National Institute of Standards & Technology

Certificate of Analysis

Standard Reference Material® 2855

Additive Elements in Polyethylene

This Standard Reference Material (SRM) is intended for the calibration or evaluation of methods for elemental analysis of polymers. A unit of SRM 2855 consists of one bottle of Level I low-density polyethylene, one bottle of Level II high-density polyethylene, and one bottle of Level III high-density polyethylene. Each bottle contains approximately 80 g of material in pellet form.

Certified Mass Fraction Values: Certified values for constituents in SRM 2855 Level II and Level III are reported in Table 1. Value assignment categories are based on the definition of terms and modes used at NIST for chemical reference materials [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 investigated or 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 using instrumental test methods.

Reference Mass Fraction Values: Reference values for SRM 2855 Level II and Level III are reported in Table 2. Reference values are non-certified values that are the present 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 [1].

Information Mass Fraction Values: Information values for constituents in SRM 2855 Level I are reported in Table 3. Information values for SRM 2855 Level II and Level III are reported in Table 4. An information value is considered to be a value that will be of interest to the SRM user, but insufficient information is available to assess the uncertainty associated with the value [1]. Information values cannot be used to establish metrological traceability.

Expiration of Certification: The certification of **SRM 2855** is valid, within the measurement uncertainty specified, until **01 June 2025**, provided the SRM is handled and stored in accordance with instructions given in this certificate (see "Instructions for Storage, Handling, 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 this certificate, NIST will notify the purchaser. Registration (see attached sheet) will facilitate notification.

Coordination of technical measurements for certification of SRM 2855 was under the direction of J.R. Sieber of the NIST Chemical Sciences Division and T.H. Palmgren of ASTM International Subcommittee D20.70.

Analytical measurements for certification of this SRM were performed at NIST by J.L. Molloy, J.R. Sieber, R.L. Temple, Jr., and L.J. Wood of the NIST Chemical Sciences Division, and Y. Li (NIST Guest Researcher) of the National Institute of Metrology, Beijing, China.

Statistical consultation for the value assignment of SRM 2855 was provided by D.L. Duewer of the NIST Chemical Sciences Division and by S.D. Leigh of the NIST Statistical Engineering Division.

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

Carlos A. Gonzalez, Chief
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Gaithersburg, MD 20899
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Certificate Revision History on Last Page

Steven J. Choquette, Director
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INSTRUCTIONS FOR STORAGE, HANDLING, AND USE

Polyethylene is a thermoplastic that is often prepared for analysis by grinding at cryogenic temperatures or by compression molding with heating. Polyethylene can oxidize at high temperatures in the presence of air. Guidance for compression molding is available from ASTM International D 4703 [2].

Homogeneity testing was performed at NIST using X-ray fluorescence spectrometry. On the basis of the homogeneity test results and the results of quantitative analyses, it is recommended to use a quantity of material greater than 100 mg to ensure that results obtained can be related to assigned values on this Certificate of Analysis.

Store material in its original, tightly-capped container at room temperature (15 ºC to 35 ºC) and away from direct illumination.

Testing of Restricted Substances

Although the three materials comprising SRM 2855 were not formulated with the intention of making the SRM applicable for testing of restricted substances, SRM 2855 can be used for that purpose. The elements of concern (Cr, Br, Cd, Hg, and Pb) were not intentionally added to the polyethylene blends. Chromium is present in Level II and Level III as a result of contact with the polymerization catalyst. The assigned values for the element Cr are provided in Table 1 and Table 3 as total Cr. Assigned values for the elements Br, Cd, Hg, and Pb are provided in Table 3 and Table 4 as information values after careful measurements using XRF at NIST. These elements were not present above the detection limits of the NIST XRF method.

Table 1. Certified Values for SRM 2855 Level II and Level III

Constituent	Mass Fraction[(a)] (mg/kg)
Level II	
Sodium (Na)	16.0 ± 1.5
Phosphorous (P)	22.0 ± 1.5
Sulfur (S)	21.0 ± 1.4
Calcium (Ca)	37.6 ± 5.1
Titanium (Ti)	10.4 ± 0.3
Chromium (Cr)	2.4 ± 0.5
Zinc (Zn)	415 ± 20
Level III	
Sodium (Na)	16.4 ± 1.3
Phosphorous (P)	41.6 ± 2.9
Sulfur (S)	41.2 ± 3.1
Calcium (Ca)	77.2 ± 2.4
Titanium (Ti)	10.4 ± 0.3
Chromium (Cr)	2.4 ± 0.5
Zinc (Zn)	807 ± 15

[(a)] Values are reported as mass fractions [3]. For all elements except Cr, the assigned value is an unweighted mean of the results from two or three analytical methods. The uncertainty listed with the value is an expanded uncertainty about the mean, with coverage factor $k = 2$, calculated by combining a between-method variance with a pooled, within-method variance [4,5] following the JCGM Guide [6]. For the element Cr, the assigned value is the median of the set of laboratory mean results, and the uncertainty is an expanded uncertainty about the median, with coverage factor $k = 2$, calculated using the inflated standard deviation of the mean of the laboratory mean results. See "Combining Results" below. The certified values are the measurands and are metrologically traceable to the SI derived unit of mass fraction (expressed as milligram per kilogram).

Table 2. Reference Values for SRM 2855 Level II and Level III

Constituent	Mass Fraction[a] (mg/kg)
Level II	
Silicon (Si)	186.7 ± 3.8
Level III	
Silicon (Si)	183.1 ± 4.1

[a] Values are reported as mass fractions [1]. Each assigned value is an unweighted mean of the results from two analytical methods. The uncertainty listed with the value is an expanded uncertainty about the mean, with coverage factor $k = 2$, calculated by combining a between-method variance with a pooled, within-method variance [4,5] following the JCGM Guide [6]. See "Combining Results" below. The reference values are the measurands as determined by the methods indicated below and are metrologically traceable to the SI derived unit of mass fraction (expressed as milligram per kilogram).

Table 3. Information Values for SRM 2855 Level I

Constituent	Mass Fraction (mg/kg)
Sodium (Na)	< 4
Silicon (Si)	< 6
Phosphorous (P)	1
Sulfur (S)	< 2
Calcium (Ca)	< 1
Titanium (Ti)	< 1
Chromium (Cr)	< 1
Zinc (Zn)	< 0.5
Bromine (Br)	< 2
Cadmium (Cd)	< 3
Mercury (Hg)	< 3
Lead (Pb)	< 2

Table 4. Information Values for SRM 2855 Level II and Level III

Constituent	Mass Fraction (mg/kg)
Bromine (Br)	< 2
Cadmium (Cd)	< 3
Mercury (Hg)	< 3
Lead (Pb)	< 2

PLANNING, PREPARATION, TESTING, AND ANALYSIS[1]

The materials for SRM 2855 were compounded under the direction of R. Ziegler, Westlake Chemicals, (Longview, TX). The materials were designed in collaboration with ASTM International Committee D20 on Plastics, Subcommittee 70 on Analytical Methods. Additives compounds used in the formulations of Level II and Level III high-density polyethylene blends included calcium stearate, sodium benzoate, zinc oxide, distearyl thiodipropionate, and tris-(2,4-di-tert-butylphenyl) phosphite.

[1] Certain commercial equipment, instruments, or materials are identified in this certificate in order to specify adequately 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.

Test Methods Employed at NIST and the Collaborating Laboratories

Inductively coupled plasma optical emission spectrometry (ICPOES): Ca, Cr, Na, P, S, Si, Ti, Zn
Instrumental neutron activation analysis (INAA) at collaborating laboratories: Ca, Na, S, Si, Ti, Zn
X-ray fluorescence spectrometry (XRF) at collaborating laboratories: Ca, Cr, Na, P, S, Si, Ti, Zn
X-ray fluorescence spectrometry (XRF) at NIST: Br, Ca, Cd, Cr, Hg, Na, P, Pb, S, Si, Ti, Zn

Collaborating Laboratories

Cooperative testing was coordinated by ASTM International Committee D20.70 in conjunction with the Interlaboratory Study Program of ASTM International, West Conshohocken, Pennsylvania, USA. The following laboratories participated in an ASTM International interlaboratory study (ILS).

Chevron Phillips Chemical Co. (Kingwood, TX) J. Ilger
Chevron Phillips Chemical Co. (Baytown, TX) C. Ball
Chevron Phillips Chemical Co. (Orange, TX) G. MacMurtrie
Chevron Phillips Singapore Chemicals (Singapore, Malaysia) L. Hua
Dow Chemical (Freeport, TX) D. Burns
Dow Chemical (Midland, MI) L. Brehm
Dow Chemical (Piscataway, NJ) C. Taylor
Dow Chemical (Terneuzen, The Netherlands) M. Van Os
Dow Corporation, Union Carbide Div. (South Charleston, WV) W-L. Shen
DSM Resolve (Geleen, The Netherlands) H. Vanwersch
Exxon Mobil (Baton Rouge, LA) S. Chang
INEOS Chemical Company (Houston, TX) M. Bothwell
Lyondell-Basell (Cincinnati, OH) B. Fulton
Nova Research & Technology Centre (Calgary, Alberta, Canada) G. Yamashita
PANalytical, Inc. (Almelo, The Netherlands) T. Van der Maten
Qatar Chemical Co. (Doha, Qatar) A. Rana
Westlake Chemical Co. (Longview, TX) R. Ziegler, D. Todd

Combining Results

Results provided by the participants of the D20.70 ILS were obtained using ICPOES, INAA, and XRF test methods. The results of this study underwent technical evaluation at NIST followed by statistical analysis to obtain an ILS consensus value for each element in each material. Critical evaluation of data from the ILS was aided by software created by D.L. Duewer of the NIST Chemical Sciences Division [4]. The software contains statistical tools for describing the distribution of data and a number of published algorithms for calculating consensus values and estimates of uncertainty of the consensus values.

For Level I, results from two NIST methods (XRF and ICPOES) were combined with the ILS data set and included in the consensus values calculations using the software described above. For phosphorus in Level I, the median of the laboratory mean results was assigned as the information value shown in Table 3. For the other elements, the pooled, within-laboratory variance was used to estimate the limits of detection shown as "less than" (<) values in Table 3.

For each element in Level II and in Level III except Cr, the mean of the laboratory mean values was chosen as the consensus value for the ILS. This consensus value was used as a single estimate and assumed to be from a single method, although in reality three methods contributed to most consensus values. The consensus value was then combined with results from two NIST methods (XRF and ICPOES), using the method of Levenson et al. [5] to calculate the assigned value and the estimate of uncertainty shown in Table 1 or Table 2. For Cr in Level II and in Level III, all ILS results from individual laboratories from both Level II and Level III materials along with the NIST results were combined into a single data set. This was done because the mass fraction of Cr was known *a priori* to be the same in both high-density polyethylene (HDPE) blends and because there were insufficient results to treat each level separately. In Table 1, the assigned value for Cr is the median of this combined set of results.

REFERENCES

[1] 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 https://www.nist.gov/srm/upload/SP260-136.PDF (accessed June 2019).

[2] ASTM Standard D 4703, *Standard Practice for Compression Molding Thermoplastic Materials into Test Specimens, Plaques or Sheets*; ASTM International, West Conshohocken, PA.

[3] 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 https://www.nist.gov/pml/pubs/sp811/index.cfm (accessed June 2019).

[4] Duewer, D.L., *A Comparison of Location Estimators for Interlaboratory Data Contaminated with Value and Uncertainty Outliers*; Accred. Qual. Assur.; Vol. 13, pp. 193-216 (2008).

[5] Levenson, M.S.; Banks, D.L.; Eberhardt, K.R.; Gill, L.M.; Guthrie, W.F.; Liu, H.-K.; Vangel, M.G.; Yen, J.H.; Zang, N.F.; *An Approach to Combining Results from Multiple Methods Motivated by the ISO GUM*; J. Res. Natl. Inst. Stand. Technol., Vol. 105, pp. 571–579 (2000).

[6] 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 https://www.bipm.org/utils/common/documents/jcgm/JCGM_100_2008_E.pdf (accessed June 2019); 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 https://www.nist.gov/pml/nist-technical-note-1297 (accessed June 2019).

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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 https://www.nist.gov/srm.