U. S. Department of Commerce
Philip M. Klutznick
Secretary

National Bureau of Standards
Ernest Ambler, Director

National Bureau of Standards Certificate of Analysis

Standard Reference Material 1580

Organics in Shale Oil

This 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.

Certified Values of Constituent Organic Compounds: The certified values for selected organic constituents are shown in Table 1. These values are based on results obtained by two independent, analytical methods (see Table 2). Non-certified values, which are given for information only, are listed in Table 3.

NOTICE AND WARNINGS TO USER

Expiration of Certification: This certification is valid, within the limits certified, for 3 years from the date of purchase. In the event that the certification should become invalid before then, purchasers will be notified by NBS.

Storage: Sealed ampoules, as received, should be stored in the dark at temperatures between 10-30 °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Use: Samples for analysis should be withdrawn from ampoules immediately after opening and processed without delay for any certified value in Table 1 to be valid within the stated uncertainty.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

The shale oil for this SRM came from a 150-ton retort for *in-situ* simulated combustion of oil shale, operated by the Laramie Energy Technology Center, Laramie, Wyoming. The shale was from the Mahogany Zone of the Colorado Green River Formation. The shale oil had been 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 NBS by Bruce R. Clark, ORNL, Oak Ridge, Tennessee.

At NBS, the centrifuged sample was filtered through fine filter paper and mixed in a 20-liter, 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 shale oils, SRM 1580 provides a typical specimen of this matrix for use in developing analytical methods.

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

Two independent techniques were employed for the determination of the certified values for the organic constituents. Three 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; and a high performance liquid chromatographic fractionation. The following techniques were employed for the final quantitative analysis: gas chromatography (GC), gas chromatography/mass-spectrometry (GC/MS) with single ion monitoring for selective detection, and high performance liquid chromatography (HPLC) with selective fluorescence detection. All GC/MS analyses used the standard addition method for quantitation. The GC and HPLC analyses employed either internal standard, external standard, or standard addition methods. The analytical methods and the corresponding values are summarized in Table 2.

Consultation on the statistical design of the experimental work was provided by K. R. Eberhardt of the Statistical Engineering Division.

The coordination of the technical measurements leading to certification were performed under the direction H. S. Hertz, S. N. Chesler, L. R. Hilpert, W. E. May, and S. A. Wise.

The technical and support aspects involved in preparation, certification, and issuance of this Standard Reference Material were coordinated through the Office of Standard Reference Materials by R. Alvarez.

Washington, D.C. 20234
March 10, 1980

George A. Uriano, Chief
Office of Standard Reference Materials

(over)

The following members of the staff of the Center for Analytical Chemistry, Organic Analytical Research Division, performed the analytical determinations.

1. J. M. Brown
2. S. N. Chesler
3. F. R. Guenther
4. L. R. Hilpert
5. W. E. May
6. R. M. Parris
7. K. Richie

TABLE 1. Certified Values of Organic Constituents

Compound	Concentration ($\mu g/g$)[a]
Fluoranthene	54 ± 10
Benzo[a]pyrene	21 ± 6
Benzo[e]pyrene	18 ± 8
Phenol	407 ± 50
o-Cresol	385 ± 50

[a]The estimated uncertainty listed for a constituent is based on judgment and represents an evaluation of the combined effects of method imprecision, possible systematic errors among methods, and material inhomogeneity. The estimated uncertainty is intended to correspond to approximately 95% confidence limits.

TABLE 2. Summary of Results by the Analytical Methods Used in Certification

Compound	Concentration ($\mu g/g$)[a]	Number of Ampoules Analyzed	Sample Preparation Technique	Analytical Technique
Fluoranthene	55 ± 5	6	Direct Injection	GC/MS
	53 ± 2	9	HPLC	HPLC
Benzo[a]pyrene	20 ± 1	6	Direct Injection	GC/MS
	23 ± 1	8	HPLC	HPLC
Benzo[e]pyrene	17 ± 1	6	Direct Injection	GC/MS
	20 ± 3	8	HPLC	HPLC
Phenol	412 ± 35	8	HPLC	GC/MS
	402 ± 4	8	Acid/Base Extraction	GC
o-Cresol	386 ± 42	8	HPLC	GC/MS
	384 ± 9	8	Acid/Base Extraction	GC

[a]Uncertainty is the standard deviation of a single measurement.

TABLE 3. Non-Certified Values of Organic Compounds in Shale Oil

NOTE: The values shown in this table are not certified because they are not based on the results of two independent methods. These values are included for information only.

Compound	Concentration ($\mu g/g$)
p-Cresol	(270)[a]
m-Cresol	(330)[a]
2,5-Dimethylphenol	(320)[a]
Pyrene	(100)[b]

[a]Acid/base extraction - GC analysis
[b]Direct injection - GC/MS analysis