Designation: B825 – 13

# Standard Test Method for Coulometric Reduction of Surface Films on Metallic Test Samples[1]

This standard is issued under the fixed designation B825; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

## 1. Scope

1.1 This test method covers procedures and equipment for determining the relative buildup of corrosion and tarnish films (including oxides) on metal surfaces by the constant-current coulometric technique, also known as the cathodic reduction method.

1.2 This test method is designed primarily to determine the relative quantities of tarnish films on control coupons that result from gaseous environmental tests, particularly when the latter are used for testing components or systems containing electrical contacts used in customer product environments.

1.3 This test method may also be used to evaluate test samples that have been exposed to indoor industrial locations or other specific application environments. (See 4.6 for limitations.)

1.4 This test method has been demonstrated to be applicable particularly to copper and silver test samples (see **(1)**).[2] Other metals require further study to prove their applicability within the scope of this test method.

1.5 The values stated in SI units are the preferred units. The values provided in parentheses are for information only.

1.6 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to become familiar with all hazards including those identified in the appropriate Material Safety Data Sheet (MSDS) for this product/material as provided by the manufacturer, to establish appropriate safety and health practices, and determine the applicability of regulatory limitations prior to use.*

## 2. Referenced Documents

2.1 *ASTM Standards:*[3]

B808 Test Method for Monitoring of Atmospheric Corrosion Chambers by Quartz Crystal Microbalances

B809 Test Method for Porosity in Metallic Coatings by Humid Sulfur Vapor (“Flowers-of-Sulfur”)

B810 Test Method for Calibration of Atmospheric Corrosion Test Chambers by Change in Mass of Copper Coupons

B827 Practice for Conducting Mixed Flowing Gas (MFG) Environmental Tests

D1193 Specification for Reagent Water

## 3. Summary of Test Method

3.1 In constant-current coulometry, a fixed reduction-current density is applied to the sample in an electrolytically conductive solution, and the resulting variations in potential—measured against a standard reference electrode in the same solution—are followed as a function of time. Typically, with well-behaved surface films, the voltage-time plot should show a number of horizontal portions, or steps, each corresponding to a specific reduction potential or voltage (Fig. 1). The final potential step, which is always present with all substances, corresponds to the reduction of hydrogen ions in the solution (to form hydrogen gas), and represents a limit beyond which no higher potential reduction process can occur.

NOTE 1—As shown in Figs. 1 and 2, a differential circuit is recommended to help in resolving the individual voltage steps by pinpointing the corresponding inflection points on the main reduction curve (see 6.2.3).

3.2 From the elapsed times at the various steps, conclusions can often be drawn regarding the corrosion processes that have taken place to produce the surface films. Also, calculations can be made from the time at each voltage step in order to calculate the number of coulombs of electrical charge required to complete the reduction process at that particular voltage.

---

[1] This test method is under the jurisdiction of ASTM Committee B02 on Nonferrous Metals and Alloys and is the direct responsibility of Subcommittee B02.11 on Electrical Contact Test Methods.

Current edition approved Aug. 1, 2013. Published August 2013. Originally approved in 1997. Last previous edition approved in 2008 as B825 – 02 (2008). DOI: 10.1520/B0825-13.

[2] The boldface numbers in parentheses refer to the list of references at the end of this standard.

[3] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard’s Document Summary page on the ASTM website.

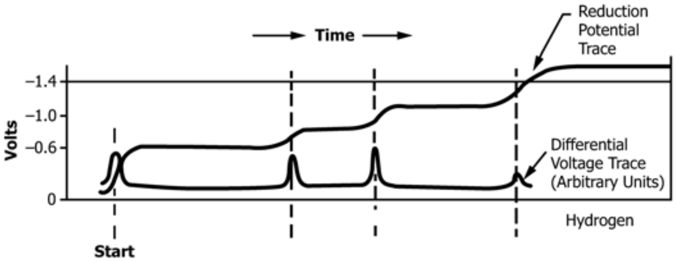


FIG. 1 Ideal Reduction Behavior of Oxide and Sulfide Films on Copper (from Ref 1)

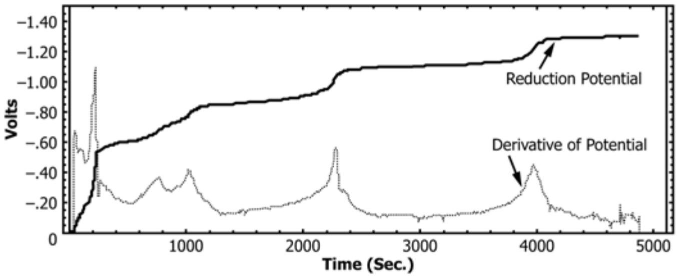


FIG. 2 Typical Reduction Behavior of Films on Copper from 72-h Exposure to the Humid Sulfur Vapor Test (see Test Method B809)

Furthermore, since the reduction of any particular chemical compound takes place at a characteristic reduction potential or voltage range, this voltage can be used to indicate the presence of a compound or compounds whose characteristic reduction potential has already been established under the conditions of the test. Under ideal conditions it may also be possible to determine the number of reducible compounds present in the tarnish film.

3.3 For the purpose of this test method, tarnish films shall be defined as the corrosion products of the reactions of oxygen or sulfur (or of other reactive gases or vapors) with the metallic surface that adhere to the surface and do not protrude significantly from it.

3.4 The basic techniques for the reduction of films on copper and silver were described as early as the late 1930s by Miley (**2**) and by Campbell and Thomas (**3**). Important observations of the effects of changing experimental variables were later reported by Albano (**4**) and by Lambert and Trevoy (**5**) in the 1950s. The details and recommendations in this test method are primarily from a recently published papers (**1**) and (**6**).

## 4. Significance and Use

4.1 The present trend in environmental testing of materials with electrically conductive surfaces is to produce, under accelerated laboratory conditions, corrosion and film-forming reactions that are similar to those that cause failures in service environments. In many of these procedures the parts under test are exposed for days or weeks to controlled quantities of both water vapor and pollutant gases, which may be present in extremely dilute concentrations.

NOTE 2—Descriptions of such tests can be found in Practice B827.

4.2 Many of these environmental test methods require monitoring of the conditions within the chamber during the test in order to confirm that the intended environmentally related reactions are actually taking place. The most common type of monitor consists of copper, silver, or other thin metallic coupons of a few square centimeters that are placed within the test chamber and that react with the corrosive environment in much the same way as the significant surfaces of the parts under test.

4.3 In practice, a minimum number of control coupons are placed in each specified location (see Test Method B810) within the chamber for a specified exposure time, depending upon the severity of the test environment. At the end of this time interval, the metal samples are removed and analyzed by the coulometric reduction procedure.

4.4 Other corrosion film evaluation techniques for metallic coupons are also available. The most common of these is mass gain, which is nondestructive to the surface films, but is limited to the determination of the total amount of additional mass acquired by the metal as a result of the environmental attack. The most common is weighing using high performance microbalances or for purposes of real-time monitoring, quartz crystal microbalances (see Specification B808).

NOTE 3—Detailed instructions for conducting such weighings, as well as coupon cleaning and surface preparation procedures, are included as part of Test Method B810.

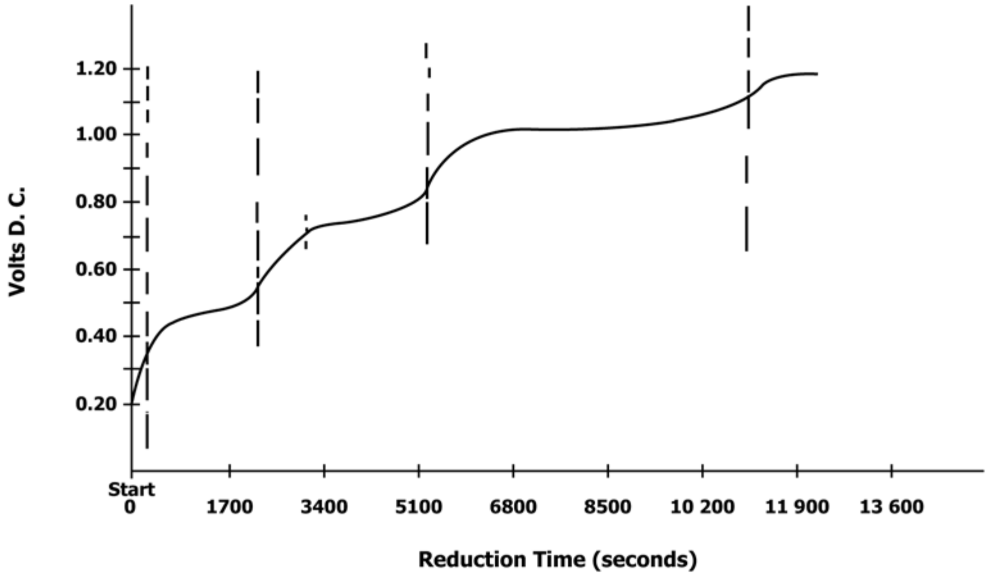
NOTE 4—Some surface analytical techniques (such as X-ray methods) can provide nondestructive identification of some compounds in the films, but such methods, for example, X-ray diffraction, can miss amorphous compounds and compounds present in quantities less than 5 % of the tarnish film volume.

4.5 With the coulometric technique, it is possible to resolve the complex total film into a number of individual components (Fig. 1) so that comparisons can be made. This resolving power provides a *fingerprint* capability for identifying significant deviations from intended test conditions, and a comparison of the corrosive characteristics of different environmental chambers and of different test runs within the same chamber.

4.6 The coulometric reduction procedure can also be used in test development and in the evaluation of test samples that have been exposed at industrial or other application environments (**7**). However, for outdoor exposures, some constraints may have to be put on the amount and type of corrosion products allowed, particularly those involving moisture condensation and the possible loss of films due to flaking (also see 4.9 and 8.3.2).

4.7 In laboratory environmental testing, the coulometric-reduction procedure is of greatest utility after repeated characterizations of a given corrosive environment have been made to establish a characteristic reduction curve for that environment. These multiple runs should come from both the use of multiple specimens within a given test exposure as well as from several consecutive test runs with the same test conditions.

4.8 The coulometric-reduction procedure is destructive in that the tarnish films are transformed during the electrochemical reduction process. Nondestructive evaluation methods, such as mass gain, can be carried out with the same samples



NOTE 1—The vertical lines correspond to major peaks in the differential curve (not shown) and delineate the main reducible film types from this environment.

**FIG. 3 Typical Reduction Curve of Copper from 48-h Exposure to High Sulfide (100 ppb $H_2S$) Mixed Flowing Gas (with 20 ppb $Cl_2$ and 200 ppb $NO_2$)**

that are to be tested coulometrically. However, such procedures must precede coulometric reduction.

4.9 The conditions specified in this test method are intended primarily for tarnish films whose total nominal thickness is of the order of $10^2$ to $10^3$ nm ($10^3$ to $10^4$ Å). Environmentally produced films that are much thicker than $10^3$ nm are often poorly adherent and are more likely to undergo loosening or flaking upon placement in the electrolyte solution.

## 5. Interferences

5.1 For reproducible results the following precautions shall be taken in order to avoid interferences.

5.1.1 Remove dissolved oxygen gas from the electrolyte solution (see 8.1.3), and prevent it from reentering the solution by keeping the cell closed, with an inert gas flowing over the solution during the reduction (see 8.3.2 and 8.3.3).

5.1.2 Use fresh electrolyte solution for each new coupon in order to avoid contamination from the reduction of previous coupons (see 8.3.5).

5.1.3 Do not apply masking finishes or other nonmetallic coatings to the coupons, prior to environmental exposure.

5.1.4 Do not use this test method to analyze poorly adherent films (see 4.9).

5.1.5 If the sample had been exposed to environments that were likely to deposit soluble particulates (in addition to the underlying insoluble overall films), care must be taken to remove most of the particulates prior to coulometric reduction (see 8.3.2 for procedure).

## 6. Apparatus

6.1 *Electrolytic Reduction Cell and Ancillary Equipment:*

6.1.1 *Reduction Cell,* preferably of glass, with a total internal volume of at least 600 mL. The cell shall be enclosed, but should have a sufficient number of entry ports or tubes to accommodate the required ancillary equipment (see Figs. 4 and 5 for examples of typical cell systems).

6.1.2 *Reference Electrode*—A silver/silver-chloride reference is preferred since much of the data in the technical literature have been obtained with this type of electrode. It can be obtained commercially or made in-house from pure silver strip or wire (see Appendix X1).

6.1.2.1 In-house electrodes must be checked periodically by testing them against a standard reference electrode (for example, saturated calomel electrode) using a potentiometer or pH meter. The potential exhibited when measuring these silver/silver-chloride electrodes in 0.1-M potassium chloride solution against a saturated calomel reference should be 0.05 V (±0.01 V) (**8**).

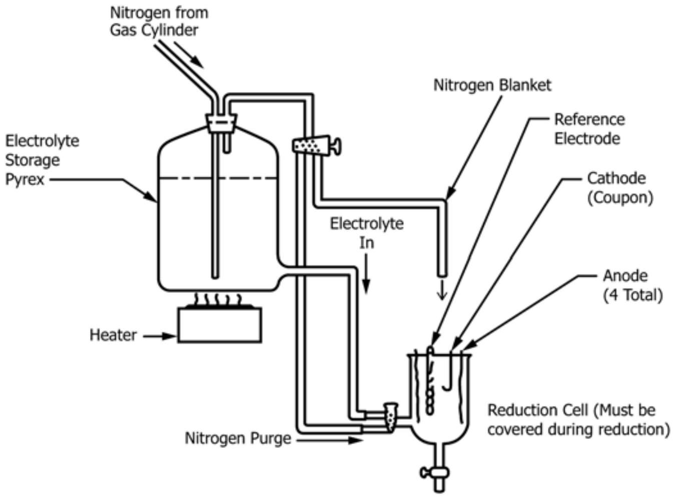


**FIG. 4 Schematic of Reduction Cell with Storage Reservoir, for Procedure A (8.1.3.1)**

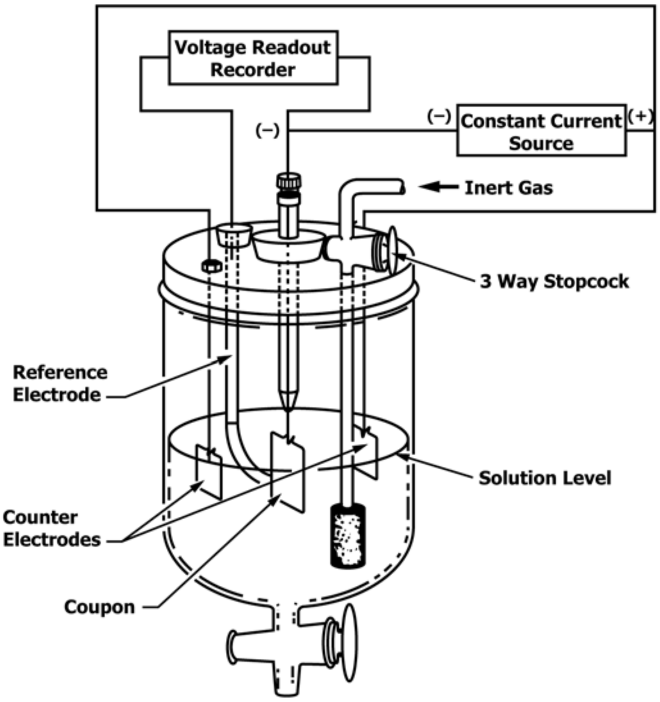


**FIG. 5 Schematic of Reduction Cell for Procedure B (8.1.3.2)**

6.1.3 *Inert-Gas Purging Tube*—The end that is in the electrolyte should be fitted with fritted glass or drawn to a fine tip (for example, 0.5-mm inner diameter or less).

6.1.4 *Counter-Electrodes*—Pure platinum foil or wire shall be used. The number of counter-electrodes may vary from 2 to 4 and shall be positioned symmetrically around the sample. The area of the counter-electrodes preferably should be equal to or greater than the sample area.

6.1.5 *Wire Hook or Clip for Holding the Sample*—The upper part of the hook or clip shall be attached to a wire (inserted into a glass or plastic tube) for ultimate connection to the negative output of the power supply. If the wire hook is to be immersed in the solution, it shall be made of the same metal as the sample. If a clip is used, it shall be heavily gold plated (3 µm or more in thickness) and attached to a platinum wire hook for electrical contact.

6.2 *Electronic Equipment*—For producing the constant cathodic current and measuring the resulting voltages as a function of time comprises three basic functional modules whose recommended characteristics (for routine tarnish-film analysis) are listed as follows:

6.2.1 *Constant Current Power Supply,* such as, a potentiostat/galvanostat, capable of supplying a constant direct current, and adjustable from 0.02 to 2 mA with a precision of ±1 %. However, for certain limited applications (for example, very large area samples), currents greater than 20 mA might conceivably be required, see 8.2.1.

6.2.2 *Strip Chart or Digital Recorder, or Both*—For a strip-chart recorder, two pens are preferred, one pen for voltage and the other for a voltage-time derivative curve. The chart recorder shall have variable speed capability, from 10 mm/h to 100 mm/min, and full-scale voltage ranges from 0.5 to 2 V. A resolution of the order of 0.5 % (namely, 10 mV with 2-V full scale), though not essential, is helpful in data evaluation, and is obtained easily with any 250-mm chart recorder. A *digital recording system*, capable of data storage and graphic representation can be used instead of, or in conjunction with, the strip chart recorder system. Both systems shall have input impedance of at least $10^6$ Ω, preferably higher.

6.2.3 *Differential Circuit, or Commercial Differential Voltage Output Apparatus*—If a digital recording system is used in conjunction with, or to replace, an analog recording system, the following method can be used to create a differential curve. After the reduction is recorded completely, each data point, except for the first and last, must be analyzed. For a given point, $X$, determine the slope to the previous point, $X_p$, and the subsequent point, $X_s$. Knowing the time interval, $T$, between each reading, the required slopes are as follows:

$$S_p = (X - X_p)/T \quad S_s = (X_s - X)/T \tag{1}$$

An approximation of the slope at $X$ is then found by taking the average of the slopes $S_p$ and $S_s$ as follows:

$$S = (S_p + S_s)/2 \tag{2}$$

Each value of $S$ is recorded with the concurrent value of $X$ for later analysis. Slopes at the first and last data points can be assumed to be zero. A method for enhancing these digitally produced differential curves can be found in Appendix X2.

## 7. Reagents

7.1 The only reagents required for routine procedures are ACS reagent-grade potassium chloride (for the electrolyte), Pre-Purified-grade nitrogen[4] or other inert gas, and a source of distilled or deionized water (Type IV or better as specified in Specification D1193).

## 8. Procedure

8.1 *Cell Preparation:*

8.1.1 Assemble the reduction cell in accordance with either Fig. 4 or Fig. 5, making sure that all components are chemically clean. For each sample size or geometry, determine in advance the level of liquid that is required to cover the specified sample surface. Mark this level on the outside of the cell. A minimum volume of 300-mL solution is recommended for each analysis.

8.1.2 Attach the tubing system for the inert gas (assembled in advance) to the regulator of the gas tank.

8.1.3 *Potassium Chloride Solution 0.1 M*—Deaerate 0.1-M KCl solution, prepared in advance, with the inert gas (to displace dissolved oxygen) using either Method A (8.1.3.1) or Method B (8.1.3.2).

NOTE 5—If any oxygen gas ($O_2$) is present in the working electrolyte, it will tend to interfere with the coulometric determinations, since $O_2$ is easily reduced in the same voltage range as many oxide or tarnish film components. Dissolved oxygen is eliminated by deaerating the electrolyte solution prior to use and by running the reduction in a closed cell under an inert atmosphere.

---

[4] Pre-Purified is a designation of Matheson Gas Co., East Rutherford, NJ, for a specific grade of purity of gas. Other vendors, such as AIRCO, have equivalent purities available sold under different terminology.

8.1.3.1 *Procedure A* (Fig. 4)—Boil the solution in the storage reservoir of Fig. 4 for 30 min, while inert gas is bubbled through the system. Cool the electrolyte solution to room temperature while maintaining the inert gas purge. After cooling, keep the solution in a covered glass container and continually purge slowly with inert gas, prior to use. Unused electrolyte solution can be stored in the glass container (with inert gas purging) for up to 7 days, after which it shall be discarded.

8.1.3.2 *Procedure B* (Fig. 5)—Transfer the electrolyte solution to the reduction cell so that the solution level is slightly above the specified mark. Close the cell and bubble the inert gas through the purging tube (whose end is at the bottom of the solution) for 50 min or more.

NOTE 6—Smaller purge times can be used, but their adequacy should be verified by measuring the oxygen reduction current on a nonfilmed sample.

8.1.4 Calculate the current to be applied, and preset the controls on the electronic equipment accordingly. This current is the absolute current that shall be applied to produce the desired current density on the particular sample used.

8.1.4.1 For the most common types of mixed flowing gas control coupons (that is, 24 to 96-h exposure in moderate to severe environments), a current density of 50 µA (0.05 mA)/cm$^2$ of *immersed* metal is required. This same current density is also commonly used to analyze tarnish films from other types of environmental tests. For very thick films, the current density might be increased (up to a maximum of 0.25 mA/cm$^2$) so that the reduction can proceed at a reasonable rate of not more than 4 to 6 h for the total reduction time of any one sample. Since the observed reduction potentials will become more negative with increasing current density, exercise care when comparing samples reduced at different current densities. List all deviations from the preferred current density of 0.05 mA/cm$^2$ in the test report.

8.2 *Coupon Preparation (Prior to Exposure to the Test Atmosphere):*

8.2.1 The metallic coupons shall normally be prepared from sheets or strips of at least 99.9 % purity, and preferably at least 10 mm wide and 0.1 mm thick. Preferred areas range from 300 to 1000 mm$^2$ maximum per flat side, and preferred thicknesses, in accordance with Test Method B810, are 0.1 to 0.6 mm (0.005 to 0.030 in.). However, coupon dimensions shall not exceed 32 mm (1.25 in.) in width and 77 mm (3 in.) in length.

8.2.2 It is essential that samples of the same shape and thickness shall be used for all tests for which sample-to-sample comparisons are made.

8.2.3 Prepare and clean the metallic coupons in accordance with standard procedures, such as those in **Ref (1)** or Test Method B810. If no standard procedure is available for the metal used, describe the cleaning and preparation procedure in detail in the test report.

8.2.4 Do not apply masking lacquers (or similar nonmetallic coatings) to the coupons.

8.3 *Reduction Procedures (Following Exposure to the Test Atmosphere):*

8.3.1 If a hook is used to suspend the sample coupon, ream the hole in the latter with a round file (such as a jeweler's file) in order to remove the insulating tarnish film from the hole wall and ensure good electrical contact between the coupon and the wire hook.

8.3.2 If the sample had been exposed to field environments, it shall be examined (at 3X) for the presence of particulates. If a significant number of particulates are observed, the sample shall be immersed for a few seconds in a beaker of fresh DI water just prior to placement in the reduction cell.

8.3.3 For the setup of Fig. 4, suspend the sample from the hook or clip, using clean forceps to avoid contaminating the sample, and insert into the empty cell. Introduce inert gas through the lower port of the empty cell to purge the air for a minimum of 2 min, after which divert the gas to the upper part of the cell. The recording system is then engaged and turned on. Introduce the deaerated electrolyte solution into the reduction vessel to the preset mark.

8.3.4 For the cell design of Fig. 5, first divert the inert gas so that it passes over the deaerated solution in the cell. Attach the sample to the hook or gold-plated clip then lower the solution level to the preset mark by opening the bottom stopcock. The recording system is then engaged and turned on.

8.3.5 Apply the precalculated current between the sample and the counter-electrodes, and mark the start time on the recorder chart, if used. Allow the reduction to proceed until the hydrogen reduction step is established, before turning off the current. Hydrogen reduction is determined by the presence of an "endless" flat or gently rising constant voltage step, which is often accompanied by the evolution of masses of small bubbles from the sample. Once this hydrogen step is reached no higher potential reduction process can occur.

8.3.6 At the completion of each coulometric run, remove the sample and drain and clean the cell in preparation for the next run.

## 9. Data Evaluation

9.1 The results of the constant-current coulometry procedure can be expressed directly as the elapsed time, in seconds, required to complete the reduction of a particular film component at its observed voltage step (see 9.4 for method), as well as the total time needed to complete the reduction of all the reducible components of the film. The elapsed time values can also be multiplied by the total applied current to give the number of coulombs of electrical charge required to complete the reduction processes at the various respective voltages as follows:

$$q = it \tag{3}$$

where:

$q$ = charge, mC,
$i$ = current, mA, and
$t$ = time, in s.

9.2 If the chemical identity of the reducible component is known (**1**), calculations can be made of both the mass of that substance and its thickness (assuming that it is present as an homogeneous layer in the film). Methods of calculation are given in Appendix X3.

9.3 *Voltage Determinations*—Record a reduction potential or potential range, in volts, for each voltage step or arrest (Fig.

1). The portion of the curve corresponding to this potential or potential range shall encompass at least 75 % of the reduction time for that segment of the total curve.

9.4 *Reduction Time Determinations:*

9.4.1 For simple films, the substance having the lowest (least negative) reduction potential will reduce first, the reduction going to completion before the substance having the next greater potential begins to reduce. The differential voltage indicator, which shows where the reduction potentials are changing most rapidly, indicates the beginning and the end of a reduction, and is thus used to determine reduction times (Fig. 1).

NOTE 7—See Ref 1-5 for proposed chemical identities for the films in Fig. 1.

9.4.2 With many environmentally produced films there may be some overlap between the reductions of the different film constituents, and the reduction steps may not be sharply defined. This will generally occur with thicker films, where the thicknesses of the various components might not be uniform over the sample area. This is often indicated by a rounding of the differential voltage peaks in Fig. 1 as the reduction potential changes gradually between the two voltage arrests or steps. If this should occur, one or both of the following methods may be used to determine the transition points.

9.4.2.1 The approximate midpoints of the differential maxima for the beginning and end of the particular reduction arrest can be estimated by inspection and measurement.

9.4.2.2 The voltage-time traces may be inspected at a nearly grazing angle to the line of sight, using a straightedge to lay out lines that best fit the steps. The transitions will then be seen and their midpoints estimated (and recorded as the beginning and end times for that particular step). When transitions are determined by this technique, they shall be reported as *graphical transitions* or *transitions by graphical analysis* to alert the test specifier to additional considerations when comparisons are to be made.

## 10. Report

10.1 Complete a report using a format similar to that shown in Fig. 6.

## 11. Precision and Bias

11.1 *Precision*—The precision of the coulometric reduction test method was determined for copper coupons exposed to the humid sulfur vapor test atmosphere in accordance with Test Method B809 for 72 h (**1**).

11.1.1 The voltage level determinations for four different reduction steps (all greater than 0.5 V) showed a maximum standard deviation (really a coefficient of variation) of 5 % for 3 separate tests involving a total of 26 samples. The average of the 12 coefficients of variation (4 levels from each of the 3 tests) was 1.8 %.

11.1.2 The reduction times for these four voltage levels showed a maximum coefficient of variation of 46 %, with an average coefficient of 27 % for the 12 reduction times. However, these reduction-time numbers are not necessarily related to the precision of the coulometric reduction method itself, because the reduction times depend upon the different tarnish thicknesses imparted to the individual samples during the environmental exposure. Independent measurements of total film thicknesses on each sample by the mass gain method in accordance with Test Method B810 showed a coefficient of variation (*S/X*) of 27 % for Test No. 2 and 23 % for Test No. 3 (Table 1), in good agreement with the values observed for coulometric reduction times. It can be inferred that the coefficients of variation for the coulometric reduction times can be

Job/Project # ______ Date Samples Received ______ Date Completed ______ Sample Dimensions ______

Current Density ______ Absolute Current Applied ______ Environmental Exposure ______

| Sample No. | Date Reduced | Mass Gain before Reduction (if available) | Product #1 | | Product #2 | | Product #3 | | Etc. | Total Reduction Time | Hydrogen Reduction Voltage |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | Pot 'l | Time | Pot 'l | Time | Pot 'l | Time | | | |
| | | | | | | | | | | | |
| | | | | | | | | | | | |
| | | | | | | | | | | | |
| | | | | | | | | | | | |
| | | | | | | | | | | | |
| | | | | | | | | | | | |
| | | | | | | | | | | | |

Size of Cell ______ Volume of Electrolyte ______

Sample Dimensions ______

FIG. 6 Coulometric Reduction of Films on Copper

**TABLE 1 Total Reduction Time versus Mass Gain for Copper Coupons in the Humid Sulfur Vapor (Test Method B809) Test Atmosphere (1)**

| | | Total Reduction Time | Weight Gain |
|---|---|---|---|
| Test 2 | Mean (*X*) | 2855.0 s | 116.3 µg |
| (12 samples) | Standard Deviation (*s*) | 768.0 s | 31.0 µg |
| | *s/X* | 26.9 % | 26.7 % |
| Test 3 | Mean (*X*) | 3853.0 s | 166.0 µg |
| (6 samples) | Standard Deviation (*s*) | 884.0 s | 38.6 µg |
| | *s/X* | 23.0 % | 23.3 % |

expected to be less than 2 % on the basis of these results, in close agreement to the coefficients of variation in the voltage level determinations.

11.1.3 Results as precise as these may not be achieved for films formed in mixed flowing gas environments due to the increased complexity of the tarnish films. Under these circumstances, do not expect to obtain exactly the same voltage values for corresponding steps of different samples. The main reason for this is the variation in the real areas of the filmed specimens (and the corresponding changes in the true current density) as the metal surfaces are etched by the corrosive environments, and films of different surface roughnesses are produced. In addition, the various films may not have uniform thicknesses over the entire surface of the sample (see 11.1.2).

11.1.4 The precision for coupons exposed to mixed flowing gas test environments is being determined as part of a planned interlaboratory (round-robin) test program.

11.2 *Bias*—Since there is no accepted standard reference material for adherent tarnish films, the bias in the reduction potentials and reduction times have not been determined.

## 12. Keywords

12.1 atmospheric corrosion; atmospheric test evaluation; cathodic reduction; control coupon evaluation; corrosion film analysis; environmental testing; monitoring environmental tests

# APPENDIXES

## (Nonmandatory Information)

## X1. FABRICATION OF IN SITU SILVER/SILVER CHLORIDE REFERENCE ELECTRODE

X1.1 Immerse two pieces of pure silver, of approximately the same size and shape, in a saturated KCl solution, keeping them at least 3 cm apart. Apply 2 to 4 V, using batteries or a d-c power supply. After a few seconds, reverse the electrical connections. Repeat this procedure, reversing the direction of current flow at least three times. The silver that was last connected to the positive terminal of the power source is covered with a mixture of silver chloride and metallic silver.

## X2. PROCEDURES FOR ENHANCING DIGITALLY PRODUCED DIFFERENTIAL CURVES

X2.1 The differential curve values are typically a few hundredths of a volt per second, which is well below those of the reduction curve. Therefore, when plotted on the same scale (normally 0 to 1.5 V, it is difficult to analyze the differential curve. The following procedure has been developed to enhance the differential curve resolution when plotted with this scaling. While the difference between high and low values is exaggerated, the overall character of the curve is unaffected.

X2.1.1 Determine the maximum value of the differential curve.

X2.1.2 Divide 2.75 by the value determined.

X2.1.3 Multiply all points in the differential curve by the value determined in X2.1.2.

X2.1.4 (*a*) Take all points in the differential curve with positive values to the 0.4 power. (*b*) All other points (negative and zero values) are set equal to zero.

X2.1.4.1 This procedure results in the following: The new maximum differential curve value is approximately 1.5 (matching the full-scale maximum). Paragraph X2.1.4 (*a*) allows small peaks to be enhanced without causing larger peaks to go off scale.

## X3. CALCULATING THE MASS AND THICKNESS OF KNOWN FILMS

X3.1 For the mass of a known substance,

$$W = it\frac{10^3\ M}{NF} \qquad (X3.1)$$

where:

$W$ = mass, µg,
$I$ = current, mA,
$t$ = time, s, to reduce a known substance,
$M$ = gram-molecular weight of that substance,
$F$ = Faraday's constant ($9.65 \times 10^4$ C), and
$N$ = number of faradays required to reduce a gram-molecular weight of the substance, for example, 1 for AgCl; 2 for $Cu_2O$, CuO, and $Ag_2S$.

X3.2 For the equivalent film thickness of the known substance,

$$T = \frac{itK}{a} \qquad (X3.2)$$

where:

$T$ = thickness, Å, ($10^{-8}$ cm)
$i$ = current, mA,
$t$ = time, s,
$a$ = area, $cm^2$, and
$K$ = conversion factor (see Eq X3.3).

$$K = \frac{10^5\ M}{NFd} \qquad (X3.3)$$

where $d$ = density of substance being reduced, g/$cm^3$, and $M$, $N$, and $F$ have the same meaning as in Eq X3.1.

X3.3 The total mass of all the components and the apparent thickness of the entire film can be obtained by adding the respective values for these known or inferred constituents. If weight gains have previously been determined for the samples, these can be compared with the total mass values of the respective samples, and appropriate correlations made.

## REFERENCES

**(1)** Krumbein, S. J., Newell, B., and Pascucci, V., "Monitoring Environmental Tests by Coulometric Reduction of Control Samples," *Journal of Testing and Evaluation*, Vol 17, No. 6, November 1989, p. 357.

**(2)** Miley, H. A., "Cooper Oxide Films," *Journal of the American Chemical Society* , Vol 59, 1937, p. 2626.

**(3)** Campbell, W. E., and Thomas, U. B., "Tarnish Studies: Electrolytic Reduction Method for the Accurate Analysis of Thin Films on Metal Surfaces," *Transactions of the Electrochemical Society*, Vol 76, 1939, p. 303.

**(4)** Campbell, W. E., and Albano, V. J., "Applications of Coulometric Reduction to Analysis of Films on Tarnished Metals," presented at Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, 1954, Abstract in *Analytic Chemistry*, Vol 26, 1954, p. 423; Albano, V. J., "A Study of the Characteristic Reduction Potentials during the Coulometric Analysis of Films on Metals," Preliminary paper to the preceding citation.

**(5)** Lambert, R. H., and Trevoy, D. J., "Analysis of Films on Copper by Coulometric Reduction," *Journal of the Electrochemical Society*, Vol 105, 1958, p. 18.

**(6)** Lee, S. and Staehle, R. W., "Coulometric Reduction of Oxide Formed on Copper, Nickel, and Iron," *J. Electrochem. Soc.*, Vol 142, 1995, pp. 2189-2195.

**(7)** Abbott, W. H., "The Development and Performance Characteristics of Mixed Flowing Gas Test Environments," *Proceedings of 33rd IEEE Holm Conference on Electrical Contacts*, Chicago, 1987, p. 63.

**(8)** Discussions of reference electrodes and their use can be found by consulting the indices in most basic textbooks of physical chemistry or chemical analysis. Examples of such texts are:
(a) Maron, S., and Lando, J., *Fundamentals of Physical Chemistry*, Macmillan, New York, NY, 1974, especially Chapter 14.
(b) Bauer, H., Christian, G., and O'Reilly, J., *Instrumental Analysis*, Allyn and Bacon, Boston, MA, 1979, especially Chapter 2.
(c) Ewing, G. W., *Instrument Methods of Chemical Analysis*, McGraw-Hill, New York, NY, 1975, Chapter 13.