



Designation: D7639 – 22

Standard Test Method for Determination of Zirconium Treatment Weight or Thickness on Metal Substrates by X-Ray Fluorescence¹

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1. Scope

1.1 This test method covers the use of X-ray fluorescence (XRF) spectrometry for the determination of the mass of zirconium (Zr) coating weight per unit area of metal substrates.

1.2 Coating treatments can also be expressed in units of linear thickness provided that the density of the coating is known, or provided that a calibration curve has been established for thickness determination using standards with treatment matching this of test specimens to be analyzed. For simplicity, the method will subsequently refer to the determination expressed as coating weight.

1.3 XRF is applicable for the determination of the coating weight as zirconium or total coating weight of a zirconium containing treatment, or both, on a variety of metal substrates.

1.4 The maximum measurable coating weight for a given coating is that weight beyond which the intensity of the characteristic X-ray radiation from the coating or the substrate is no longer sensitive to small changes in weight.

1.5 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

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 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.*

¹ This test method is under the jurisdiction of ASTM Committee D01 on Paint and Related Coatings, Materials, and Applications and is the direct responsibility of Subcommittee D01.53 on Coil Coated Metal.

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2. Referenced Documents

2.1 *ASTM Standards:*²

E177 Practice for Use of the Terms Precision and Bias in ASTM Test Methods

E691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method

3. Summary of Test Method

3.1 The test specimen is placed in the X-ray beam, and the resultant peak intensity of the zirconium Ka line (at 0.0786 nm or 15.747 keV) or the zirconium La line (at 0.606 nm or 2.042 keV) is measured. The intensity (in counts or counts per second) is then compared to a previously prepared calibration curve or equation to obtain the coating weight of zirconium treatment in mg/m^2 or mg/ft^2 (or μm or nm).

3.2 The exact relationship between the measured number of counts and the corresponding coating weight (or coating thickness) must be established for each individual combination of substrate and zirconium-containing treatment. Usually determined by the treatment supplier, this relationship is established by using primary standards having known amounts of the same treatment applied to the same substrate composition as the test specimens to be measured.

4. Significance and Use

4.1 The procedure described in this test method is designed to provide a method by which the coating weight of zirconium treatments on metal substrates may be determined.

4.2 This test method is applicable for determination of the total coating weight and the zirconium coating weight of a zirconium-containing treatment.

5. Apparatus

5.1 *X-Ray Fluorescence Spectrometer*, capable of measuring the intensity of zirconium Ka or La line, and establish the

² 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.

relationship between peak intensity and coating weight. The spectrometer's design must include, as a minimum, the following features:

5.1.1 *Source of X-Ray Excitation*, X-ray tube with excitation above 2.55 keV if measuring the zirconium La line, or above 18 keV if measuring the zirconium Ka line.

5.1.2 *X-Ray Detector*, with high sensitivity and capable of discriminating between zirconium La or Ka radiation and other X-rays of higher or lower energies.

5.1.2.1 In the case of wavelength dispersive X-ray fluorescence (WDXRF), this can be an analyzing crystal (for example, fixed channel, goniometer) setup to detect the zirconium X-rays (La or Ka line). Germanium 111 has been found to be acceptable for the Zirconium La line and LiF220 or LiF200 for the zirconium Ka line.

5.1.2.2 In the case of energy dispersive X-ray fluorescence (EDXRF), it can be a proportional counter, or a semiconductor such as a PIN diode or a silicon-drift detector.

5.1.3 *Pulse-Height Analyzer*, or other means of energy discrimination.

5.1.4 *Optical Path*, specified by manufacturer. A helium or vacuum path is recommended when measuring the zirconium La line in order to minimize the attenuation of the X-rays by the air in the optical path. The zirconium Ka line has a higher energy and its intensity will not be affected by air.

5.1.5 *Signal Conditioning and Data Handling System*, whereby a coating weight versus X-ray counts curve may be established within the system for the direct readout of coating weight.

5.1.6 *Sample Spinner (optional)*, to reduce the effects of coating weight variation across the test specimen.

6. Calibration Standards and Test Specimens

6.1 *Calibration Standards*—should be specimens for which the coating weight has been well characterized by other analytical procedures such as x-ray photoelectron spectroscopy, Auger emission spectroscopy, glow discharge optical emission spectrometry, weigh-strip-weigh method, or other depth-profiling analytical technique.

6.2 *Blank (bare and untreated) Specimen (optional)*, should be of the same metal substrate on which the treatment coating weight is to be determined. It may be necessary to prepare a blank specimen from a treated specimen if an untreated specimen is not available. To best imitate a bare, untreated blank, abrade a treated specimen that is from the same metal specimen as the test specimen using a small abrasive pad or zirconium-free rotating sanding disc.

NOTE 1—When using an abrasive pad, the first abrading is made parallel with the rolling direction of the metal, the second abrading is made perpendicular to the rolling direction of the metal, and the third abrading is made parallel with the rolling direction of the metal. This procedure should be repeated until constant readings are obtained. Always use the same side of the metal substrate from which the readings of the treated specimen will be taken.

6.3 *Calibration Standards and Test Specimens*—shall be cut to the required size, if necessary, for measurement by the instrument.

6.4 All calibration standards and test specimens shall be flat in the area of measurement and free of burrs and distortions

that would prevent proper seating in the analysis chamber or the specimen holder, or proper seating of the handheld analyzer on the standard's surface.

6.5 The treatment on the substrate should be uniform in the area of measurement. If the coating weight might vary across the surface, it is recommended to analyze the test specimen in three different areas and use the average reading as the result.

6.6 The area of measurement should be maintained free of foreign materials. The test specimen shall be handled only by the edges that are outside of the area to be measured.

6.7 The coated area of the test specimen should be larger than the measured area.

6.8 The calibration standards and test specimens should be measured over the X-ray port using the same rolling direction of the metal. This is not necessary for instruments operating with a sample spinner.

NOTE 2—The orientation of the X-ray tube and detector is specified by the XRF manufacturer.

7. Calibration Procedure

7.1 Set up the instrument calibration and operating parameters according to the chemical supplier and instrument manufacturer's recommendations.

7.2 Establish calibration curve by carefully determining the intensity of the emitted zirconium radiation from each of the calibration standards (a minimum of five standards is recommended). Obtain three readings for each standard (measured across the standard's surface if it is suspected that the zirconium coating weight might be varying).

7.3 Construct a calibration by using the software and algorithms supplied by the equipment manufacturer, establishing the relationship between zirconium intensity and zirconium treatment coating weight.

7.4 When using drift correction monitors, determine the intensity of the drift correction monitor sample(s).

7.5 Immediately after completing the calibration, determine the zirconium coating weight of one or more calibration check sample. Check samples can be stable, well-characterized materials. The differences between two measured values shall be within the repeatability of this test method. When this is not the case, the stability of the instrument and the repeatability of the sample preparation should be investigated and corrective measures taken. Calibration check samples should have the same substrate and same treatment as calibration standards and samples to be measured.

8. Preparation of Apparatus

8.1 *Instrument Setup*—Before using any XRF spectrometer, it is essential that the instrument is performing to the manufacturer's specifications. Consult with the manufacturer on how to perform spectrometer quality control checks.

9. Procedure

9.1 Immediately after a change to the metal substrate which is being coated, measure a blank specimen of the new metal substrate following the procedure in 9.2 and 9.3.

TABLE 1 Precision Data (units: nm)

Material	Average ^A		Repeatability Standard Deviation	Reproducibility Standard Deviation	Repeatability Limit	Reproducibility Limit
	\bar{X}	$S\bar{X}$	s_r	S_R	r	R
F4	34.26	0.95	1.79	1.95	5.01	5.46
F8	91.11	5.87	5.82	8.06	16.29	22.55

^A Average of laboratories' calculated averages.

NOTE 3—The value of the measured blank specimen may be negative, positive or 0.

NOTE 4—A large negative or positive value of the measured blank specimen may indicate that the substrate is substantially different than the calibration standards. Evaluate if the calibration is valid for the new substrate.

9.2 Following manufacturer's instructions, place the test specimen in the spectrometer for analysis or, in the case of handheld spectrometers, place the instrument's analysis head against the test specimen to measure. If the instrument does not operate with a sample spinner, ensure that test specimens are measured with the same rolling orientation. If coating weight is even, measure each test specimen once to obtain the zirconium coating weight in the unknown test specimen. If coating weight is not even, measure three sub-specimens (or three different locations on the same specimen if spectrometer allows this), once each, and obtain the average of the readings.

9.3 It is recommended to measure a quality control sample periodically, typically on a daily basis, to verify that the method is in statistical control.

10. Calculation

10.1 The zirconium coating weight on the test specimen is automatically calculated from the calibration curve.

10.2 Subtract the value of the blank specimen measured in 9.1 from the calculated zirconium coating weight.

NOTE 5—Some XRF instruments have software that can perform this subtraction automatically. Follow the manufacturer's instructions.

11. Report

11.1 Report the results as zirconium treatment coating weight (in mg/m² or mg/ft²) or thickness (in μm or nm).

12. Precision and Bias³

12.1 The precision of this test method is based on a preliminary interlaboratory study conducted in 2009, which included eight laboratories. All laboratories calibrated their spectrometers using the same calibrations standards and measured the same test specimens (sent from one laboratory to another in order to prevent errors due to differences in coating thickness from set to set). The laboratories reported ten replicate test results for each of the two different materials provided. Every "test result" reported represents an individual determination. Except for the use of data representing just two materials, Practice E691 was followed for the design and

analysis of the data; the details are given in ASTM Research Report No. RR:D01-1151. Only the coating thickness was known for the calibration standards (that is, coating treatment density or coating weight were not known), therefore this precision study only shows data in thickness units (nm).

12.1.1 *Repeatability Limit (r)*—Two test results obtained within one laboratory shall be judged not equivalent if they differ by more than the "r" value for that material; "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.

12.1.1.1 Repeatability limits are listed in Table 1.

12.1.2 *Reproducibility Limit (R)*—Two test results shall be judged not equivalent if they differ by more than the "R" value for that material; "R" is the interval representing the critical difference between two test results for the same material, obtained by different operators using different equipment in different laboratories.

12.1.2.1 Reproducibility limits are listed in Table 1.

12.1.3 The above terms (repeatability limit and reproducibility limit) are used as specified in Practice E177.

12.1.4 While any judgment in accordance with statement 12.1.1 and 12.1.2 would have an approximate 95 % probability of being correct, due to the limited number of materials tested, the precision statistics for this ILS must not be treated as exact mathematical quantities which are applicable to all circumstances and uses. The scope of the results guarantees that there will be times when differences greater than predicted by the ILS results will arise, sometimes with considerably greater or smaller frequency than the 95 % probability limit would imply. Consider the repeatability and reproducibility limits as a general guide, and the associated probability of 95 % as only a rough indicator of what can be expected.

12.2 *Bias*—At the time of the study, there was no accepted reference material suitable for determining the bias for this test method, therefore no statement on bias is being made.

12.3 The precision statement was determined through statistical examination of 160 results, from eight laboratories, on two different materials, described as:

F4: ZrOx-coated cold-rolled steel

F8: ZrOx-coated electro-galvanized steel

13. Keywords

13.1 benchtop; coating weight; EDXRF; handheld; pre-treatment; substrate; thickness; treatment; WDXRF; X-ray fluorescence; zirconium

³ Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D01-1151. Contact ASTM Customer Service at service@astm.org.