. E. Michaelis, who selected the high grade silver standard sample for us; to B. F. Field, R. L. Driscoll, R. D. Cutkosky, L. H. Lee, N. B. Belecki, T. E. Wells, A. Skapars, W. G. Eicke, P. T. Olsen, and E. R. Williams, all of the Electrical Measurements and Standards Division, for a variety of calibrations, advice on refinements of circuitry, and general support; to E. L. Garner, L. P. Dunstan, T. J. Murphy, and I. L. Barnes of the Center for Analytical Chemistry, for the mass spectrometric analysis; to P. J. Paulsen, of the same Center, for mass spectrometric analysis, and for providing unpublished data which materially assisted in the statistical interpretation of our results; to C. Eisenhart for the calculation of the statistics of Paulsen's data and for guidance in other statistical calculations; to W. F. Koch and G. Marinenko, both of the Center for Analytical Chemistry, and themselves authors of Faraday experiments [2, 3, 28], for helpful discussions; and to B. N. Taylor, for administrative support and helpful discussion over the protracted period of the experiment.

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