National Institute of Standards & Technology

Certificate of Analysis

Standard Reference Material® 2861

Restricted Elements in Polyvinyl Chloride

This Standard Reference Material (SRM) is intended primarily for use in validation of chemical and instrumental methods of analysis of polyvinyl chloride (PVC) and materials of similar matrix for restricted, additive and tramp element contents. It can be used to validate value assignment of in-house reference materials. A unit of SRM 2861 consists of one bottle containing approximately 25 g of PVC pellets.

Certified Mass Fraction Values: Certified values for constituents of SRM 2861 are reported in Table 1 as mass fractions of the elements in a PVC matrix [1]. 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 taken into account [2]. A certified value is the present best estimate of the true value. The certified values are the measurands and are metrologically traceable to the SI derived unit of mass fraction (expressed as percent). The expanded uncertainty estimates are expressed at a confidence level of approximately 95 %.

Table 1. Certified Mass Fraction Values for SRM 2861 Restricted Elements in Polyvinyl Chloride

Constituent	Mass Fraction (%)	Expanded Uncertainty (%)
Antimony (Sb)	0.00678	0.00040
Arsenic (As)	0.00239	0.00051
Barium (Ba)	0.0740	0.0013
Cadmium (Cd)	0.00651	0.00036
Calcium (Ca)	3.33	0.14
Chromium (Cr)	0.00504	0.00031
Iron (Fe)	0.0058	0.0012
Lead (Pb)	0.00883	0.00047
Mercury (Hg)	0.00556	0.00030
Selenium (Se)	0.02441	0.00032
Sulfur (S)	0.1006	0.0090
Tin (Sn)	0.1294	0.0010

Expiration of Certification: The certification of **SRM 2861** is valid, within the measurement uncertainty specified, until **01 July 2024**, provided the SRM is handled and stored in accordance with instructions given in this certificate (see "Instructions for Handling, Storage, and Use"). Reference values are expected also to remain valid within this period. Periodic recalibration or recertification of this SRM is not required. The certification is nullified if the SRM is damaged, contaminated, or otherwise modified.

Coordination of technical measurements for certification was performed by J.R. Sieber of the NIST Chemical Sciences Division.

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Gaithersburg, MD 20899
Certificate Issue Date: 09 August 2017

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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 this certificate, NIST will notify the purchaser. Registration (see attached sheet or register online) will facilitate notification.

Statistical consultation for this SRM was provided by N.A. Heckert of the NIST Statistical Engineering Division.

Support aspects involved in the issuance of this SRM were coordinated through the NIST Office of Reference Materials.

INSTRUCTIONS FOR HANDLING, STORAGE, AND USE

Polyvinyl chloride pellets may be analyzed either in as-received form, cryogenically ground to powder for methods requiring dissolution, or melt pressed for methods that require a larger area of measurement, such as X-ray fluorescence spectrometry (XRF). To relate analytical determinations to the certified values in this Certificate of Analysis, a minimum test portion of 100 mg should be used when it has been prepared as powder. See below for additional information on melt pressing and exposure to X-rays. A bottle containing unused material should be recapped immediately and stored at room temperature away from light.

To use the uncertainty estimates given in this certificate, divide the expanded uncertainty by $k = 2$ to obtain the combined standard uncertainty. The effective degrees of freedom of the combined standard uncertainty are ≥ 60.

Heterogeneity of SRM 2861 is such that measurements of very small quantities will be subject to high variance. The elements Ba, Fe, and Se are characterized by discrete locations of high concentrations. These locations range in size from approximately 50 µm to several hundred micrometers, and they may contain 10 times to 100 times the overall mass fraction of the element. Multiple measurements of small spots on a sample may exhibit widely varying results. To obtain a test result representative of the overall composition of SRM 2861, the user must make measurements of different locations until the mean of the measurements and the standard deviation no longer change.

CAUTION TO USERS

Polyvinyl chloride is damaged by exposure to X-rays of sufficient power density for a sufficient duration. When radiation damage is suspected, do not make repeat measurements of the same location of a specimen. Both microbeam XRF and high power wavelength dispersive XRF spectrometers use direct excitation and cause sufficient damage to alter the composition of the PVC. An energy dispersive XRF spectrometer of the secondary target design may not damage the PVC. Damage from irradiation is characterized by discoloration of the PVC that may be accompanied by a faint odor of burned material. Sample mass loss may be observed. Excessive irradiation was observed to cause loss of Cl and Hg from SRM 2861 as well as reduction of the hexavalent Cr originally added as $Na_2Cr_2O_7$ prior to extrusion. Losses of Cl and Hg can be observed as decreasing X-ray count rates from repeat measurements. Increasing count rates for Ca were observed when Cl was lost.

ADDITIONAL CONSTITUENTS: Noncertified values are provided for the following additional constituents in SRM 2861.

Information Mass Fraction Values: Information values for constituents in SRM 2861 are reported as mass fractions in Table 2. An information value is a value that may be of interest to the SRM user, but insufficient information is available to assess the uncertainty associated with the value [2]. Information values cannot be used to establish metrological traceability. The information values reported in Table 2 for Cl and Na were determined using a single test method at one laboratory: Cl by XRF and Na by inductively coupled plasma optical emission spectrometry (ICPOES). The values listed for Br and Cu are the estimated limits of detection of both test methods. These two elements were not added intentionally to this PVC formulation.

Table 2. Information Mass Fraction Values for SRM 2861 Restricted Elements in Polyvinyl Chloride

Constituent	Mass Fraction (%)
Bromine (Br)	<0.001
Chlorine (Cl)	35
Copper (Cu)	<0.0003
Sodium (Na)	0.006

PREPARATION AND ANALYSIS[(1)]

The material for SRM 2861 was prepared by combining a master blend with a dry blend in a mixer at 85 ºC, followed by extrusion at 175 ºC, cooling in a water bath and chopping, then a second extrusion, cooling, and chopping. Blending and extrusion were performed by Polymers Center of Excellence (Charlotte, NC). The master blend was prepared from virgin PVC powder to which organometallic compounds of Ba, Cd, Hg, and Pb, an aqueous solution of $Na_2Cr_4O_7$ (containing a surfactant), and a copper phthalocyanine bromide dye were added. The dry blend consisted of PVC with added $CaCO_3$ and methyltin mercaptide. The approximate density of SRM 2861 is 1.3 g/cm^3. The PVC pellets were blended and bottled at NIST.

Homogeneity testing was performed at NIST using XRF to measure disks made from 6.2 g of pellets melt-pressed at 175 ºC. Additional evaluation of heterogeneity was performed using microXRF at NIST. Material heterogeneity was sufficiently low for value assignment. Quantitative determinations were done at NIST by XRF after melt-pressing and at collaborating laboratories by ICPOES after cryogenic grinding and microwave-assisted acid digestion.

Each certified value is a weighted mean of the results from the three laboratories [3]. The uncertainty listed with each certified value is an expanded uncertainty about the mean [4], with coverage factor, $k = 2$, calculated following the ISO/JCGM Guide [5].

Analyses leading to the certification of this SRM were performed at NIST by J.R. Sieber, J.L. Molloy, C. Bibb, and M. Boyce of the NIST Chemical Sciences Division. Analytical determinations were also performed by D. Cobb, U.S. Consumer Product Safety Commission (CPSC, Rockville, MD), and C.S. Helt and K. Leung, Underwriters Laboratories (Melville, NY).

NOTICE TO USERS

NIST strives to maintain the SRM inventory supply, but NIST cannot guarantee the continued or continuous supply of any specific SRM. Accordingly, NIST encourages the use of this SRM as a primary benchmark for the quality and accuracy of the user's in-house reference materials and working standards. As such, the SRM should be used to validate the more routinely used reference materials in a laboratory. Comparisons between the SRM and in-house reference materials or working measurement standards should take place at intervals appropriate to the conservation of the SRM and the stability of relevant in-house materials. For further guidance on how this approach can be implemented, contact NIST by email at srms@nist.gov.

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

REFERENCES

[1] Thompson, A.; Taylor, B.N.; *Guide for the Use of the International System of Units (SI)*; NIST Special Publication 811; U.S. Government Printing Office: Washington, DC (2008); available at http://www.nist.gov/pml/pubs/sp811/index.cfm (accessed Aug 2017).

[2] May, W.; Parris, R.; Beck II, C.; Fassett, J.; Greenberg, R.; Guenther, F.; Kramer, G.; Wise, S.; Gills, T.; Colbert, J.; Gettings, R.; MacDonald, B.; *Definition of Terms and Modes Used at NIST for Value-Assignment of Reference Materials for Chemical Measurements*; NIST Special Publication 260-136 U.S. Government Printing Office: Washington, DC (2000); available at http://www.nist.gov/srm/upload/SP260-136.PDF (accessed Aug 2017).

[3] DerSimonian, R. and Laird, N.; *Meta-analysis in Clinical Trials*; Control Clin. Trials, Vol. 7, pp. 177–188 (1986).

[4] 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).

[5] JCGM 100:2008; *Evaluation of Measurement Data - Guide to the Expression of Uncertainty in Measurement*; (GUM 1995 with Minor Corrections), Joint Committee for Guides in Metrology (JCGM) (2008); available at http://www.bipm.org/utils/common/documents/jcgm/JCGM_100_2008_E.pdf (accessed Aug 2017); see also Taylor, B.N.; Kuyatt, C.E.; *Guidelines for Evaluating and Expressing the Uncertainty of NIST Measurement Results*; NIST Technical Note 1297, U.S. Government Printing Office: Washington, DC (1994); available at http://www.nist.gov/pml/pubs/index.cfm (accessed Aug 2017).

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.