



# National Institute of Standards & Technology

## Certificate of Analysis

### Standard Reference Material<sup>®</sup> 2860

#### Phthalates in Polyvinyl Chloride

This Standard Reference Material (SRM) is intended primarily for use in validating methods for determining six phthalate esters in polyvinyl chloride (PVC). The phthalates esters are di-*n*-butyl phthalate (DnBP), benzyl butyl phthalate (BBP), bis(2-ethylhexyl) phthalate (DEHP), di-*n*-octyl phthalate (DnOP), diisononyl phthalate (DINP), and diisodecyl phthalate (DIDP). A unit of SRM 2860 consists of shredded material as follows: one jar containing approximately 2 g of BLANK (PVC) with no phthalates added; and two jars each containing approximately 2 g of Level I (Nominal Concentration 0.1 % Phthalates in PVC) and Level II (Nominal Concentration 2 % Phthalates in PVC) respectively, for a total of three jars.

**Certified Values:** Certified values are provided in Table 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 [1]. The certified values are metrologically traceable to the SI derived unit of mass fraction (expressed as micrograms per gram).

Table 1. Certified Values for Bis(2-ethylhexyl) and Di-*n*-octyl phthalates in SRM 2860  
PVC with Nominal Concentration of 0.1 % Phthalates Added

Analyte	Acronym	Mass Fraction, ( $\mu\text{g/g}$ ) <sup>(a)</sup>
Bis(2-ethylhexyl) phthalate	DEHP	1514 $\pm$ 33
Di- <i>n</i> -octyl phthalate	DNOP	1171 $\pm$ 83

<sup>(a)</sup> Values are expressed as  $x \pm U_{95\%}(x)$ , where  $x$  is the certified value and  $U_{95\%}(x)$  is the expanded uncertainty of the certified value.

The true value of the analyte is believed to lie within the interval  $x \pm U_{95\%}(x)$  with 95 % confidence [2]. To propagate this uncertainty, treat the certified value as a normally distributed random variable with mean  $x$  and standard deviation  $U_{95\%}(x)/k$ , where  $k$  is the coverage factor, 2.0 for DEHP and DNOP above.

**Expiration of Certification:** The certification of **SRM 2860** is valid, within the measurement uncertainty specified, until **31 December 2025**, 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 this certificate, NIST will notify the purchaser. Registration (see attached sheet or register online) will facilitate notification.

Production of this SRM was performed by B.A. Benner, Jr., M.M. Shantz (retired), L.C. Sander, R.D. van Zee, R. Isenberg, and P.C. Bryant of the NIST Chemical Sciences Division and D. Owen, K. Stahl, and K. Utecht of BASF (Pasadena, TX).

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Statistical analysis 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.

**Non-Certified Values:** Tables 2-5 list values that do not meet NIST's criteria for certification [1] but are the best currently available estimates for measurands of interest. Diisononyl phthalate and diisodecyl phthalate consist of industrial mixtures of multiple isomers and thus their mass fractions cannot be designated as certified. Values are metrologically traceable to the measurement methods, calibration procedures, and standards used.

Table 2. Non-Certified Values for Bis(2-ethylhexyl) Phthalate in SRM 2860 PVC Blank with No Phthalates Added

Analyte	Acronym	Mass Fraction, ( $\mu\text{g/g}$ ) <sup>(a)</sup>
Di- <i>n</i> -butyl phthalate	DBP	$\leq$ detection limit <sup>(b)</sup>
Benzyl butyl phthalate	BBP	$\leq$ detection limit <sup>(c)</sup>
Bis(2-ethylhexyl) phthalate	DEHP	$64.4 \pm 4.3$
Di- <i>n</i> -octyl phthalate	DNOP	$\leq$ detection limit <sup>(b)</sup>
Diisononyl phthalate	DINP	$\leq$ detection limit <sup>(d)</sup>
Diisodecyl phthalate	DIDP	$\leq$ detection limit <sup>(d)</sup>

<sup>(a)</sup> Values are expressed as  $x \pm U_{95\%}(x)$ , where  $x$  is the assigned value and  $U_{95\%}(x)$  is the expanded uncertainty of the value. The true value of the analyte is believed to lie within the interval  $x \pm U_{95\%}(x)$  with 95 % confidence [2]. To propagate this uncertainty, treat the certified value as a normally distributed random variable with mean  $x$  and standard deviation  $U_{95\%}(x)/k$ , where  $k$  is the coverage factor, 2.0 for DEHP in the Level I material.

<sup>(b)</sup> Less than estimated detection limit of 20  $\mu\text{g/g}$ .

<sup>(c)</sup> Less than estimated detection limit of 10  $\mu\text{g/g}$ .

<sup>(d)</sup> Less than estimated detection limit of 50  $\mu\text{g/g}$ .

Table 3. Non-Certified Values for Di-*n*-butyl, Benzyl butyl, Diisononyl and Diisodecyl phthalates in SRM 2860 PVC with Nominal Concentration of 0.1 % Phthalates Added

Analyte	Acronym	Mass Fraction, ( $\mu\text{g/g}$ ) <sup>(a)</sup>
Di- <i>n</i> -butyl phthalate	DBP	$1074 \pm 275$
Benzyl butyl phthalate	BBP	$1243 \pm 342$
Diisononyl phthalate	DINP	$1222 \pm 235$
Diisodecyl phthalate	DIDP	$1156 \pm 355$

<sup>(a)</sup> Values are expressed as  $x \pm U_{95\%}(x)$ , where  $x$  is the assigned value and  $U_{95\%}(x)$  is the expanded uncertainty of the value. The true value of the analyte is believed to lie within the interval  $x \pm U_{95\%}(x)$  with 95 % confidence [2]. To propagate this uncertainty, treat the certified value as a normally distributed random variable with mean  $x$  and standard deviation  $U_{95\%}(x)/k$ , where  $k$  is the coverage factor, 2.0 for DBP, BBP, DINP, and DIDP in the Level II material.

Table 4. Non-Certified Values for Six Phthalates Esters in SRM 2860 PVC with Nominal Concentration of 2 % Phthalates Added

Analyte	Acronym	Mass Fraction, (%) <sup>(a)</sup>
Di- <i>n</i> -butyl phthalate	DBP	1.82 ± 0.10
Benzyl butyl phthalate	BBP	1.60 ± 0.09
Bis(2-ethylhexyl) phthalate	DEHP	1.89 ± 0.19
Di- <i>n</i> -octyl phthalate	DNOP	1.84 ± 0.08
Diisononyl phthalate	DINP	1.78 ± 0.13
Diisodecyl phthalate	DIDP	1.65 ± 0.20

<sup>(a)</sup> Values are expressed as  $x \pm U_{95\%}(x)$ , where  $x$  is the assigned value and  $U_{95\%}(x)$  is the expanded uncertainty of the value. The true value of the analyte is believed to lie within the interval  $x \pm U_{95\%}(x)$  with 95 % confidence [2]. To propagate this uncertainty, treat the certified value as a normally distributed random variable with mean  $x$  and standard deviation  $U_{95\%}(x)/k$ , where  $k$  is the coverage factor, 2.0 for the six phthalates above.

Table 5. Non-certified Characteristics of PVC in Individual and Composite Sheets and Oxy 240F Precursor Resin<sup>(a)</sup>

Material	$M_n^{(b)}$ (g mol <sup>-1</sup> )	$M_w^{(c)}$ (g mol <sup>-1</sup> )	$M_w/M_n^{(d)}$	$R_{\eta,w}^{(e)}$ (nm)	$R_{\eta,z}^{(f)}$ (nm)	$R_{\eta,w}/R_{g,z}^{(g)}$	$[\eta]_w^{(h)}$ (mL g <sup>-1</sup> )
PVC Blank	69200 ± 4800	132800 ± 4200	1.92 ± 0.15	12 ± <1	23 ± 1	0.52 ± 0.02	91 ± 2
0.1 % Phthalates Added	62900 ± 5900	126900 ± 6900	2.02 ± 0.22	11 ± <1	23 ± 1	0.48 ± 0.02	88 ± 3
2 % Phthalates Added	64500 ± 4700	128300 ± 6100	1.99 ± 0.17	11 ± <1	23 ± 1	0.48 ± 0.02	89 ± 2
PVC Blank Composite <sup>(i)</sup>	66800 ± 4200	124500 ± 4800	1.86 ± 0.14	12 ± <1	22 ± 1	0.55 ± 0.02	90 ± 2
0.1 % Phthalates Composite <sup>(i)</sup>	65800 ± 4800	122600 ± 2500	1.86 ± 0.14	11 ± <1	23 ± <1	0.48 ± ≤0.01	89 ± 2
2 % Phthalates Composite <sup>(i)</sup>	65400 ± 4400	124400 ± 3800	1.90 ± 0.14	11 ± <1	23 ± <1	0.48 ± ≤0.01	88 ± 2
Oxy 240F precursor resin	64300 ± 2000	114000 ± 1100	1.77 ± 0.06	12 ± <1	21 ± <1	0.57 ± ≤0.01	89 ± 1

<sup>(a)</sup> Results from size-exclusion chromatographic measurements. Analyses conducted in tetrahydrofuran (THF) at 25 °C.

<sup>(b)</sup>  $M_n$  = number-average molar mass.

<sup>(c)</sup>  $M_w$  = weight-average molar mass.

<sup>(d)</sup>  $M_w/M_n$  = molar mass dispersity.

<sup>(e)</sup>  $R_{\eta,w}$  = weight-average viscometric radius.

<sup>(f)</sup>  $R_{g,z}$  = z-average radius of gyration.

<sup>(g)</sup>  $R_{\eta,w}/R_{g,z}$  = dimensionless radii ratio.

<sup>(h)</sup>  $[\eta]_w$  = weight-average intrinsic viscosities

<sup>(i)</sup> Multiple aliquots from the three material levels, respectively, were combined prior to measurements.

Figure 1 shows that the presence of dioctyl adipate (DOA) and phthalates does not affect statistically-relevant changes upon the molar mass averages, dispersity ( $= M_w/M_n$ ), or distribution of PVC, when comparing data for the resin vs. the various composite samples. The “C” in Figure 1 refers to “Composite” for the multiple aliquots from each level, that were combined, respectively, prior to measurements.

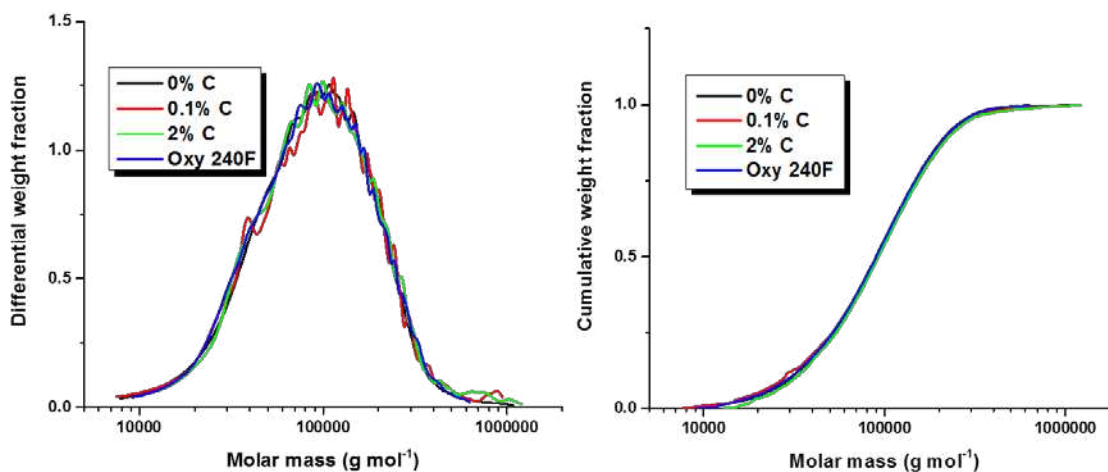


Figure 1. Molar Mass Distributions of Select PVC Samples

## INSTRUCTIONS FOR HANDLING, STORAGE AND USE

**Handling and storage:** Until required for use, SRM 2860 should be stored in the dark at room temperature but not above 30 °C. A recommended minimum sample size of 0.1 g can be generated by cutting pieces from the PVC shredded materials using a razor blade or scalpel.

**Use:** SRM 2860 is provided as a suite of three matrix shredded materials for validating measurements of six phthalates in PVC.

## NOTICE AND WARNING TO USERS

**Warning:** The shredded materials composing SRM 2860 should be handled with cloth or nitrile gloves. These materials are potentially flammable and should be kept away from open flame.

## PREPARATION AND ANALYSIS<sup>(1)</sup>

**Material Formulation and Processing:** This SRM was formulated and milled at BASF (Pasadena, TX), producing 6 to 9 sheets of the three levels of phthalate plasticizers in PVC. These sheets were subdivided and packaged at NIST (Gaithersburg, MD). Solutions of the six phthalate esters in bis(2-ethylhexyl) adipate (DOA) were prepared at NIST after consulting with D. Owen (BASF). These solutions were used to achieve intended phthalate mass fractions in the PVC sheets of 0 % (DOA neat with no phthalates added), 0.1 % phthalates, and 2 % phthalates in PVC from batch formulations of 300 g vinyl resin (Oxy 240F), 150 g plasticizer (phthalates in DOA), and 9 g heat stabilizer (Baerlocher 1760A).

After combining and manually mixing the components for 5 min, the formulations were further mixed using a professional grade metal food processor for 2 min, 2 min, and 11 min. Oxy 240F is a suspension resin. This type of resin absorbs the liquid plasticizer to form a “dry blend”. These PVC formulations would require the phthalate solutions used in the 0.1 % phthalates in PVC to have phthalate mass fraction concentrations of 0.305 % in DOA, and the solutions used in the 2 % phthalates in PVC preparation to have phthalate mass fraction concentrations of 6.21 % in DOA. The phthalate solutions and DOA with no phthalates added were shipped to BASF’s Pasadena, TX facility on September 19, 2013. The PVC sheets were milled using a LabTech Engineering Co. LTD (Thailand) Two Roll Mill. The mill’s counter-rotating rollers, heated at approximately 172 °C, fused the dry blend into flexible sheets of approximately 450 g each. From 6 to 9 individual PVC sheets were milled each for the 0.1 % phthalate, 2 % phthalate, and 0 % phthalate (100 % DOA) formulations. The PVC sheets were shipped to NIST.

<sup>(1)</sup>Certain commercial organizations, services, equipment, or materials are identified in this certificate in order to adequately specify the experimental procedure. Such identification does not imply recommendation or endorsement by the NIST, nor does it imply that the organizations, services, materials, or equipment identified are necessarily the best available for the purpose.

Processing of the PVC sheets involved cutting them into strips approximately 20 cm wide, freezing the sheets to -80 °C, and shredding with a heavy-duty cross-cutting paper shredder. The resulting segments of the PVC shredded materials were packaged in 10 mL amber vials in 2 g to 2.5 g masses.

**NIST Analytical Approaches for Determination of six phthalates in PVC materials:** Sampling of the PVC samples involved cutting small pieces of the shredded PVC using a solvent-cleaned stainless steel scalpel for the 0.1 g aliquots and combining multiple pieces until their masses totaled approximately 1 g (accurately determined) for the 1 g samplings. The method employed for this work [3] involved spiking the 0 %, and 0.1 % phthalates in PVC samples with known masses of benzyl benzoate followed by dissolution of the PVC matrices with THF (for example, 10 mL for 0.1 g PVC sample size) using sonication (5 to 10) min, after which the polymer resin was precipitated with hexanes (20 mL for 0.1 g PVC sample size). For 1 g sample aliquots, the dissolution solvents were scaled up to 65 mL THF and 130 mL hexanes. Aliquots of the supernate of the samples were then passed through 0.45 µm syringe filters into 2 mL amber glass vials. A spiked blank and calibrants were prepared with each set of samples. Quadruplicate extractions were performed for the 0 % and 0.1 % phthalate materials.

For the NIST Method 1 gas chromatography/mass spectrometry (GC/MS) measurements, 1 µL aliquots were injected onto a 60 m x 0.25 mm (inner diameter), 0.25 µm phase, 50 % phenylmethyl-substituted polysiloxane, with helium at a constant flow of 1.5 mL min<sup>-1</sup>. The GC temperature program began at 66 °C for a 1 min hold then increased at 50 °C min<sup>-1</sup> to 150 °C then 5 °C min<sup>-1</sup> to 300 °C for a 15 min hold. The interface, source and quadrupole temperatures were set at 300 °C, 200 °C, and 150 °C, respectively. For Method 1, selected ions were monitored for benzyl benzoate [mass/charge (*m/z*) 105], di-*n*-butyl phthalate (*m/z* 223), benzyl butyl phthalate (*m/z* 206), bis(2-ethylhexyl) phthalate (*m/z* 279), di-*n*-octyl phthalate (*m/z* 279), diisononyl phthalate (*m/z* 293), and diisodecyl phthalate (*m/z* 307).

The GC/MS measurements using Method 2 began with a 0.5 µL to 1.0 µL splitless injection at a temperature of 275 °C (0.80 min splitless time), a constant flow of helium of 1.5 mL min<sup>-1</sup>, an oven temperature program beginning at 150 °C for a 1 min hold followed by a 5 °C min<sup>-1</sup> ramp to 300 °C for a 15 min hold. The mass spectrometer's source and interface were both set at 300 °C and the Q3 quadrupoles were scanned from *m/z* 40 to *m/z* 550. For SRM 2860, reconstructed ion chromatograms for benzyl benzoate (*m/z* 105), di-*n*-butyl phthalate (*m/z* 149), benzyl butyl phthalate (*m/z* 149), bis(2-ethylhexyl) phthalate (*m/z* 149), di-*n*-octyl phthalate (*m/z* 149), diisononyl phthalate (*m/z* 293), and diisodecyl phthalate (*m/z* 307) were used to generate peaks and associated areas for the quantification of the six phthalates.

**CPSC Analytical Approach for Determination of six phthalates in PVC materials:** The CPSC laboratory used the same spiking and extraction procedures of the PVC shredded materials as described above [3]. In addition, the CPSC performed nine extractions for 0.05 mg aliquots of the 0.1 % nine and eight extractions for the 0.05 g samplings of the 2 % materials. CPSC also performed nine extractions each for the 0.1 g aliquots of the 0.1 % and 2 % materials and three extractions each for the 1 g samples of the two materials.

The GC/MS measurements involved a 1.0 µL splitless injection at a temperature of 290 °C (0.80 min splitless time), a constant flow of helium of 1.0 mL min<sup>-1</sup>, an oven temperature beginning at 50 °C for a 1 min hold followed by a 30 °C min<sup>-1</sup> ramp to 280 °C then a 15 °C min<sup>-1</sup> ramp 310 °C for a 4 min hold. The same ions were monitored as those for NIST Method 1 (above). The interface, source, and quadrupole temperatures were set at 320 °C, 200 °C, and 150 °C, respectively.

**Diablo Analytical and Frontier Laboratories Analytical Approaches for Determination of six phthalates in PVC materials:** These laboratories performed measurements of phthalates in the Level II material (2 % phthalates in PVC) using an external calibration and standard addition procedure followed by thermal desorption (TD)-GC/MS [4]. 20 mg PVC/mL solutions of the Level II material were prepared by dissolving in THF. These solutions were then diluted by a factor of five, resulting in 0.5 mg PVC/mL solutions from which 10 µL aliquots were sampled, spiked with known amounts of a phthalate standard (for the standard addition procedure), dried at 50 °C and analyzed by TD-GC/MS. Thermal desorption took place during a 100 °C - 320 °C thermal ramp at 20 °C/min with a 5 min hold at the final temperature. The GC/MS measurements involved a split injection onto a 30 m x 0.25 mm i.d. Ultra ALLOY-5 column (0.25 µm film) at a temperature of 320 °C, a constant flow of helium of 1.2 mL min<sup>-1</sup>, an oven temperature beginning at 80 °C for a 1 min hold followed by a 50 °C min<sup>-1</sup> ramp to 200 °C then a 15 °C min<sup>-1</sup> ramp 320 °C for a 2 min hold. The MS was scanned from *m/z* 29 to *m/z* 600, with the same ions used as those specified in NIST Method 1 (above) for quantitation of the six phthalates. The interface, source and quadrupole temperatures were set at 320 °C, 230 °C, and 150 °C, respectively.

**NIST Analytical Approaches for Characterization of the PVC Matrix (Table 5 and Figure 1, above):** For size-exclusion chromatography (SEC) analysis, the precursor PVC (Oxy 240F) was dissolved in THF (high performance liquid chromatography (HPLC) grade) at a concentration of 2.3 mg mL<sup>-1</sup>. Punches (diameter from 4 to 5 mm) from the PVC sheets were weighed (mass range of punches was from 16.6 mg to 41.3 mg) and dissolved in 10 mL of THF.

Thus, the concentration of the samples varied between 1.66 mg mL<sup>-1</sup> and 4.13 mg mL<sup>-1</sup>. The critical overlap concentration ( $c^*$ ) of PVC, which was determined from the intrinsic viscosity data of the precursor PVC (inverse of intrinsic viscosity of the highest molar mass species in the sample), was 5.3 mg mL<sup>-1</sup>. Before SEC analysis, all the samples were allowed to dissolve and solvate overnight, with mixing by occasional gentle inversion. Two punches were obtained from each sheet, and two SEC injections were performed from the solution of each punch.

The multi-detector SEC instrument consisted of an HPLC pump, a manual injector with 100  $\mu$ L injection loop, a multi-angle static light scattering detector (MALS), a quasi-elastic light scattering (QELS) detector, a differential viscometer (VISC), and differential refractive index (DRI) detector. The delay reservoir volume in the viscometer was 27 mL. The columns used were three PLgel 10  $\mu$ m-particle size columns connected in series. The columns and detectors were temperature-regulated to 25 °C. The normalization of MALS detector, and determination of interdetector delays and interdetector band broadening, was accomplished using a narrow dispersity ( $M_w/M_n \leq 1.06$ ) polystyrene with nominal  $M_w$  of 30000 g mol<sup>-1</sup>. THF was used as eluent.

## REFERENCES

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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](mailto:srminfo@nist.gov); or via the Internet at <https://www.nist.gov/srm>.*