National Institute of Standards & Technology

Certificate of Analysis

Standard Reference Material® 2569

Lead Paint Films for Children's Products

This Standard Reference Material (SRM) is intended for use in the evaluation of lead in paint on films or similar matrices using non-destructive, instrumental methods of analysis. SRM 2569 consists of three different paint films each containing a specified amount of lead (Pb) and each supported on polyester sheet. SRM 2569 is not intended for use in test method calibration for thickness and density. A unit of SRM 2569 consists of three coupons of paint on polyester and five coupons of uncoated polyester. The coupons are approximately 73 mm long by 52 mm wide. The paint films are cured lacquer having a specified thickness in the range of 20 µm to 45 µm.

Certified Values: Certified values for amount of Pb as mass fraction in the paint film, mass of Pb per unit area of paint film, and paint film thickness of the three coated components of SRM 2569 are reported in Table 1 [1]. Value assignment categories are based on the definitions of terms and modes used at NIST for certification of chemical reference materials [2]. A NIST certified value is a value for which NIST has the highest confidence in its accuracy, in that all known or suspected sources of bias have been investigated and taken into account. A certified value is the present best estimate of the true value based on the results of analyses performed at NIST and collaborating laboratories.

Reference Values: Reference values for paint film density are reported in Table 2. Reference values are non-certified values that are the best estimates of the true values; however, the values do not meet the NIST criteria for certification and are provided with associated uncertainties that may not include all sources of uncertainty [2].

Information Value: An information value for the nominal thickness of the polyester sheet supporting the paint films is reported in Table 3. An information value is considered a value that will be of interest to the SRM user, but insufficient information is available to assess the uncertainty associated with the value.

Expiration of Certification: The certification of **SRM 2569** is valid, within the measurement uncertainty specified, until **16 August 2021**, provided the SRM is handled and stored in accordance with the instructions given in this certificate (see "Instructions for Handling, Storage, and Use"). The certification is nullified if the SRM is damaged, contaminated, or otherwise modified.

Maintenance of SRM Certification: NIST will monitor this SRM over the period of its certification. If substantive technical changes occur that affect the certification before the expiration of the certificate, NIST will notify the purchaser. Registration (see attached sheet) will facilitate notification.

Coordination of the technical measurements for certification of SRM 2569 was performed by J.R. Sieber of the NIST Analytical Chemistry Division.

Measurements for homogeneity testing and value assignment of SRM 2569 were performed by S.E. Long, A.F. Marlow, J.L. Molloy, K.E. Murphy, and J.R. Sieber of the NIST Analytical Chemistry Division; D. Cobb of the U.S. Consumer Product Safety Commission (CPSC), Rockville, MD, and M. Van de Mark of Rolla Coatings, Rolla, MO. Additional homogeneity measurements were performed by Z. Chen, D. Li, and A. Vershinin of X-Ray Optical Systems, East Greenbush, NY and by K. McIntosh at the New York State Department of Health, Albany, NY.

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Certificate Revision History on Last Page

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Statistical consultation for the value assignment of SRM 2569 was provided by S.D. Leigh and A.L. Rukhin of the NIST Statistical Engineering Division.

Support aspects involved in the issuance of this SRM were coordinated through the NIST Measurement Services Division.

INSTRUCTIONS FOR HANDLING, STORAGE, AND USE

The following instructions cover the use, handling, and storage of SRM 2569. Further explanations of the properties of this material and its uses are provided in "A Guide to Using SRM 2569 to Validate Analytical Methods" [3]. Each coupon of SRM 2569 is labeled on the side opposite to the paint coating using a small, self-adhesive label. The paint film is certified across the entire coupon area; however, measurements must not be made at the area behind the label. The coupons are flexible and may be curved to conform to a cylinder ≥1 cm diameter. To use the SRM to simulate measurement of a single layer of paint on a plastic substrate, measure the side of a coupon opposite to the labeled side. For determinations of Pb, the coupons were designed to provide at least four unique measurement locations for X-ray spectrometers viewing an area of 1 cm^2. Larger and smaller areas may be measured. The recommended minimum measurement area is 0.75 mm^2. Use of a viewing area <1 cm^2 requires measuring three or more separate locations and calculating the median of the results. A useful approximation of the standard uncertainty of the median is the standard deviation of the mean multiplied by 1.25 [4].

Level 2 Heterogeneity: The Level 2 coupons contain regions roughly spherical and approximately 50 µm diameter and smaller with high Pb concentrations that are scattered randomly across the surface of the coupon. The recommended minimum measurement area and the requirement to calculate the median of three or more measurements serve to ensure that the spatial heterogeneity caused by these regions does not influence measurement accuracy. In the event that one measurement out of three produces a result greater than twice the median of three measurements, the high value should be replaced by a new measurement of a different location. See reference 3 for additional information.

Store the SRM in a cool, dry location, preferably in its original container. When handling coupons, wear gloves to prevent contamination by body oils and moisture. Avoid exposure to light during storage. In the normal course of handling a coupon, it may become contaminated with dust, dirt, or oil. If it is necessary to clean a coupon, first place it on a soft cloth on a smooth, flat surface. Use a clean, dry, soft cloth to gently brush dust or dirt from the film. A gentle stream of air from a clean supply will work also. ***Do not*** blow from the mouth because this results in moisture and oils being directed at the coupon. To remove oily residues, use a clean soft cloth to gently rub the surface until the oil is no longer visible. ***Do not*** use alcohol or organic solvents because they will destroy the paint. Frequent cleaning will shorten the useful life of the paint layer.

Care must be taken to avoid damage to the paint film when using a procedure that requires direct contact of equipment with the paint surface. SRM 2569 paint films are not protected by a clear coating layer. Physical abrasion of the coupons' surfaces must be avoided. ***Do not*** fold or crease the material. ***Do not*** cut coupons because cutting results in chipping of the paint at the cut edge that worsens with repeated handling. The presence of loose flakes of paint, however small, in a measured area will cause biased results. ***Do not*** measure areas that include visible voids or cracks in the green coating.

Five coupons of uncoated polyester are provided to enable users to simulate paint on thicker polymer substrates by stacking one or more uncoated coupons beneath a coated coupon, and measuring the coated side. Measurements of paint layers hidden beneath a layer of polymer may be simulated by measuring Pb through the uncoated coupons. Stacked coupons must be in close contact to each other. A single coupon of the supplied polyester will attenuate Pb L-series X rays by approximately 3 % to 5 % for measurements made normal to the surface. Cl K-series X rays from the paint will be attenuated approximately 95 % by a sheet of the polyester substrate. Pb M-series X rays will be difficult to detect when measuring the substrate side of a Pb-containing coupon because the polyester absorbs approximately 99 % of Pb M-series X rays passing into it from the paint.

Exposure to X rays from low-power sources, including sources used in handheld spectrometers, small beam semi-monochromatic sources, and secondary target sources, can be made repeatedly without noticeable damage to the lacquer. However, exposure to X rays from high-power sources, such as direct irradiation from side- and end-window X-ray tubes operated at 0.5 kW and higher, will result in observable darkening of the paint and polyester. Experience has shown that 10 exposures of a single location to a high-power source for 600 s does not change the measured Pb count rates for L-series and M-series lines. Additional exposures are not recommended.

Prolonged exposure (>30 min) to a 3 kW Rh tube source caused damage including substantial blackening and flaking of the paint film.

SOURCE, PREPARATION, AND ANALYSIS[(1)]

The material for SRM 2569 was created for NIST by Rolla Coatings by applying specially formulated lacquer compositions to cleaned, uncoated polyester panels (Leneta Corp., Mahwah, NJ, cat. no. P300-7C) using an automated draw down technique. Lead was added to the lacquer as lead 2-ethylhexanoate. The lacquers also contain chlorinated dye to impart the green color and to enhance X-ray contrast between the coating and the polyester substrate. For Level 1 and Level 2 compositions, a chlorinated paraffin wax was added to the lacquers to further enhance X-ray contrast.

During the characterization of paint films and polyester substrate material, elements other than Pb were detected but not quantified. Elements detected in the uncoated polyester coupons are Na, P, S, Mn, Fe, Cu, Sr, and Sb. Elements detected in the coated SRM coupons are Na, Al, Si, P, S, Cl, Mn, Fe, Cu, Sr, Sn, and Sb. Of these elements, Cl and Cu are present in the dye compound used in all three levels, Cl was intentionally added to the lacquer formulations for Level 1 and Level 2 (see above), and Sb is present as residual catalyst in polyester.

Measurements for homogeneity testing of SRM 2569 were performed at NIST using wavelength dispersive X-ray fluorescence (XRF), multiple monochromatic beam energy dispersive XRF, and microbeam XRF (microXRF). Additional homogeneity measurements were performed by collaborating laboratories using multiple monochromatic beam energy dispersive XRF and handheld XRF instrumentation. Measurements for uniformity of coating thickness were made during manufacturing at Rolla Coatings using ultraviolet light absorption spectrometry. The manufacturer visually inspected all coupons and rejected those containing trapped particles and fibers.

Test Methods Employed at NIST and Collaborating Laboratories: Determinations of mass fraction of Pb in paint were performed at NIST using isotope dilution inductively-coupled plasma mass spectrometry (ID-ICPMS) [5]. Determinations of mass of Pb per unit area were performed at NIST using XRF. Independent values of mass of Pb per unit area were obtained by calculation using ID-ICPMS values of Pb mass fraction, the weighed total mass of cured paint per coupon performed by Rolla Coatings, and the mean measured area of a coupon. Measurements of thickness were performed at NIST using an outside micrometer gauge with the paint film thickness determined by difference between coated and uncoated coupons. Independent values of thickness were calculated from experimentally determined values for paint density performed at NIST, the weighed total mass of cured paint per coupon, and the mean measured area of a coupon. Density determinations were performed at NIST by weighing cured paint films in air and in water and applying Archimedes' principle of buoyancy.

Value Assignments: Each certified value for mass fraction of Pb is the mean of results obtained at NIST using ID-ICPMS [5]. For Level 2 and Level 3, the uncertainty listed with each mass fraction is an expanded uncertainty about the mean with coverage factor $k = 2$ (approximately 95 % confidence), calculated by combining sources of uncertainty characteristic of the test method and the material according to the ISO Guide [6]. For Level 1, the certified value for mass fraction of Pb is an upper confidence bound (approximately 99 % confidence) based on the variance of ID-ICPMS results.

The certified values for mass of Pb per unit area and for paint thickness are the means of sets of results obtained using the test methods and calculations listed above [6]. For Level 1, the certified value for mass of Pb per unit area is an upper confidence bound (approximately 99 % confidence) based on the variance of NIST XRF results. For Level 2 and Level 3, the uncertainty listed with each value of mass of Pb per unit area and paint thickness is an expanded uncertainty about the mean, with coverage factor $k = 2$ (approximately 95 % confidence), calculated following the ISO Guide [6] by combining a between-method variance incorporating differences among methods with a pooled, within-method variance and a component of variance accounting for coupon-to-coupon differences measured during homogeneity testing [8,9].

Each reference value for density of the paint is the result obtained at NIST using a gravimetric procedure. The uncertainty listed with each density value is an expanded uncertainty about the mean with coverage factor $k = 2$ (approximately 95 % confidence), calculated by combining sources of uncertainty characteristic of the test method and the material according to the ISO Guide [6].

[(1)] Certain commercial equipment, instruments or materials are identified in this certificate to adequately specify the experimental procedure. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

Table 1. Certified Values for SRM 2569 Lead Paint Films for Children's Products

Constituent	Value	Unit
Level 1		
Pb Mass Fraction	<0.2[(a)]	mg/kg
Mass of Pb per Unit Area	<0.02[(a)]	µg/cm^2
Paint Thickness	40.17 ± 0.66	µm
Level 2		
Pb Mass Fraction	85.0 ± 3.8	mg/kg
Mass of Pb per Unit Area	0.225 ± 0.043	µg/cm^2
Paint Thickness	22.9 ± 2.4	µm
Level 3		
Pb Mass Fraction	314.4 ± 3.6	mg/kg
Mass of Pb per Unit Area	1.453 ± 0.073	µg/cm^2
Paint Thickness	39.4 ± 2.4	µm

[(a)] The value is an upper confidence bound (approximately 99 % confidence) based on the variance of measured results.

Table 2. Reference Values for SRM 2569 Lead Paint Films for Children's Products

Constituent	Value (g/cm^3)
Level 1	
Density of Paint	1.145 ± 0.008
Level 2	
Density of Paint	1.158 ± 0.020
Level 3	
Density of Paint	1.160 ± 0.012

Table 3. Information Value for SRM 2569 Lead Paint Films for Children's Products

Constituent	Value (µm)
Polyester Substrate	
Thickness	167

REFERENCES

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[9] Horn, R.A.; Horn, S.A.; Duncan, D.B.; *Estimating Heteroscedastic Variance in Linear Models*; J. Am. Stat. Assoc., Vol. 70, pp. 380–385 (1975).

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Users of this SRM should ensure that the Certificate of Analysis in their possession is current. This can be accomplished by contacting the SRM Program: telephone (301) 975-2200; fax (301) 948-3730; e-mail srminfo@nist.gov; or via the Internet at http://www.nist.gov/srm.