Designation: B825 – 19

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, health, and environmental practices, and determine the applicability of regulatory limitations prior to use.*

1.7 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

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

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[1] This test method is under the jurisdiction of ASTM Committee B02 on Nonferrous Metals and Alloys and is the direct responsibility of Subcommittee B02.05 on Precious Metals and Electrical Contact Materials and Test Methods.

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[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.

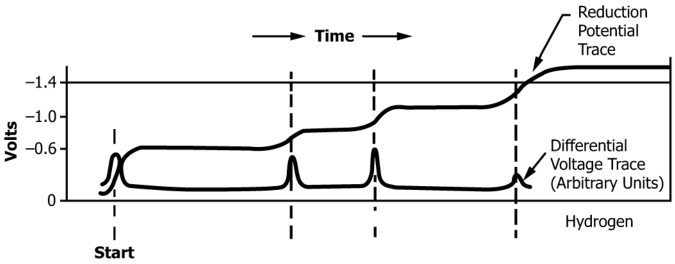


FIG. 1 Ideal Reduction Behavior of Oxide and Sulfide Films on Copper (from Ref 1)

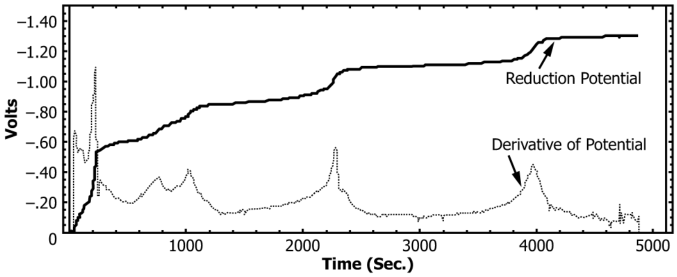


FIG. 2 Typical Reduction Behavior of Films on Copper from 72-h Exposure to the Humid Sulfur Vapor Test (see Test Method B809)

complete the reduction process at that particular voltage. 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.

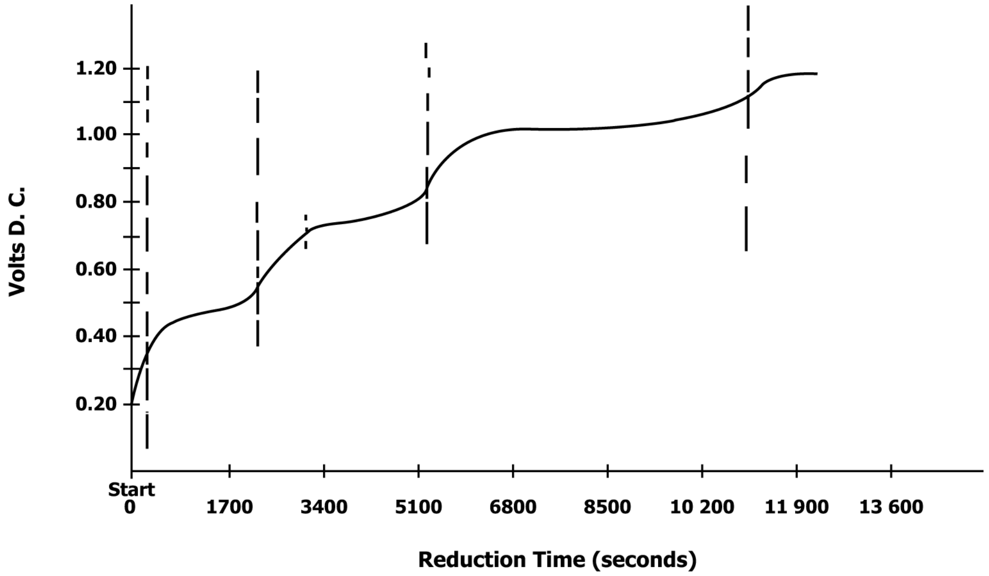
NOTE 4—Some surface analytical techniques (such as X-ray methods) can provide nondestructive identification of some compounds in the films, but such methods, for example, X-ray diffraction, can miss amorphous compounds and compounds present in quantities less than 5 % of the tarnish film volume.

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**).

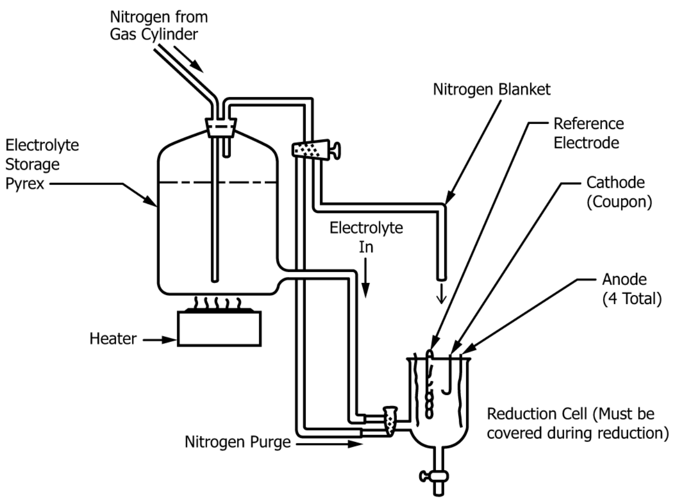


FIG. 4 Schematic of Reduction Cell with Storage Reservoir, for Procedure A (8.1.3.1)

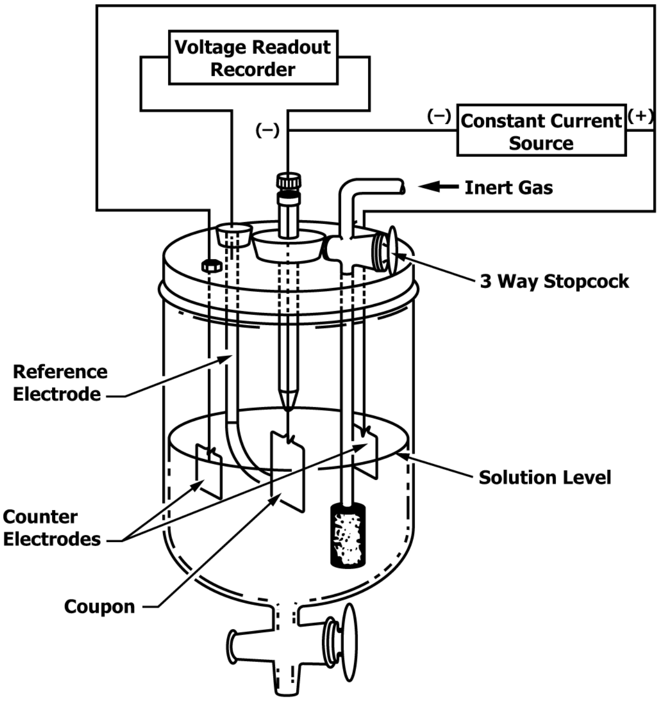


FIG. 5 Schematic of Reduction Cell for Procedure B (8.1.3.2)

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:

$$S_p = (X - X_p)/T \quad S_s = (X_s - X)/T \qquad (1)$$

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

$$S = (S_p + S_s)/2 \qquad (2)$$

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.

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[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.