National Institute of Standards & Technology

Certificate of Analysis

Standard Reference Material® 2777

Weathered Gulf of Mexico Crude Oil in Toluene

This Standard Reference Material (SRM) 2777 is a naturally weathered Gulf of Mexico crude oil that is diluted in toluene. SRM 2777 is intended for use in evaluating analytical methods for the determination of polycyclic aromatic hydrocarbons (PAHs) in weathered crude oil matrices. All the constituents for which certified and reference values are provided are naturally present in the weathered oil. A unit of SRM 2777 consists of five ampoules, each containing approximately 1.2 mL of crude oil solution.

Certified Mass Fraction Values: Certified mass fraction values for PAHs 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]. The certified values are based on the agreement of results obtained at NIST using multiple analytical techniques.

Reference Mass Fraction Values: Reference mass fraction values are provided for additional PAHs and 17α(H),21β(H)-hopane 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].

Expiration of Certification: The certification of **SRM 2777** is valid, within the measurement uncertainty specified, until **30 September 2027**, 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.

Overall direction and coordination of technical measurements leading to certification were performed by J.A. Murray, M.M. Schantz and S.A. Wise of the NIST Chemical Sciences Division.

Evaluation of the data was provided by 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.

Analytical measurements were performed by J.A. Bowden, J.A. Murray, and S.S. Schuur of the NIST Chemical Sciences Division.

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Certified Values: The certified mass fractions and uncertainty interval of PAHs are given in Table 1. For each certified value, the estimate was derived by fitting a statistical model to the results of measurements using two to three analytical methods. The Bayesian paradigm was used for statistical inference [2]. The expanded uncertainty is calculated in a manner consistent with the ISO/JCGM Guide [3,4], and it expresses contributions from all recognized sources of uncertainty. Sample analysis methods are denoted by the footnotes in the table. Metrological traceability is to the SI derived unit for mass fraction, expressed as mg/kg, through certified values of PAHs in SRM 2260a and SRM 1491a that were used to prepare calibrants.

Table 1. Certified Mass Fraction Values for PAHs in SRM 2777

	Mass Fraction[a] (mg/kg)		
Phenanthrene[b,c,]	0.585	±	0.091
1-Methylphenanthrene[b,c,d]	2.43	±	0.29
2-Methylphenanthrene[b,c,d]	1.63	±	0.18
3-Methylphenanthrene[b,c,d]	3.15	±	0.29
9-Methylphenanthrene[b,c,d]	4.18	±	0.51
Benzo[ghi]perylene[c,d]	0.106	±	0.015

[a] Values are expressed as $x \pm U_{95\%}(x)$, where x is the certified value and $U_{95\%}(x)$ is the expanded uncertainty corresponding to a symmetric 95 % coverage interval. To propagate uncertainty, treat the certified value as normally distributed with mean x and standard deviation $U_{95\%}(x)/2$.
[b] GC/MS (I) analysis on an Rxi-17sil MS column.
[c] GC/MS (II) using SPE clean-up followed by analysis on a DB-XLB column.
[d] GC/MS (III) using LC fractionation followed by analysis on a Rxi-17 column.

Reference Values: The reference mass fractions and uncertainty interval of additional PAHs and $17\alpha(H),21\beta(H)$-hopane are given in Table 2. For each reference value, the estimate was derived by fitting a statistical model to the results of measurements using one to three analytical methods. The Bayesian paradigm was used for statistical inference [2]. The expanded uncertainty is calculated in a manner consistent with the ISO/JCGM Guide [3,4]. Values in Table 2 are metrologically traceable to the measurement methods.

Table 2. Reference Mass Fraction Values for Additional PAHs and $17\alpha(H),21\beta(H)$-Hopane in SRM 2777

	Mass Fraction (mg/kg)[a]		
Dibenzothiophene[b]	0.379	±	0.025
Pyrene[b,c]	0.443	±	0.073
1-Methylpyrene[b,c]	0.190	±	0.032
4-Methylpyrene[b,c]	0.73	±	0.13
Chrysene[b,c,d]	1.92	±	0.19
Triphenylene[b,c,d]	3.37	±	0.33
Benzo[b]fluoranthene[b,d]	0.504	±	0.088
Picene[c,d]	0.167	±	0.023
$17\alpha(H),21\beta(H)$-Hopane[c,d]	7.9	±	1.1

[a] Values are expressed as $x \pm U_{95\%}(x)$, where x is the certified value and $U_{95\%}(x)$ is the expanded uncertainty corresponding to a symmetric 95 % coverage interval. To propagate uncertainty, treat the certified value as normally distributed with mean x and standard deviation $U_{95\%}(x)/2$.
[b] GC/MS (I) analysis on an Rxi-17sil MS column.
[c] GC/MS (II) using SPE clean-up followed by analysis on a DB-XLB column.
[d] GC/MS (III) using LC fractionation followed by analysis on a Rxi-17 column.

INSTRUCTIONS FOR HANDLING, STORAGE, AND USE

Handling: This material is a dilution of naturally weathered crude oil and may contain constituents of unknown toxicities; therefore, caution and care should be exercised during its handling and use.

Storage: Sealed ampoules, as received, should be stored in the dark at temperatures between 4 °C and 30 °C.

Use: Samples for analysis should be withdrawn **immediately** after opening ampoules and should be processed without delay for the certified values in Table 1 to be valid within the stated uncertainties. Certified values are not applicable to material stored in ampoules that have been opened, even if they are resealed.

PREPARATION AND ANALYSIS[(1)]

Sample Collection and Preparation: The weathered petroleum crude oil sample that was used to prepare SRM 2777 was provided by C. M. Reddy of Woods Hole Oceanographic Institution (Woods Hole, MA). The weathered oil was extracted from oil-soaked sand that was collected 31 August 2012 at Gulf Shores Beach, AL which had been impacted by the Deepwater Horizon oil spill in April 2010. Geochemical analysis by Aeppli et al., revealed that the residue is weathered Macondo Well oil [5]. Soxhlet extraction (90:10 dichloromethane/methanol v:v) was used to extract the weathered oil from the sand. Solvent was removed to yield a dark, syrupy liquid. This source material was then delivered to NIST and diluted in toluene at approximately 71.3 mg/g. The resulting oil solution was homogenized by stirring overnight. The mixed oil solution was then transferred and sealed into 2 mL amber glass ampoules that had been flushed with argon.

Determination of PAHs and 17α(H),21β(H)-hopane: The general approach used for value assignment of the PAHs and 17α(H),21β(H)-hopane in SRM 2777 consisted of combining results from analyses using various combinations of different cleanup/isolation procedures and chromatographic separation techniques [6]. Three sets of gas chromatography/mass spectrometry (GC/MS) results, designated as GC/MS (I), GC/MS (II), and GC/MS (III), were obtained at NIST.

For the GC/MS (I) determination of the PAHs, two test portions (80 mg) from six ampoules were transferred to a vial and spiked with a known amount of internal standard solution consisting of perdeuterated PAHs and further diluted with toluene. This oil mixture was then analyzed by GC/MS using a 0.25 mm i.d. × 60 m fused silica capillary column with a 50 % (mole fraction) phenyl methylpolysiloxane phase (0.25 μm film thickness; Rxi-17sil MS, Restek, Bellefonte, PA). Results using this method are denoted as GC/MS (I).

For the GC/MS (II) analyses, one test portion (260 mg) from each of six ampoules of SRM 2777 was transferred to a vial, spiked with a known amount of internal standard solution consisting of perdeuterated PAHs. An aliquot of the diluted oil (0.1 mL) was fractionated using an aminopropyl solid-phase extraction (SPE) column to isolate the fraction of interest. Following a concentration step, the isolated fraction was analyzed by GC/MS using a 0.25 mm i.d. × 60 m fused silica capillary column with a proprietary phase (0.25 μm film thickness; DB-XLB column, Agilent Technologies, Santa Clara, CA). Results using this method are denoted as GC/MS (II).

For GC/MS (III) analyses, duplicate test portions of 260 mg from 10 ampoules of SRM 2777 were transferred to a vial, spiked with a known amount of an internal standard solution consisting of perdeuterated PAHs and 17β(H),21β(H)-hopane. The oil mixture was loaded on an aminopropyl SPE column to isolate the fraction of interest. Following a concentration step, the processed extract was then fractionated using liquid chromatography on a semi-preparative scale aminopropyl silane column. Three fractions were collected: (1) aliphatics, hopanes, and steranes; (2) low molecular PAHs through fluorene; and (3) the remainder of the PAHs through molecular mass 302 g/mol. Following concentration, each fraction was then analyzed by GC/MS using a 0.25 mm i.d. × 60 m fused silica capillary column with a proprietary stationary phase (0.10 μm film thickness; Rxi-PAH, Restek, Bellefonte, PA). Results using this method are denoted as GC/MS (III).

In addition to the analyses performed at NIST, SRM 2777 was used in an interlaboratory comparison exercise in 2014-2015 sponsored by the Gulf of Mexico Research Initiative [7, 8]. The results obtained from the interlaboratory study were not included in the value assignment; however, they were used for confirmation of the NIST measurements.

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

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; or via the Internet at https://www.nist.gov/srm.