



# National Institute of Standards & Technology

## Certificate of Analysis

### Standard Reference Material<sup>®</sup> 1580

#### Organics in Shale Oil

This Standard Reference Material (SRM) is intended primarily for evaluating the reliability of analytical methods for the determination of trace-level organic compounds in an oil matrix (i.e., shale oil, petroleum crude oil, or coal-derived liquids). A unit of SRM 1580 consists of five ampoules, each containing approximately 1.2 mL of shale oil.

**Certified Mass Fraction Values:** Certified values for eight organic constituents 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 investigated or taken into account [1].

**Reference Mass Fraction Values:** Reference values for 12 polycyclic aromatic hydrocarbons (PAHs) are provided in Table 2. Reference values are noncertified values that are estimates of the true value. However, the values do not meet the NIST criteria for certification and are provided with associated uncertainties that may reflect only measurement precision, may not include all sources of uncertainty, or may reflect a lack of sufficient statistical agreement among multiple analytical methods [1].

**Information Mass Fraction Values:** Information values for seven organic compounds are provided in Table 3. 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 or only a limited number of analyses were performed [1].

**Expiration of Certification:** The certification of **SRM 1580** is valid, within the measurement uncertainty specified, until **31 March 2027**, provided the SRM is handled and stored in accordance with 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) will facilitate notification.

The coordination of the technical measurements leading to the update of the certification of SRM 1580 was performed by B.A. Benner, Jr. and L.C. Sander of the NIST Analytical Chemistry Division.

Analytical measurements for the update of SRM 1580 were performed by B.A. Benner, Jr. of the NIST Analytical Chemistry Division; the original certification measurements were performed by J.B. Thomas, S.N. Chesler, F.R. Guenther, L.R. Hilpert, P.L. Konash, W.E. May, R.M. Parris, and K.L. Richie of the NIST Analytical Chemistry Division.

Evaluation of the data was provided by S.D. Leigh, N.A. Heckert, and A.L. Pintar of the NIST Statistical Engineering Division.

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

Stephen A. Wise, Chief  
Analytical Chemistry Division

Robert L. Watters, Jr., Chief  
Measurement Services Division

Gaithersburg, MD 20899  
Certificate Issue Date: 26 June 2012  
*Certificate Revision History on Last Page*

## INSTRUCTIONS FOR HANDLING, STORAGE, AND USE

**Handling:** Shale from the Mahogany Zone of the Colorado Green River Formation was processed by partial combustion resulting in a shale oil that was subsequently centrifuged, filtered, and mixed. This material may contain constituents of unknown toxicities; therefore, caution and care should be exercised during its handling and use. Consult the Material Safety Data Sheet (MSDS), enclosed with the SRM shipment, for details.

**Storage:** Sealed ampoules, as received, should be stored in the dark at temperatures between 10 °C to 30 °C.

**Use:** Samples for analysis should be withdrawn from ampoules immediately after opening and processed without delay for any certified value in Table 1 to be valid within the stated uncertainty. Certified values are not applicable to ampoules stored after opening, even if resealed.

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

The shale oil for SRM 1580 came from a 150-ton retort for *in-situ* simulated combustion of shale oil, operated by the Laramie Energy Technology Center, Laramie, WY. The shale was from the Mahogany Zone of the Colorado Green River Formation. The shale oil was supplied in November 1975 to the Oak Ridge National Laboratory (ORNL) where it underwent centrifugation to separate the oil from water and sludge. The shale oil was provided to NIST by Bruce R. Clark, ORNL, Oak Ridge, TN.

At NIST, the centrifuged sample was filtered through fine filter paper and mixed in a 20 L, Teflon-stoppered, glass bottle by rolling for 40 hours. Samples were aliquoted into 2 mL amber glass ampoules. Although not intended to be representative of all shales oils, SRM 1580 provides a typical specimen of this matrix for use in developing analytical methods.

Randomly selected ampoules were analyzed. Each analyst examined from three to six ampoules, sometimes measuring replicates from one ampoule. No trend was found in measured values with the ampouling sequence.

At least two independent techniques were employed for the determination of the certified values for the organic constituents. Four different methods of sample preparation were used prior to analysis: simple dilution of the shale oil with methylene chloride (or other suitable solvent); acid/base extraction to isolate acidic, basic, and neutral components; a liquid chromatographic fractionation; and, a solid-phase extraction preparation. The following techniques were employed for the final quantitative analysis: gas chromatography with flame ionization detection (GC-FID), gas chromatography/mass spectrometry (GC/MS) with selected ion monitoring for detection, and liquid chromatography (LC) with selective fluorescence detection. The GC/MS analyses used either the standard addition or internal standard methods for quantitation. The GC-FID and LC analyses employed either internal standard, external standard, or standard addition methods.

The details of the original certification of SRM 1580 are described in Hertz et al. [2]. Results for recent analyses by GC/MS using internal standards for quantitation were combined with the results from the original certification measurements to update the certified values for the PAHs in Table 1. The reference values in Table 2 were assigned based only on the recent GC/MS analyses.

---

<sup>(1)</sup> 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 Mass Fraction Values of Organic Constituents in SRM 1580

	Mass Fraction (mg/kg)		
Fluoranthene	53.1	±	1.0 <sup>(a,b)</sup>
Pyrene	99	±	10 <sup>(a,b)</sup>
Benzo[ <i>a</i> ]pyrene	21.5	±	2.4 <sup>(a,b)</sup>
Benzo[ <i>e</i> ]pyrene	16.7	±	3.3 <sup>(a,b)</sup>
Phenol	402	±	9 <sup>(c,d)</sup>
<i>o</i> -Cresol	384	±	12 <sup>(c,d)</sup>
2,6-Dimethylphenol	174	±	15 <sup>(a,d)</sup>
Benzo[ <i>f</i> ]quinoline (5,6-Benzoquinoline)	15.5	±	1.0 <sup>(a,e)</sup>

<sup>(a)</sup> The certified value is a weighted mean of the average mass fractions, with one average each from two to three analytical methods [3,4]. The standard uncertainty is the estimated standard deviation of the sampling distribution of the weighted mean [3,4]. The expanded uncertainty is twice the standard uncertainty which is consistent with the ISO Guide [5,6].

<sup>(b)</sup> Methods used were GC/MS and LC-fluorescence.

<sup>(c)</sup> The certified value is a weighted mean of average mass fractions, with one average each from two analytical methods [3,4]. The expanded uncertainty is the half width of a symmetric 95 % parametric bootstrap confidence interval [7], which is consistent with the ISO Guide [5,6]. The effective coverage factor *k* is 2.37 for phenol and 2.19 for *o*-cresol.

<sup>(d)</sup> Methods used were GC-FID and GC/MS with standard addition.

<sup>(e)</sup> Methods used were GC-FID and LC-Fluorescence

Table 2. Reference Mass Fraction Values for Selected PAHs in SRM 1580

	Mass Fraction <sup>(a)</sup> (mg/kg)		
Naphthalene	889	±	107
Phenanthrene	274	±	22
Anthracene	75.0	±	13.4
Benz[ <i>a</i> ]anthracene	45.5	±	4.8
Chrysene/Triphenylene <sup>(b)</sup>	38.4	±	9.0
Benzo[ <i>b</i> ]fluoranthene	11.7	±	1.5
Benzo[ <i>k</i> ]fluoranthene	2.53	±	0.37
Benzo[ <i>j</i> ]fluoranthene	8.9	±	1.0
Benzo[ <i>a</i> ]fluoranthene	4.30	±	0.75
Perylene	1.85	±	0.32
Indeno[1,2,3- <i>cd</i> ]pyrene	4.73	±	0.70
Benzo[ <i>ghi</i> ]perylene	8.29	±	0.97

<sup>(a)</sup> The reference mass fraction value is the mean of results using one analytical technique, GC/MS using internal standards. The expanded uncertainty, *U*, is calculated as  $U = k u_c$ , where  $u_c$  is one standard deviation of the analyte mean, and the coverage factor, *k*, is determined from the Student's *t*-distribution corresponding to the associated degrees of freedom (df = 2) and a 95 % confidence level for each analyte.

<sup>(b)</sup> Represents the combined mass fraction values of these two PAHs as they co-elute under the chromatographic conditions used for this work.

Table 3. Information Mass Fraction Values for Organic Compounds in Shale Oil

	Mass Fraction (mg/kg)
<i>p</i> -Cresol	270 <sup>(a)</sup>
<i>m</i> -Cresol	330 <sup>(a)</sup>
2,5-Dimethylphenol	320 <sup>(a)</sup>
2,4-Dimethylphenol	380 <sup>(a)</sup>
2,5,6-Trimethylphenol	360 <sup>(a)</sup>
2,4,6-Trimethylphenol	120 <sup>(a)</sup>
Phenanthridine	45 <sup>(b)</sup>

<sup>(a)</sup> Acid/base extraction – GC analysis<sup>(b)</sup> LC extraction – LC analysis

## REFERENCES

- [1] May, W.; Parris, R.; Beck, C.; Fassett, J.; Greenberg, R.; Guenther, F.; Kramer, G.; Wise, S.; Gills, T.; Colbert, J.; Gettings, R.; MacDonald, B.; *Definitions 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 June 2012).
- [2] Hertz, H.S.; Brown, J.M.; Chesler, S.N.; Guenther, F.R.; Hilpert, L.R.; May, W.E.; Parris, R.M.; Wise, S.A.; *Determination of Individual Organic Compounds in Shale Oil*; Anal. Chem. Vol. 52, pp. 1650-1657 (1980).
- [3] Dersimonian, R.; Laird, N.; *Meta-Analysis in Clinical Trials*; Control Clin. Trials, Vol. 7, pp. 177–188 (1986).
- [4] Rukhin, A.L.; *Weighted Means Statistics in Interlaboratory Studies*; Metrologia, Vol. 46, pp. 323–331 (2009).
- [5] JCGM 100:2008; *Evaluation of Measurement Data — Guide to the Expression of Uncertainty in Measurement* (ISO GUM 1995 with Minor Corrections); Joint Committee for Guides in Metrology (2008); available at [http://www.bipm.org/utis/common/documents/jcgm/JCGM\\_100\\_2008\\_E.pdf](http://www.bipm.org/utis/common/documents/jcgm/JCGM_100_2008_E.pdf) (accessed June 2012); 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/tn1297/index.cfm> (accessed June 2012).
- [6] JCGM 101:2008; *Evaluation of measurement data – Supplement 1 to the Guide to Expression of Uncertainty in Measurement*; Propagation of Distributions Using a Monte Carlo Method; Joint Committee for Guides in Metrology (BIPM, IEC, IFCC, ILAC, ISO, IUPAC, IUPAP and OIML), International Bureau of Weights and Measures (BIPM), Sèvres, France (2008); available at [http://www.bipm.org/utis/common/documents/jcgm/JCGM\\_101\\_2008\\_E.pdf](http://www.bipm.org/utis/common/documents/jcgm/JCGM_101_2008_E.pdf) (accessed June 2012).
- [7] Efron, B.; Tibshirani, R.J.; *An Introduction to the Bootstrap*; Chapman & Hall (1993).

**Certificate Revision History:** 26 June 2012 (Updated certified values and changed the perylene value from a certified to reference value; updated and added reference values; added expiration date; editorial changes); 24 November 1980 (This technical revision provides the addition of certified and non-certified organic compounds and an update to the table of “Summary of Results by Analytical Methods”); 10 March 1980 (Original certification date).

*Users of this SRM should ensure that the Certificate 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 <http://www.nist.gov/srm>.*