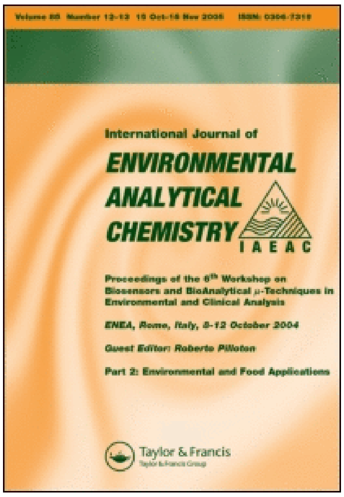

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Analytical Standards and Methods for the Determination of Polynuclear Aromatic Hydrocarbons in Environmental Samples†

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Standard reference materials (SRM's) have been produced, certified, and issued by the United States National Bureau of Standards (NBS) since 1905. NBS currently issues more than 1000 SRM's of various types, including nuclear materials, rubber, clinical and environmental trace metal standards. The most recent addition to this group is a series of environmental trace organic materials with certified concentrations of selected polynuclear aromatic hydrocarbons (PAH), phenols, and N-heterocyclic compounds. Until recently, trace organic SRM's were non-existent due to the lack of analytical methodology necessary for certification. Details concerning the analytical methods developed and used for certification of the concentrations of several PAH in SRM's 1580 (Organics in Shale Oil), 1644 (Generator Columns for PAH in water), 1647 (PAH in Acetonitrile), and 1649 (Urban Particulate Matter) are given along with some suggested uses for these SRM's.

KEY WORDS: Gas chromatography/mass spectrometry, generator columns, high performance liquid chromatography, polynuclear aromatic hydrocarbons, priority pollutants, shale oil, standard reference materials, urban particulate matter.

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†Paper presented at the Workshop on the Chemistry and Analysis of Hydrocarbons in the Environment. Barcelona, November 1981.

INTRODUCTION

We have previously reported on the state-of-the-art in the frontier area of quantitative trace organic analysis.[1] In recent years, the Organic Analytical Research Division of the National Bureau of Standards (NBS) has been involved in a number of collaborative analytical studies whose purpose was to further assess the accuracy of data obtained from the trace organic analysis of environmental samples. The results of these studies revealed the existence of biases among laboratories involved in the measurement of polycyclic aromatic hydrocarbons (PAH), phenols, and nitrogen containing PAH compounds in environmental samples.[2-4] It has been demonstrated, particularly in the trace metals area, that the use of appropriate quality assurance standards or Standard Reference Materials (SRM's) can enhance the accuracy of analytical measurements.[5] However, until recently, SRM's for environmental trace organic analyses were nonexistent due to the lack of the analytical methodology necessary for certification.

At NBS three modes of measurements have historically been used to assure that certified values of SRM properties are accurate. These are: (a) definitive methods, (b) reference methods, (c) two or more independent and reliable methods.

In the first mode, measurement of the property is made using a method of analysis based on "first principles". A definitive method is one in which all major significant parameters have been related directly, or by a solid chain of evidence, to the base or derived units of the International System of Units (SI). Direct determination by mass is an example of a definitive method. At NBS, isotope dilution mass spectrometry (ID/MS) has been used as a definitive method for the measurement of organic and inorganic constituents at trace levels in several matrices.[5] In this procedure, all chemical manipulations are done on a weight basis. All mass spectrometric determinations involve ratios, not absolute measurement of the individual isotopes. Therefore, no known instrumental corrections or errors are involved. However, ID/MS has not been investigated at NBS as a definitive method for environmental trace organic analysis mainly due to the unavailability of appropriate internal standards for many of the important analytes.

Reference methods (as defined by NBS) are those methods whose accuracy have been substantiated by comparison with a definitive method or by analysis of a previously certified SRM. These methods are generally more cost and time-effective than definitive methods, and usually do not require highly specialized equipment. Since reference methods require the existence of either a definitive method and/or an appropriate

SRM, environmental trace organic reference methods (as defined by NBS) are also non-existent.

The third possible mode for certification, and the one currently being used for the certification of environmental trace organic SRM's, is measurement by at least two totally independent and reliable methods. This approach is based on the rationale that the likelihood of two independent methods being biased by the same amount in the same direction is small. When the analytical results agree, we can state with some assurance that they are indeed accurate.

The interlaboratory comparison or "round-robin" mode is a subset of mode C and has also been used at NBS for certification of some SRM's. However, this procedure is normally used only for the purpose of reissuing an SRM, with the old certified SRM's being used by NBS as a quality control check on the participating laboratories. The use of this mode in an uncontrolled manner would yield results of questionable accuracy and poor precision as shown by the data given in Table I from an interlaboratory comparison of the determination of several PAH in a shale oil sample.

In this paper, details concerning the analytical methods developed and used for certification of the concentrations of several PAH in SRM's 1580 (Organics in Shale Oil), 1644 (Generator Columns for PAH in Water), 1647 (Priority Pollutant PAH in Acetonitrile), and 1649 (Urban Particulate Matter) are presented along with some suggestions for the use of these materials.

SRM 1580, ORGANICS IN SHALE OIL

The shale oil for this SRM is from a 150-ton retort for *in situ* simulated combustion of oil shale, operated by the Laramie Energy Technology Center, Laramie, Wyoming. The shale oil was obtained by Oak Ridge National Laboratory (ORNL) in November 1975, where it underwent centrifugation to separate water and sludge from the oil.

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 in the certification process. Each analyst examined at least six ampoules and made a minimum of three replicate measurements from each ampoule. No correlation was found between the measured values and the ampouling sequence. The PAH measured in this sample are pyrene, fluoranthene, benzo[a]pyrene, benzo[e]pyrene, and perylene.

TABLE I

Interlaboratory comparison of shale oil analyses (Concentrations in $\mu g/g$).

		Laboratory									
	NBS[a]	2	3[b]	3[c]	3[d]	4	5	6	7	8	9
Compound			b	c	d						
fluoranthene	61 ± 8	102	247	75		80	108	126	122	116	380
pyrene	102 ± 5	155	161	138	147	150	168	177	141	185	620
benzo[a]pyrene	22 ± 2	—		19	13	—			3.3		
benzo[e]pyrene	21 ± 1								1.3		

[a] Results reported by NBS represent the mean of values obtained by GC, GC/MS, and HPLC uncertainties represent the standard deviation of the mean.

[b] Quantification by GC/MS.

[c] Quantification by HPLC.

[d] Quantification by laser excited spectroscopy.

Certification

Two methods of analytical sample preparation were used. Dilution of the sample in methylene chloride was the only sample preparation step necessary prior to analysis by gas chromatography/mass spectrometry (GC/MS). Samples to be analyzed by high performance liquid chromatography (HPLC) were prepared by HPLC fractionation. Samples containing approximately 14 mg of shale oil were injected onto a 300 mm × 8 mm aminosilane (NH_2) column using a loop injector. The mobile phase was composed of two to five percent methylene chloride in hexane. Standards of the compounds to be measured were injected prior to the shale oil to determine the appropriate elution volumes for fraction collection. The fractions were collected in centrifuge tubes and reduced to 50–500 μL by passing nitrogen over the sample.

The GC/MS determinations were performed using selected ion monitoring and a standard addition technique for quantification. The polynuclear aromatic hydrocarbons of interest were separated on a 30 m SE-52 wall coated open tubular column interfaced to a quadrupole mass spectrometer.

Liquid chromtographic analysis was performed using an instrument equipped with a gradient pumping system, loop injector, and a spectrofluorimetric detector. A digital integrator and strip chart recorder were used for data acquisition. As mentioned previously, PAH were initially isolated from the shale oil matrix by chromatography on an aminosilane column using hexanemethylene chloride as the mobile phase. The analytes were then separated from the PAH by chromatography on an octadecylsilane column (C-18) with a water-acetonitrile mobile phase. Further selectivity was obtained by monotoring the chromatographic effluent fluorometrically with excitation and emission wavelengths optimized for detection of each analyte. External standard and standard addition methods were used for quantification.

A summary of the results obtained using the two analytical methods are given in Table II. Further details concerning these methods can be found elsewhere.[3,4] The certified values for five PAH along with values for three phenols and one N-heterocyclic compound are given in Table III.

Uses

SRM 1580 is intended primarily for evaluating the reliability of analytical methods used for the determination of trace level organic compounds in an oil matrix. In addition to PAH, several phenols and N-heterocycles have been certified in SRM 1580. These compounds are representative of acidic, basic, and neutral organic species which are isolated in most extraction schemes.

TABLE II

Summary of results of analytical methods used in certification.

Compound	Conc.[a] (μg/g)	Sample preparation technique	Analytical technique
fluoranthene	55 .±5	Direct Injection	GC/MS
	53 ±2	HPLC	HPLC
pyrene	101 ±5	Direct Injection	GC/MS
	107 ±8	HPLC	HPLC
benzo[a]pyrene	20 ±1	Direct Injection	GC/MS
	23 ±1	HPLC	HPLC
benzo[e]pyrene	17 ±1	Direct Injection	GC/MS
	20 ±3	HPLC	HPLC
perylene	2.8±0.5	Direct Injection	GC/MS
	3.9±0.6	HPLC	HPLC

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

TABLE III

Certified values of PAH in SRM 1580.

Compound	Concentration (μg/g)[a]
fluoranthene	54 ±10
pyrene	104 ± 9
benzo[a]pyrene	21 ± 6
benzo[e]pyrene	18 ± 8
perylene	3.3± 1.1
phenol	407 ±50
o-cresol	385 ±50
2,6-dimethylphenol	175 ±30
5,6-benzoquinoline	16 ± 4

[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 homogeneity. The uncertainty given represents the best estimates of possible systematic errors and the 95% confidence level of the means.

As efforts to develop alternate fuels intensify, the number of laboratories required to perform single species quantitative analyses will increase dramatically, and new measurement techniques and methods will continue to evolve. It must be emphasized that SRM 1580 will not assure accurate analysis for PAH, phenols and N-heterocyclic compounds in complex environmental matrices; however this SRM can serve as a benchmark against which the accuracy of emerging analytical techniques can be evaluated. SRM 1580 can also serve as an intercalibration material on which laboratories can evaluate the comparability of methods for compounds and classes of compounds that have not yet been certified.

SRM 1644, GENERATOR COLUMNS FOR POLYNUCLEAR AROMATIC HYDROCARBONS

SRM 1644 consists of separate generator columns for anthracene, benz(a)anthracene, and benzo(a)pyrene. These columns are 50 cm × 0.6 cm stainless steel tubes packed with 80–100 mesh quintus quartz (sea sand) and coated with 0.5% (w/w) of the PAH compound of interest. These columns were prepared commercially under the technical direction of NBS.

Saturated solutions are generated by pumping HPLC grade water through the generator column at flow rates between 0.1 and 5 mL/min. Since the acqueous solubility is a well-defined thermodynamic quantity, saturated solutions are standard solutions.

Certification

Two independent analytical techniques were used to certify the concentration of anthracene, benz(a)anthracene and benzo(a)pyrene in the acqueous effluents from their respective generator columns. The first technique involved the quantitative extraction of the PAH from the aqueous stream by an "extractor column" packed with a C-18 bonded phase; the use of an acetonitrile-water eluent to transfer components from the extractor column to an analytical C-18 column for separation of the analyte from non-analyte components; and detection of the analyte by absorbance at 254 nm. Details concerning this method have been reported elsewhere.[6–8] The second technique involved the use of a "standard addition" technique for "on stream" analysis. The effluent from the generator column was mixed with PAH standards dissolved in acetonitrile, and the resultant analyte concentration in the mixed solvent determined by fluorescence.

These methods were used to measure the concentrations of anthracene, benz(a)anthracene and benzo(a)pyrene in the aqueous effluents from their respective generator columns at temperatures between 10 to 30°C for 20 columns randomly selected from the SRM pool of 240 columns for each compound. The data obtained were combined and fitted to an empirical expression of the form $\ln[\text{Conc}] = A + B(1/T) + C(1/T)^2$ by least squares. In this equation, $\ln[\text{Conc}]$ is the natural logarithm of the concentration, T is the absolute temperature, and A, B, and C are constants. The derived equations for anthracene, benz(a)anthracene, and benzo(a)pyrene were used to calculate the certified concentrations at one degree intervals between 10 and 30°C for each compound. These certified concentrations are given in Table IV. The certification of generator columns for Indeno(1,2,3-cd)pyrene is now in progress. These columns will provide aqueous solutions of this PAH at certified concentrations between 0.05 and 0.3 μg/kg over the 10–30°C temperature range.

Uses

SRM 1644 is intended to provide accurate concentrations of anthracene, benz(a)anthracene and benzo(a)pyrene in water. Because the acqueous solubility of PAH in general and the above in particular are very low (43, 9.1, 1.6 and 0.2 μg/kg) at 25°C, respectively, such solutions are difficult to prepare and impossible to preserve for long periods of time. The use of this SRM allows the user to circumvent these problems by generating the desired solution as needed.

TABLE IV

Temperature °C	Concentration and its uncertainty,[a] μg/kg		
	Anthracene	Benz(a)anthracene	Benzo(a)pyrene
10	16.6±0.7	3.38±1.2	0.59±0.06
11	17.6±0.6	3.60±1.1	0.63±0.05
12	18.7±0.6	3.83±0.91	0.67±0.04
13	19.8±0.5	4.09±0.79	0.71±0.04
14	21.1±0.5	4.36±0.68	0.76±0.03
15	22.4±0.5	4.65±0.59	0.81±0.03
16	23.8±0.5	4.96±0.54	0.87±0.03
17	25.4±0.5	5.29±0.55	0.93±0.03
18	27.0±0.5	5.65±0.60	0.99±0.03
19	28.8±0.5	6.04±0.68	1.06±0.03
20	30.7±0.6	6.45±0.77	1.13±0.03
21	32.8±0.6	6.90±0.87	1.21±0.04
22	35.0±0.6	7.38±0.94	1.30±0.04
23	37.4±0.6	7.90±1.0	1.39±0.04
24	39.9±0.6	8.45±1.0	1.49±0.04
25	42.7±0.6	9.05±1.0	1.59±0.04
26	45.7±0.8	9.69±1.0	1.71±0.04
27	48.9±1.0	10.4±1.1	1.83±0.05
28	52.4±1.3	11.1±1.2	1.96±0.05
29	56.1±1.7	11.9±1.3	2.11±0.07
30	60.1±2.2	12.8±1.7	2.26±0.09

[a] The uncertainties are 99 percent (Working–Hotelling) confidence bands for the entire regression curve. The difference between the true and certified concentration should be less than the stated uncertainty at the 99 percent confidence level.

SRM 1647, PRIORITY POLLUTANT POLYNUCLEAR AROMATIC HYDROCARBONS (IN ACETONITRILE)

A 12.0 liter solution containing the 16 PAH on the U.S. Environmental Protection Agency's list of priority pollutants was prepared for NBS by a commercial vendor. Approximately 11 of 12 liters of this solution were dispensed (1.2 mL ampoule) into 9000 ampoules before shipment to NBS.

Samples representing the early, middle and final stages of ampouling were analyzed by HPLC immediately upon arrival at NBS. No significant differences in concentration for any of the 16 compounds was found. However, visual inspection of the residue remaining in the 12-L flask after the ampoules had been filled revealed the presence of some undissolved crystalline material. HPLC analysis of an aliquot of this residual solution revealed that the two compounds that did not dissolve completely were chrysene and dibenz(a),h)anthracene.

Certification

Three analytical methods were used in the certification of SRM 1647. The gravimentric values (corrected for compound purity) supplied by the commercial vendor were used for fourteen of the sixteen compounds. Gravimetric values for chrysene and dibenz(a,h)anthracene were rejected as a result of the preliminary HPLC determinations made on the ampouled and residual solution. HPLC separation on a polymeric C-18 column, using an acetonitrile-water mobile phase and UV (254 nm) determine response factors for each of the sixteen compounds. Six mixture were measured. Four external standard solutions were used to determine responcse factors for each of the sixteen compounds. Six replicate measurements were made on each of the external standard solutions and nine ampoules randomly selected from the SRM pool. Figure 1 is a typical chromatogram from the HPLC analysis of SRM 1647.

Gas chromatography on a fused silica SE-52 capillary column was used for the determination of eight of the sixteen compounds. Two standard solutions were used to obtain compound responses relative to 1-methylpyrene and m-tetraphenyl which were used as internal standards. Four replicate analyses were made on each of the two calibration solutions and two ampoules taken from the SRM pool.

Gas chromatography was also used to determine the purity of each of the crystalline materials used in this SRM. These purity values were used directly in the gravimetric method and in the calculation of the concentration of each of the 16 PAH in the standard solutions used in the

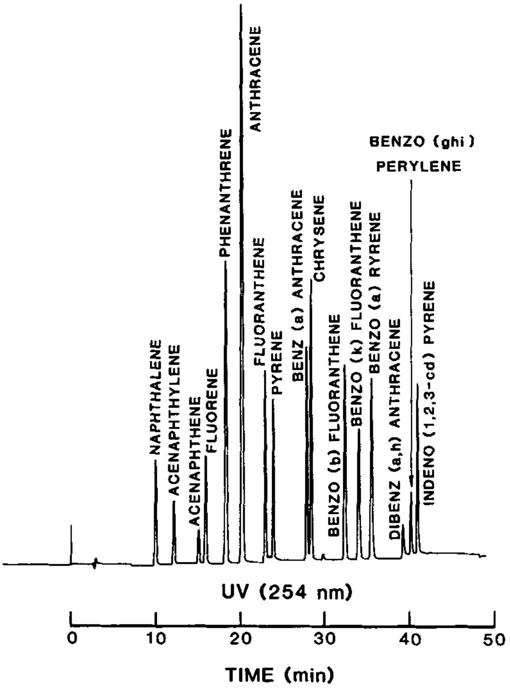

FIGURE 1 HPLC separation of 16 priority pollutant PAH.

GC and HPLC methods. The certified values along with a summary of the results obtained for the three analytical methods are given in Table V.

Uses

SRM 1647 is intended primarily for calibrating chromatographic systems used in the determination of priority pollutant PAH. This material can also be useful in PAH recovery studies. For example, because of its miscibility with water, SRM 1647 can be used to fortify aqueous samples with known amounts of these PAH. This SRM was developed at the request of the U.S. Environmental Protection Agency to support method 610 for PAH.[9]

SRM 1649, URBAN PARTICULATE MATTER

NBS has recently completed a preliminary analysis of an urban air particulate matter sample as an SRM to be certified for trace organic

TABLE V

Summary of results by the analytical methods used for certification of SRM 1647 (PAH in Acetonitrile).

	Concentration (μg/mL)			
	Gravimetry	HPLC	GC	Certified[a]
1. Naphthalene	22.5	22.4 ±0.5		22.5 ±0.2
2. Acenaphthylene	19.0	19.2 ±0.5		19.1 ±0.2
3. Acenaphthene	20.8	21.2 ±0.4		21.0 ±0.4
4. Fluorene	4.89	4.96±0.18		4.92±0.10
5. Phenanthrene	5.00	5.12±0.18		5.06±0.10
6. Anthracene	3.25	3.33±0.10		3.29±0.10
7. Fluoranthene	9.99	10.3 ±0.5		10.1 ±0.2
8. Pyrene	9.82	9.85±0.58		9.84±0.10
9. Benz(a)anthracene	4.99	5.12±0.14	4.97±0.06	5.03±0.10
10. Chrysene		4.69±0.15	4.68±0.06	4.68±0.10
11. Benzo(b)fluoranthene	5.11	5.13±0.21	5.09±0.06	5.11±0.10
12. Benzo(k)fluoranthene	5.00	5.06±0.15	4.99±0.10	5.02±0.10
13. Benzo(a)pyrene	5.28	5.32±0.13	5.31±0.19	5.30±0.10
14. Benzo(ghi)perylene	4.00	4.09±0.30	3.99±0.14	4.01±0.10
15. Dibenz(a,h)anthracene		3.73±0.12	3.63±0.07	3.68±0.10
16. Indeno(1,2,3-cd)pyrene	4.07	4.11±0.15	4.02±0.06	4.06±0.10

[a] The estimated uncertainty given for each compound is based on judgment, and represents an evaluation of the combined effects of method imprecision and possible systematic errors among methods.

constituents. SRM 1649 will consist of 10 gram quantities of this material with certified concentrations for several PAH. The particulate material for this SRM was collected in Washington, D.C. in a baghouse especially designed for this purpose. The sample was collected over a period in excess of 12 months and, therfore, is a time-integrated sample. The particulate material was removed from the filter bags by a specially designed vacuum cleaner and combined into a single lot. This material was screened through a fine mesh sieve to remove most of the fibers and other extraneous material from the bags. The sieved material was then thoroughly mixed in a V-blender, bottled, and sequentially numbered.

Certification

Randomly selected bottles have been selected for the determination of 13 PAH by at least one of two independent analytical schemes. Sample aliquots of 1 g are being extracted in a Soxhlet extractor for 48 h with a cycle time of about 20 min. Samples being prepared for GC analysis are extracted with 450 mL of a 1:1 mixture of benzene/methanol, whereas samples for HPLC analysis are extracted with a similar volume of methylene chloride. An internal standard solution of 1-methylpyrene (for GC analysis) or 7-methylfluoranthene (for LC analysis) is added to the particulate samples prior to extraction. Prior to GC analysis the extract is concentrated in a rotary evaporator, re-dissolved in cyclohexane, and liquid-liquid partitioned between N,N-dimethylformamide (DMF) and water as described by Bjørseth.[10] After the liquid-liquid partition the total PAH fraction is isolated by normal-phase HPLC on an aminosilane column. The PAH fraction is collected, concentrated, and analyzed by GC on a 30 m × 0.25 mm i.d. SE-52 fused silica column.

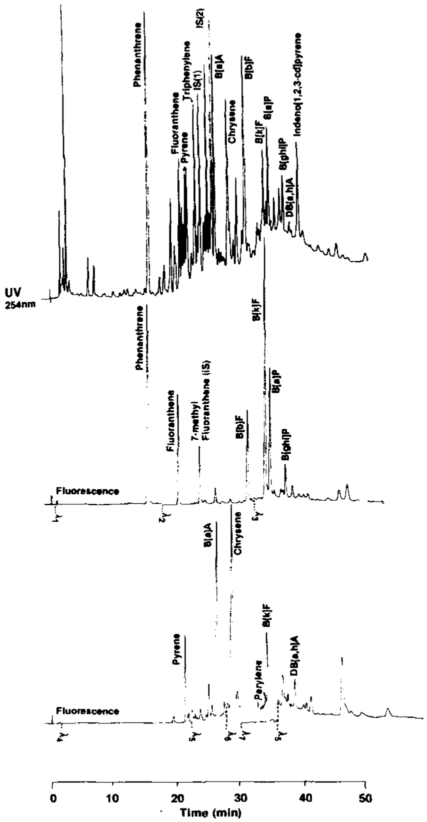

FIGURE 2 HPLC analysis of Washington Urban Dust Sample. The upper chromatogram is the UV detection at 254 nm; the middle and lower chromatograms are with fluorescence detection with excitation and emission conditions given in Table VI. (IS) = internal standard, B(b)F = benzo-(b)fluoranthene, B(k)F = benzo(k)fluoranthene, B[ghi]P = benzo(ghi)perylene and DB[a,h]A = dibenz(a,h)anthracene.

TABLE VI

Fluorescence condition for HPLC determination of PAH in air particulate extract.

	Wavelengths (nm)		
	Excitation	Emission	PAH determined
λ_1	250	360	phenanthrene
λ_2	285	450	fluoranthene, 7-methylfluoranthene (I.S.), benzo[b]fluoranthene
λ_3	295	400	benzo[k]fluoranthene, benzo[a]-pyrene, benzo[ghi]perylene
λ_4	335	385	pyrene
λ_5	285	390	benz[a]anthracene, dibenz[a,h]-anthracene
λ_6	270	360	chrysene
λ_7	400	440	perylene, benzo[k]flouranthene

TABLE VII

Preliminary results of the determination of selected PAH on Washington urban particulate matter (μg/g).[a]

	GC	HPLC
Phenanthrene		4.8 ± 0.3
Fluoranthene	7.3 ± 0.2	7.4 ± 0.7
Pyrene	7.2 ± 0.4	6.3 ± 0.4
Benzo[a]anthracene	2.4 ± 0.1	2.5 ± 0.3
Chrysene	4.6 ± 0.2[b]	3.7 ± 0.2
Benzo[b]fluoranthene		6.2 ± 0.5
Benzo[k]fluoranthene		2.0 ± 0.2
Benzo[a]pyrene	2.9 ± 0.3	2.6 ± 0.4
Benzo[e]pyrene	3.3 ± 0.2	4.1 ± 0.3
Perylene	0.8 ± 0.1	0.8 ± 0.1
Benzo[ghi]perylene	4.7 ± 0.2	3.9 ± 0.8
Indeno[1,2,3-cd]pyrene	3.3 ± 0.3	3.4 ± 0.4
Dibenz[a,h]anthracene		0.5 ± 0.1

[a] These values are *not* certified. Research is continuing to resolve discrepancies between methods. Certification will be contingent upon the agreement between methods for each compound after all analytical measurements have been made.

[b] Includes triphenylene, which co-elutes with chrysene.

Sample clean-up for the LC chloride analyses consists of evaporation of the methylene chloride to near dryness, solvent exchange to cyclohexane, and liquid-liquid partition between cyclohexane and nitromethane.[11] The nitromethane solution is concentrated to approximately 2 mL and analyzed by reversed phase HPLC on a polymeric C-18 column, with an acetonitrile/water gradient elution. A fluorescence detector is being used which is capable of changing excitation and emission wavelengths as a function of time during the chromatographic run. The excitation and emission wavelengths used for detection of each of the 13 PAH determined are listed in Table VI. Preliminary data for SRM 1649 obtained using the GC and HPLC methods on a limited number of samples are given in Table VII. Figures 2 and 3 are GC and HPLC chromatograms representing the analysis of extracts of candidate SRM 1649. Further details concerning these methods will be reported elsewhere.[12,13]

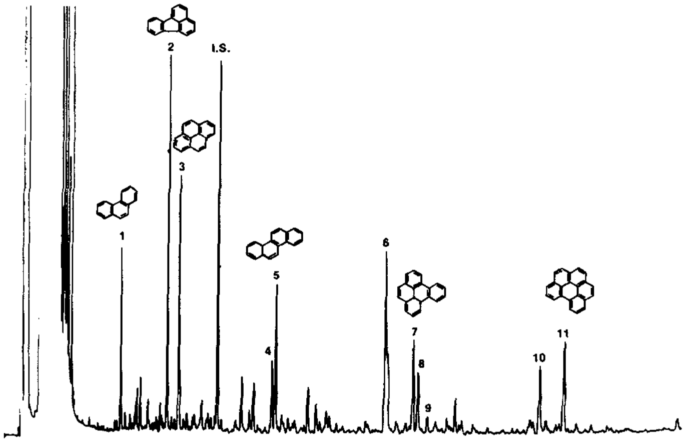

FIGURE 3 Gas chromatographic separation of fraction from Washington Urban Dust Sample. Peaks identified are (1) phenanthrene, (2) fluoranthene, (3) pyrene, (I.S.) 1-methylpyrene, (4) benz(a)anthracene, (5) chrysene/triphenylene, (6) benzofluoranthenes, (7) benzo(e)pyrene, (8) benzo(a)pyrene, (9) perylene, (10) indeno(1,2,3-cd)pyrene, and (11) benzo(ghi) perylene.

Uses

This particulate material will be useful for the validation of analytical methods for the determination of PAH on particulate matter samples. In addition the availability of this large quantity of homogeneous particulate material will provide analysts with adequate material for use in intercalibration and biological studies.

SUMMARY

The SRM's discussed in this paper are intended to serve either or both of two functions; calibration of analytical instrumentation or validation of analytical procedures for determination of individual PAH in complex samples. SRM 1647, Priority Pollutant PAH in Acetonitrile, is intended for use in the calibrating chromatographic instrumentation used in PAH analyses. SRM 1644, Generator Columns for PAH in Water, can be used for producing aqueous solutions for anthracene, benz(a)anthracene and benzo(a)pyrene. SRM's 1580, Organics in Shale Oil and 1649, Urban Particulate Matter, can be used for evaluating the reliability of analytical methods used for determining individual PAH in complex matrices. For example, several research groups have used SRM 1580 to validate new analytical procedure for determining PAH in various oil shale, coal, and petroleum derived samples.[14–19]

In our own laboratory, SRM 1580 has been used to validate an on-line multidimensional HPLC approach for the determination of PAH in oil matrices.[20] This system (shown in Figure 4) utilizes an aminosilane column in the normal phase mode for isolation of a selected fraction from a complex mixture and a C-18 column in the reversed phase mode with spectrofluorimetric detection for analytical separation and selective detection, as does the off-line sequential HPLC method that we have described previously.[3,4,21–23] In addition, this system employs a "concentrator column" (diamino) for interfacing the normal and reversed phase systems. The desired fraction is valved through, and trapped on, the

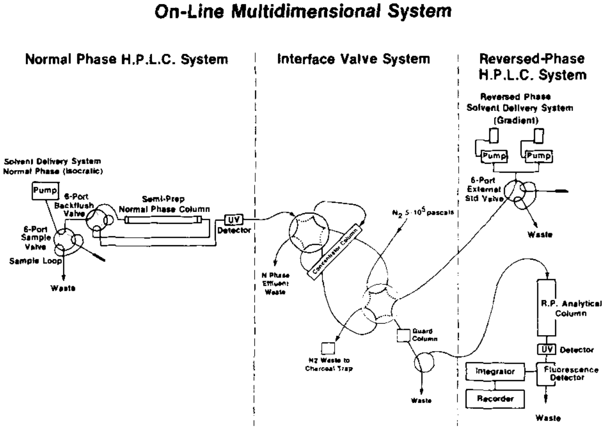

FIGURE 4 Schematic diagram of the on-line multidimensional HPLC system.

"concentrator column". The normal phase solvent is evaporated using an inert gas purge. The concentrator column is then valved into the reversed-phase analytical system and the fraction transferred to the analytical column by gradient elution focusing. SRM 1580 was used to validate this approach as shown by the data given in Table VIII.

The methods developed and/or used at NBS for certification of these SRM's can, with minor modifications, be employed for the routine determination of PAH in real-world samples.

TABLE VIII

Determination of selected PAH in three oil samples by multidimensional HPLC.

Compound	Multidimensional HPLC (on-line)[a]	Multidimensional HPLC (off-line)[a]	Certified[c]
	SRM 1580 (Shale Oil) Concentration in μg/g)		
Fluoranthene	53.8 ±3.5(3)[b]	53 ±2(9)	54 ±10
Pyrene	109.7 ±7.1(3)	107 ±8(10)	104 ±18
Perylene	2.32 ±0.15(5)	3.9 ±0.6(11)	3.4±2.2
Benzo[a]pyrene	20.7 ±2.2(8)	23 ±1(8)	21 ± 6
	SRC II Coal Liquid (Concentration in mg/g)		
Fluoranthene	3.15 ±0.04(3)	3.3 ±0.16(3)	
Pyrene	6.65 ±0.05(3)	6.0 ±0.2(3)	
Perylene	0.024±0.002(3)		
Benzo[a]pyrene	0.133±0.008(5)	0.134±0.007(3)	
Benzo[e]pyrene	0.153±0.006(3)	0.143±0.005(3)	
Benzo[k]fluoranthene	0.062±0.001(5)		
	Wilmington Crude Oil (Concentration in μg/g)		
Fluoranthene	2.4 ±0.3(3)	3 ±1(3)	
Pyrene	14.8 ±2.2(3)	14 ±2(3)	

[a] Uncertainty is 1 standard deviation.

[b] (*n*) indicates the number of replicate measurements.

[c] Certified values derived from a combination of HPLC and GC/MS values.

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