Designation: A630 – 16aᵋ1

Standard Test Methods for
Determination of Tin Coating Weights for Electrolytic Tin Plate[1]

INTRODUCTION

Four test methods for determination of tin coating weights are described. These are typical methods and represent those most commonly used in the tin plate industry. Publication of these test methods is not intended to preclude the use of any other methods such as X-ray fluorescence measurement systems for control purposes by the consumer or supplier. However, in case of dispute, the referee method is to be used to determine conformance to Specification A624/A624M and Specification A626/A626M.

Sampling procedures for tin coating-weight testing and applicable standards for the specific class designation are outlined in Specification A624/A624M and Specification A626/A626M.

1. Scope*

1.1 These test methods include four methods for the determination of tin coating weights for electrolytic tin plate as follows:

Test Method	Sections
A—Bendix Test Method	3 to 9
B—Constant-Current, Electrolytic Test Method (Referee Method)	10 to 17
C—Sellar's Test Method	18 to 27
D—Titration Test Method	28 to 36

1.2 The values stated in inch-pound units are to be regarded as standard. The values given in parentheses are mathematical conversions to SI units that are provided for information only and are not considered standard.

1.3 *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 establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

A624/A624M Specification for Tin Mill Products, Electrolytic Tin Plate, Single Reduced

A626/A626M Specification for Tin Mill Products, Electrolytic Tin Plate, Double Reduced

D1125 Test Methods for Electrical Conductivity and Resistivity of Water

METHOD A—DETERMINATION OF THE TIN COATING WEIGHTS BY THE BENDIX TEST METHOD

3. Scope

3.1 This test method covers the determination of tin coating weights on steel plate.

4. Summary of Test Method

4.1 The procedure involves dissolution of tin from a tin plate anode in a dilute hydrochloric acid solution containing a

A Summary of Changes section appears at the end of this standard

measured excess of standard potassium iodate-potassium iodide solution. Excess iodine from the iodate-iodide solution is back titrated with standard sodium thiosulfate using a starch indicator.

5. Apparatus[3]

5.1 The detinning cell consists essentially of two cathodes of carbon rod, the sample that serves as an anode, and a beaker of dilute hydrochloric acid electrolyte. The carbon rods (6 by 0.25 in. or 152 by 6.35 mm, encased in porous porcelain thimbles) are suspended from a suitable frame about 1 in. (25 mm) apart. A small glass-enclosed magnet is attached to the frame in such a manner that it will hold the sample suspended midway between the two cathodes. A movable platform permits the beaker of electrolyte to be brought up around the assembly so that the sample will be completely immersed.

5.2 A source of direct current that can be regulated to supply up to 3 A at 3 to 5 V through the deplater is required.

5.3 Although regular laboratory glassware can be used, it is advisable to use automatic dispensing pipets or burets, a motor-driven stirrer for titrations, and a timing switch when large numbers of determinations are to be made.

5.4 *Precautions*—The apparatus must be kept in continuous operation to prevent iron in the solution adhering to the porous cells from oxidizing and subsequently liberating iodine from the potassium iodate-potassium iodide solution. If the instrument has been idle for some time, it is necessary to remove the ferric iron by running a disk of tinplate through the regular procedure before test samples are run.

6. Reagents

6.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society where such specifications are available.[4] Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

6.2 *Water*—Deionized or distilled water having a volume resistivity greater than 1 MΩ·cm at 25°C as determined by Nonreferee Method of Test Methods D1125.

6.3 *Hydrochloric Acid* (1.7 to 2.0 *N*)—Add 1 part of concentrated hydrochloric acid (HCl, sp gr 1.19, 36.5 to 38.0%) to 5 parts of water and mix well.

6.4 *Potassium Iodate-Potassium Iodide, Standard Solution* (0.0975 *N*)—Dissolve 3.48 g of KIO_3, 21.74 g of KI, and 1.21 g of NaOH in 1 L of distilled water. Standardize as follows: Transfer 0.2700 g of National Bureau of Standards tin to a 500-mL Erlenmeyer flask. Add 200 mL of HCl (1+1). Connect the flask to a carbon dioxide (CO_2) system and displace the air in the flask with CO_2. While continuing the flow of CO_2, heat the flask but do not boil violently. After the tin has dissolved add 0.5 g of antimony and 2 g of high-purity aluminum. Heat until the aluminum is completely dissolved and digest for an additional 10 min. Cool the flask to room temperature in running water while maintaining an atmosphere of CO_2. Disconnect from the CO_2 system and titrate with the KIO_3-KI solution using starch as an indicator. Calculate the tin titer, *T*, as follows:

$$T = A/B$$

where:
A = tin used (0.2700 g),
B = KIO_3-KI solution used for titration, mL, and
T = tin titer for above KIO_3-KI solution, (grams of tin/mL),
T = 17.28 = lb/base box (bb)/mL, for a 4-in.^{2} (25.81-cm^2) sample.

6.5 *Sodium Thiosulfate, Standard Solution (for coatings over 0.50 lb/bb)*—Dissolve 15.11 g of $Na_2S_2O_3 \cdot 5 H_2O$ and 1.11 g of NaOH in 1 litre of distilled water in a light-proof bottle. Allow this solution to age for 72 h, remix, and standardize as follows: Connect the bottle to the Bendix apparatus and titrate 20 mL of the standardized KIO_3-KI solution with the thiosulfate solution using the same procedure as is used for making weight of coating determinations, but ignore the stripping unit. The tin equivalent of the $Na_2S_2O_3$ solution in pounds per base box is equal to: 20/A × T × 17.28, where A = millilitres of sodium thiosulfate solution used in titrating 20 mL of standard KIO_3-KI solution. A chart can be prepared showing lb/bb/mL of thiosulfate.

6.6 *Sodium Thiosulfate, Standard Solution (for coatings 0.50 lb/bb and under)*—Dissolve 6.57 g of $Na_2S_2O_3 \cdot 5 H_2O$ and 2.78 g of NaOH in 1 litre of distilled water in a light-proof bottle. Larger quantities in the same proportions may be prepared if desired. Allow that solution to age for 72 h, remix, and standardize by the same procedure used for the stronger $Na_2S_2O_3$ solution but use only 10 mL of potassium iodate-potassium iodide solution.

6.7 *Starch Solution*—Heat 200 mL of distilled water to boiling in a Florence flask and slowly add 2.5 g of soluble starch paste while the solution is agitated. Add the hot starch solution to 500 mL of distilled water containing 2.5 g of NaOH. Dilute to 1 L and thoroughly mix.

7. Test Sample

7.1 Tin plate samples for coating weight determinations are obtained by stamping disks 2.257 ± 0.001 in. (57.33 ± 0.02 mm) in diameter which is equivalent to 4 in.^{2} (25.81 cm^2) of area (8 in.^{2} (52 cm^2) of surface area). Recommended methods of obtaining representative samples are described in the Tin

---

[3] Complete details and drawings of the apparatus are contained in U. S. Patent No. 2,455,726 entitled "Method for Electrolytic Stripping and Determination of Plating Metals." A suitable commercial supplier of the apparatus has been found to be the Wilkens-Anderson Company of Chicago.

[4] *Reagent Chemicals, American Chemical Society Specifications,* American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals,* BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary,* U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

Mill Products sections of the American Iron and Steel Institute's Steel Products Manual.[5]

8. Procedure

8.1 Make required electrical connections.

8.2 Add HCl (1+1) to the porous tubes containing the carbon cathodes.

8.3 Suspend the sample disk of tin plate from the magnetic holder.

NOTE 1—If it is desired to strip on one side only, mask the opposite side and reduce the current to half its normal value. If a heavy oxide film has developed on the tin plate during storage, the plate must be cathodically cleaned prior to testing.

8.4 Place a measured quantity of standardized KIO_3-KI solution into a 400-mL beaker (see 8.10). Simultaneously add 250 mL of dilute HCl and mix thoroughly.

8.5 Raise the beaker so that the sample and porous cells are immersed.

8.6 Turn on d-c current and adjust to give 0.5 A/in.^{2} of sample.

8.7 Time for complete removal of tin (see 8.10).

8.8 Remove the beaker and add approximately 5 mL of starch indicator solution.

8.9 Titrate with standardized $Na_2S_2O_3$ solution to the disappearance of the blue color.

8.10 The stripping times and amounts of KIO_3-KI solution to use are as follows:

Product	Stripping Time, s	Amount of KIO_3-KI Solution, mL
Electrolytic 100	90	20
Electrolytic 75	75	20
Electrolytic 50	60	10
Electrolytic 25	60	10
Electrolytic 10	45	10

Stripping time should not be longer than is required to remove all of the tin. Results will be high by approximately 0.01 lb/bb for each minute of over-stripping.

9. Reproducibility of Results

9.1 Arbitrary maximum spreads in intermill check tests show the reproducibility of test results by the Bendix Method to be as follows: ±0.02 lb/bb for 0.25–lb coatings, ±0.03 lb/bb for 0.75-lb coatings, and ±0.04 lb/bb for 1.25-lb coatings. Data have not been developed for 0.10-lb coatings.

METHOD B—DETERMINATION OF THE TIN COATING WEIGHTS BY THE CONSTANT CURRENT, ELECTROLYTIC METHOD (REFEREE METHOD)

10. Scope

10.1 This test method[6] may be used to determine not only the total tin coating weight but also to determine that part of the tin coating which is present as free tin and that part which is present in the alloyed form.

11. Summary of Test Method

11.1 In this test method, the tin is stripped from a sample of tin-plate anodically at constant current in an electrolyte of the hydrochloric acid. The potential difference developed between the sample and a reference electrode is plotted against time on a strip chart recorder or an electric digital readout. The time required for stripping the free tin and alloyed tin, respectively, are read from the resulting chart (see Fig. 1) or a digital readout. Since the stripping current has been preset, the free-tin and alloy-tin coating weights are calculated by employing Faraday's law of electrolysis.

12. Calibration and Standardization

12.1 Determine the weight loss of pure tin specimens electrolyzed for a given time interval, expressing the results as milligrams or pounds of tin per base box per second.

12.2 The test specimen should be a 4-in.^{2} disk of pure tin approximately 0.20 in. (5.1 mm) thick.

12.3 The milliammeter should be frequently checked using a precision milliammeter.

13. Available Constant Current Procedures

13.1 There are three commercially available constant current, electrolytic units that are in common use. Either of the following, or equivalent equipment, can be used as an acceptable referee method:

13.1.1 *Willey & Kunze Coulometric Test Method*—Supplier will provide set up, start up and running procedures.[7]

13.1.2 *The Stannomatic Test Method*—Supplier will provide set up, start up and running procedures.[8]

---

[5] Available from American Iron and Steel Institute (AISI), 1140 Connecticut Ave., NW, Suite 705, Washington, DC 20036, http://www.steel.org.

[6] See Kunze, C. T., and Willey, A. R., "Electrolytic Determination of Tin and Tin-Iron Alloy Coating Weights on Tin Plate," *Journal*, Electrochemical Society, Vol 99, No. 9, September 1952, pp. 354–359; and "Methods for Determination of Coating Weights of Tin Plate," American Iron and Steel Institute, December 1959, pp. 19–26.

[7] Available from Coulometric Systems, Bergholtz, OH.

[8] Available from Products Distribution Service Division, Wilkens Anderson Co., 4525 West Division St., Chicago, IL 60651.
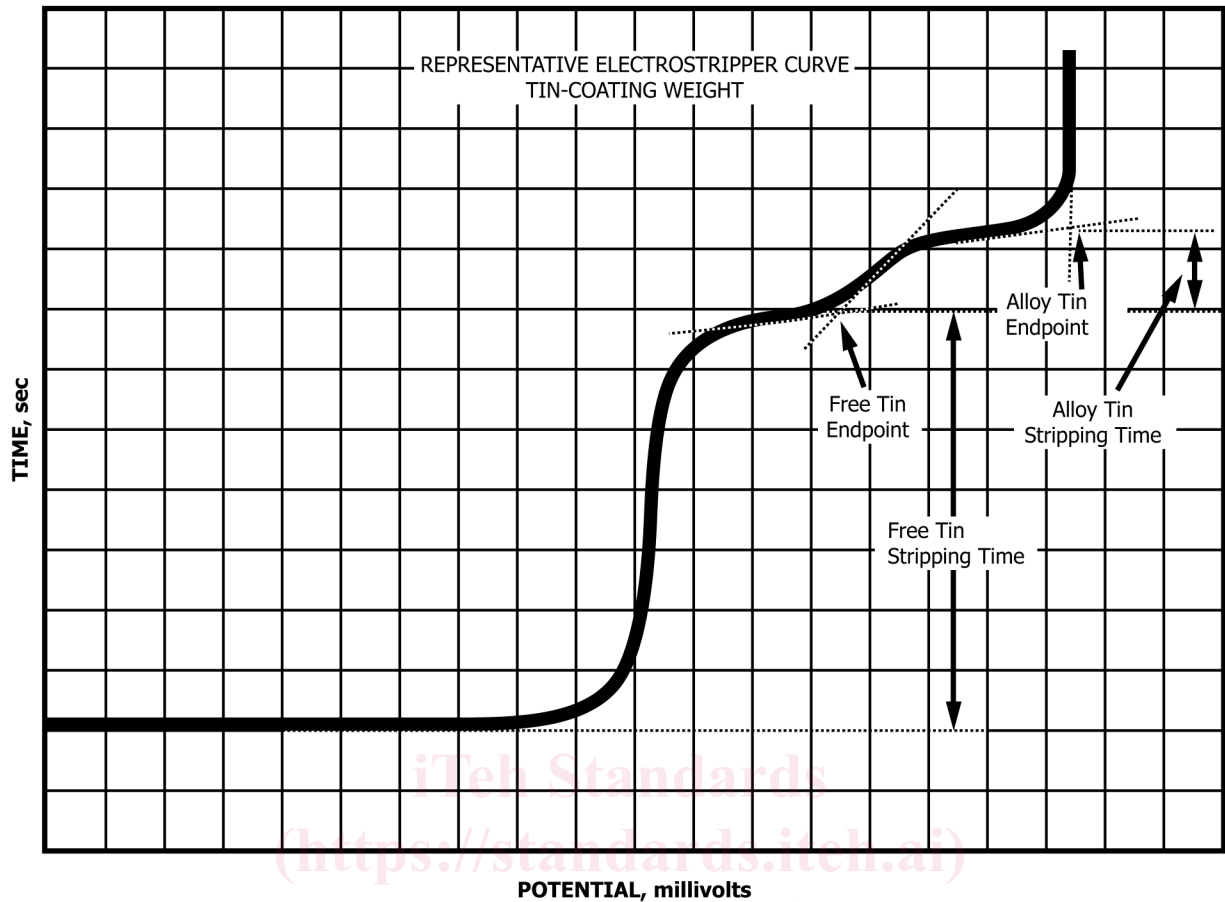
REPRESENTATIVE ELECTROSTRIPPER CURVE
TIN-COATING WEIGHT

Alloy Tin
Endpoint

Free Tin
Endpoint

Alloy Tin
Stripping Time

Free Tin
Stripping Time

TIME, sec

POTENTIAL, millivolts

FIG. 1 Representative Electrostripper Curve

13.1.3 *The Donart Test Method*—Supplier will provide setup, start, and running procedures.[9]

14. Willey & Kunze Coulometric Test Method

14.1 In this test method, the tin is electrolytically removed from a 4 in.^{2} (25.807 cm^2) circular sample of tinplate anodically at constant current in an electrolyte of 1.0 N hydrochloric acid. The potential difference developed between the sample and a glass calomel reference electrode is plotted against time on a strip chart recorder. The time required for stripping the free tin and alloy tin, respectively are read from the resulting chart (see Fig. 1) or on an electronic digital readout. Since the stripping current is constant and preset, the free tin and alloy tin coating weights are calculated by employing Faraday's law of electrolysis.

14.2 *Significance and Use:*

14.2.1 The amount of tin coating is directly associated with the economics of producing tinplate and the performance of the container or part for which such plate is used. Therefore, the test method was developed for accuracy and as a control. The amount of tin combined in the alloy layer is also essential as the continuity and amount plays an important part in its functional properties. This test method is so designed that the tin coating is determined on only one side of the specimen at a time. This is useful when determining tin coatings on differential tinplate.

14.3 *Apparatus:*

14.3.1 This instrument (Model 8014) consists of an ammeter, volt meter, constant current source and strip recorder. A cell and sample holder are provided.

14.4 *Reagents:*

14.4.1 *Electrolyte*—1.0 N hydrochloric acid (HCl).

14.5 *Sample Size:*

14.5.1 Tinplate samples for coating weight determinations are obtained by stamping discs 2.257 $\pm$ 0.001 in. (57.33 $\pm$ 0.02 mm) in diameter. This is equivalent to 4 in.^{2} (25.81 cm^2) of area of one side. Sampling procedures for tin coating weight testing and applicable standards for the specific class designation are outlined in Specifications, A624, A624M, A626, and A626M.

14.6 *Interferences:*

14.6.1 The distance of the cathode from the sample is important and should be 0.75 $\pm$ 0.25 in. (1.90 $\pm$ 0.64 cm). Also, it is important that the cathode be approximately the same shape as the sample so that all parts of the anode are equidistant from the cathode.

14.7 *Procedure:*

---

[9] Available from Donart Electronics, 1005 Robinson Hwy, McDonald PA, 15057.

4

14.7.1 Clean the tinplate sample disk by cathodically treating in 0.5% sodium carbonate solution for 10 s with a current density of 0.5 A/in.[3]

14.7.2 An alternative procedure is to wipe the surface of the sample with a clean cloth saturated with acetone, this to be followed by immersion of disk in acetone, removing, and air drying. The procedure under 16.1 is preferred as it reduces the tin oxide present on the surface to metallic tin and improves the definition of the end point.

14.7.3 After following steps under Section 10, the apparatus is ready for determining tin coating weight of the samples. Exactly the same procedure is used for samples with unknown tin coating weights as the "dummy" samples. The recommended recorder has a chart speed of 2 in./min and uses a chart having 10 divisions/in. Therefore, each division is equivalent to 3 s.

14.8 *Calculation:*

14.8.1 Calculate results as follows:

$$A = ITC \tag{1}$$

$$B = 0.65 \, IT_1C \tag{2}$$

$$D = A + B \tag{3}$$

where:

A = free tin coating weight, lb/bb
I = stripping current, A,
T = time required for the removal of free tin, s,
C = 0.02126 or the electrochemical equivalent of tin expressed in lb/bb for a 4-in.^{2} or 25.81-cm^2 area of tinplate,
B = alloy tin coating weight, lb/bb,
0.65 = that portion of the current required for removal of the alloyed tin. Since the tin-iron alloy composition is FeSn$_2$ and these elements enter the solution stoichiometrically with a two-electron loss for each atom of tin and iron, only two thirds of the current is dissipated for the dissolution of tin. Consequently, the total alloy time must be corrected to compensate for the electrolysis of the iron,
T_1 = time required for the removal of the alloy layer, s, and
D = total tin coating weight, lb/bb.

15. The Stannomatic Test Method

15.1 *Principle of Equipment Operation:*

15.1.1 The free tin and the alloy tin covering the surface of the tin plate to be examined are dissolved electrolytically. The test size is exactly defined on both sides of the sample by two precision gaskets. The free tin and iron-tin alloy results are a function of the amount of current (Coulombs) used for stripping and are displayed on a numeric readout.

15.2 *Apparatus:*

15.2.1 This instrument consists of a stripping cell with a standardized sample size control. The stripping controller has a numeric readout which displays separately free tin and alloy tin on both sides of the test sample.

15.3 *Reagent:*

15.3.1 *Electrolyte*—As specified by equipment manufacturer.

15.4 *Sample Size:*

15.4.1 Tinplate samples can be of various dimensions but must be large enough to afford a test area at least $1\frac{1}{2}$ in. in diameter. The test area must be reasonably flat. Sampling procedures for tin coating weight testing and applicable standards for the specific class designations are outlined in Specifications A624/A624M and A626/A626M.

15.5 *Preparing Sample:*

15.5.1 The surface of the tested sample shall be clean. Oil, grease and organic coating such as lacquer shall be removed with suitable solvents. Remove oxides, passivation oxide coatings, and corrosion products, by carefully burnishing the test surface with a clean, soft pencil eraser. Also, cleaning with a tissue impregnated with acetone or solvent is usually sufficient. Electrochemical cleaning may be necessary occasionally.

15.6 *Special Precautions:*

15.6.1 It should be noted that the reading of the alloy counter represents the actual weight of tin contained in the FeSn$_2$ alloy. If the tinplate has not undergone heat treatment the alloy layer does not form. Unless the instrument is adjusted to the proper setting, the alloy counter will become inoperative, and the automatic program will stop after the first layer is completely removed.

15.6.2 Automatic prepolarization and light electro-cleaning of cathodes is performed during the first 3 s after each start of the Stannomatic III or later model.

15.6.2.1 During this initial sequence the auxiliary anodes are activated against the cathodes. This operation may be extended by pressing the start button for several seconds.

15.6.2.2 Failure of this function may cause ghost layers and subsequent premature switch over of the sequence.

15.6.3 One condition for reliable results and a well-defined inflection point displayed on the instrument meters is a uniform stripping of the whole surface.

15.6.3.1 After completion of the measurement the test surface should be examined visually. If the dissolution of the coating is not complete the measurement should be discarded and repeated.

15.6.4 The following factors influence the uniformity of stripping:

15.6.4.1 Contaminated or dirty cathode.

15.6.4.2 Cathode not well fitted and located.

15.6.4.3 Cathode and fixing part substituted with non-original parts.

15.6.4.4 Sample punched too near the edges of the metal strip may have a non-uniform coating.

15.6.4.5 Sample dirty, corroded, partially or totally coated with organic coating.

15.6.4.6 Sample with a thick passivation layer.

16. The Donart Electronics Test Method

16.1 *Principle of Equipment Operation:*

16.1.1 The Model 3300 Coulometric Tester is an advanced instrument for measuring tin coating weights for electrolytic tin according to ASTM Standard A630 and ISO 2177. The Model

3300 is based on the constant current, electrolytic method. By controlling the diameter of the area to be stripped, and the use of a precision constant current source, the Model 3300 Coulometric Tester can accurately calculate tin and alloy coating weights.

16.2 *Apparatus:*

16.2.1 The unit consists of two electrolyte cells fitted with cathodes and anodes. A precision gasket is used to uniformly seal the sample. The electrolytic cells have provisions for filling the cell. Each cell is designed with an automatic decavitation cell to eliminate air bubbles from being trapped on the surface of the sample that could cause errors in measurement. Redundant grounding contacts are used to ensure good grounding of sample.

16.2.2 A custom filling valve is provided to electrically isolate cells in an effort to obtain smoother and more precise curves.

16.2.3 A precision constant current power supply is provided. Three stripping currents can be applied to both sides of sample. Using the lowest current setting will allow accurate measurements of tin coating on fully alloyed products.

16.2.4 A precision 16 bit A/D converter is provided for measuring current and voltage throughout the test. Current used for calculation is actual current measured throughout the test. By measuring actual current throughout the test and using the average value for calculations, this makes the Donart System self-calibrating.

16.3 *Reagent:*

16.3.1 Electrolyte is a mix of 420 ml of hydrochloric acid (HC1) with one gallon (3.78 L) of distilled water.

16.4 *Sample Size:*

16.4.1 Most tin mill laboratories have access to a 2 in. punch that is used for procuring samples for various tests throughout the mill. These samples work well in the Model 3300 Coulometric Tester. However, provisions in the design of the Model 3300 will allow various sizes and shapes to be tested. Custom cells have been manufactured to measure very small sample sizes.

16.5 *Preparing Sample:*

16.5.1 Cleaning the sample prior to testing with a solvent will improve curve quality and prevent false triggers.

16.6 *Software:*

16.6.1 Special software is provided so the user can easily enter data needed for the test. At the end of the test, measurements are screened, showing the actual test curve. Software provisions for modifying inflection points are provided. Software automatically stops test after complete removal of coating.

16.7 *Special Precautions:*

16.7.1 Electrolyte should not be reused more than three times.

16.7.2 Cell seals should be checked for leaks and replaced when necessary.

16.7.3 After testing, sample can be coated with copper phosphate solution to determine crispness of de-plated area.

16.7.4 Yearly calibrations of constant current source should be maintained.

17. Precision and Bias[10]

17.1 There is no bias data due to the lack of a certified reference standard for tin coating weights.

17.2 The precision of this test method is based on an intralaboratory study with a total of 13 participating laboratories.[10]

METHOD C—DETERMINATION OF THE TIN COATING WEIGHTS BY THE SELLAR'S METHOD

18. Scope

18.1 This test method covers the determination of the total weight of tin carried by a unit area of tinplate.

19. Summary of Test Method

19.1 The tinplate sample is dissolved in hydrochloride acid. The tin goes into the solution as stannous chloride. Accidental air oxidation of the tin from the stannous to the stannic form is prevented by completing the analysis under an atmosphere of carbon dioxide.

[10] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:A01-1004. Contact ASTM Customer Service at service@astm.org.

Coating Weight, each surface lb/base box [g/m²]	Average[A]	Repeatability[B] Standard Deviation	Reproducibility[C] Standard Deviation	Repeatability Limit[D]	Reproducibility Limit[E]
		sr	sR	r	R
0.05 [1.1]	0.0498 [1.1155]	0.0028 [0.0627]	0.0032 [0.0717]	0.0079 [0.1770]	0.0090 [0.2016]
0.10 [2.2]	0.0876 [1.9622]	0.0022 [0.0493]	0.0034 [0.0762]	0.0061 [0.1366]	0.0094 [0.2106]
0.20 [4.4]	0.1727 [3.8685]	0.0030 [0.0672]	0.0054 [0.1210]	0.0083 [0.1859]	0.0151 [0.3382]
0.25 [5.6]	0.2381 [5.3334]	0.0038 [0.0851]	0.0131 [0.2934]	0.0106 [0.2374]	0.0366 [0.8198]
0.50 [11.2]	0.4729 [10.5930]	0.0072 [0.1613]	0.0161 [0.3603]	0.0202 [0.4525]	0.0452 [1.0125]
0.75 [16.8]	0.7459 [16.7082]	0.0197 [0.4413]	0.0217 [0.4861]	0.0552 [1.2365]	0.0609 [1.3642]
1.00 [22.4]	0.9814 [21.9834]	0.0279 [0.6250]	0.0303 [0.6787]	0.0780 [1.7472]	0.0848 [1.8995]

[A] The average of the laboratories' calculated averages.
[B] Repeatability - addresses variability between independent test results gathered from within a single laboratory (otherwise known as intralaboratory testing).
[C] Reproducibility - addresses variability among single test results gathered from different laboratories (otherwise known as interlaboratory testing).
[D] Repeatability Limit (r) – The maximum difference between two results, obtained under repeatability conditions, that is accepted as plausible due to random causes under normal and correct operation of the test method; "r" is the interval representing the critical difference between two test results for the same material, obtained by the same operator using the same equipment on the same day in the same laboratory.
[E] Reproducibility Limit (R) – The maximum difference between two results, obtained under reproducibility conditions, that is accepted as plausible due to random causes under normal and correct operation of the test.