Validation of a Method for the Analysis of PAHs in Bulk Lake Sediments Using GC–MS

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Abstract

This work presents the validation procedures of an analytical method to determine the 16 PAHs from the US EPA's priority pollutants list in sediment samples using ultrasonic extraction coupled to gas chromatography–mass spectrometry. The extraction techniques are altered by the construction of an extraction flask adapted to the ultrasonic bath that greatly reduces losses and increases extraction efficiency of the volatile compounds, especially naphthalene. Cleanup procedures are also altered to change the polarity of the solvent mixture that contributes to reducing the elution of undesirable compounds. The PAH spiked sediment at 100 µg/kg level shows recovery rate of 68% to 108%. A certified reference material has been analyzed for those compounds showing results conforming to certified values. The optimized procedure is applied to sediment samples from different areas across Southeast Brazil and presents the results from the Ibirité Reservoir (MG, Brazil), a eutrophic water body. The total PAH concentration in these sediment samples varies between 103.96 and 180.87 µg/kg (dry weight). As the detected concentrations are relatively low, the acute toxicity detected in sediment and its pore water is not due to these compounds, but to high concentrations of ammonia, copper, and nickel according to TIE procedures.

Introduction

Polycyclic aromatic hydrocarbons (PAHs) are widespread environmental contaminants of special concern on account of their carcinogenic and mutagenic properties (1–3). For this reason, 16 PAHs have been classified by the US Environmental Protection Agency (U.S. EPA) as priority pollutants (4,5).

These compounds can be introduced into the environment by various processes, including natural ones, such as incomplete high temperature combustion of organic matter, as well as from anthropogenic sources, such as pyrolysis of fossil fuel and the resulting release of oil-derived products (2,6–8). Most PAH inputs in aquatic environments are linked to some type of human activity, such as industrial and urban wastes.

Due to their low solubility and high hydrophobicity, these compounds tend to be rapidly adsorbed by the particles of the sediment (9–11). Therefore, in aquatic ecosystems, suspended sediments (particulates) and bottom sediments can be considered the most important sinks of these contaminants, whose characteristics reflect the inputs from point and non-point sources of contaminants to those systems (12,13).

Sediments have a large number of different organic compounds, like humic acids, that make it difficult to identify and quantify PAHs (14). Various authors have already observed that PAHs are a class of organic compounds that have high affinity to organic matter in soils and sediments; therefore, an increase in the organic carbon concentrations indicate a PAHs content increase in those matrixes (15–17). Moreover, sediment grain-size distribution is also an important factor governing PAHs distribution as fine grain-size sediments have been shown to accumulate greater PAHs concentration than coarse sand (15,18).

Many analytical techniques have been developed and subsequently applied to monitor these compounds in the environment. Sample extraction is a critical step in PAHs analysis because these compounds are strongly sorbed to the matrix; consequently, their extraction is time-consuming and in many cases causes quantification errors (19).

The traditional extraction methods of these compounds in sediment samples include Soxlhet, ultrasonic extraction, and mechanical shaking (12,20,21). Currently, modern extraction techniques, such as supercritical fluid extraction, pressurized liquid extraction, and microwave-assisted extraction (13,14,17,22,23), have also been employed, although at considerable costs (24).

Each one of these techniques has its advantages and limitations, and choosing a method depends on factors such as cost, user friendly operation, amount of solvent used, and amount of time used (25). The most widely used liquid/solid extraction is Soxhlet, which requires a very long extraction time (6–48 h), consumes large amounts of organic solvent, is laborious, and can degrade thermally labile compounds (22). New approaches have been used to replace Soxlhet extraction with faster and less solvent consuming methods, which include one or more extraction cycles [e.g., ultrasonic extraction (26)]. In ultra-sonication a large number of samples can be extracted from each batch, with lower equipment costs, high extraction efficiency, and lower extraction temperature (20).

Due to the complex nature of the sediments, it is difficult to analyze extracts for trace contaminants using chromatographic techniques. Owing to their highly complicated physico-chemical structure, the processing of such samples has to be carried out in several successive stages to entirely remove any interfering substances (27).

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After extraction, clean-up steps of PAH extracts are necessary, as it enables the analysis many groups of compounds simultaneously. Many clean-up procedures have been employed to remove potential interfering polar constituents (24,28). One of the most used methods is liquid chromatography (LC), which exploits different polarities of compounds, using silica gel or aluminum oxide as a stationary phase. For different polar compound groups, elution solvents with increasing polarity are used, non-polar solvents such as hexane or pentane are used for eluting the first fraction, followed by more polar solvents or their mixtures (29).

As for the analysis step, chromatographic methods have been found to be the best choice for the determination of PAHs in environmental samples. Gas chromatography (GC) and LC have become the most widely applicable modes of chromatography for PAHs (30). The use of GC coupled to mass spectrometry (MS) for the determination of PAHs is based on a favorable combination of greater selectivity, resolution, and sensitivity (31).

To guarantee that a chosen method is adjusted for a desired analytical application, it is necessary to carry out its validation (32) in order to assure the required reliability of the obtained results (33). Thus, the work herein describes the development and validation procedures to determine the 16 PAHs of the U.S. EPA priority pollutant list in sediment samples using ultrasonic extraction and GC–MS analysis. This procedure was used to determine PAHs concentration in sediment samples from different sites of Southeast Brazil. This study presents the results from the Ibirité Reservoir, a eutrophic water body located in the metropolitan area of Belo Horizonte (MG, Brazil) as a field case.

Experimental

Chemicals

Sixteen PAHs considered of primary environmental concern according to the US EPA were analyzed: naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, indeno-[1,2,3-cd]pyrene, dibenzo[a,h]anthracene and benzo[ghi]perylene. The standard solutions of the 16 PAHs (purity > 99%), purchased from Accustandard (New Haven, CT), were used for quantification.

Deuterated internal standards (naphthalene-d_8, acenaphthene-d_{10}, phenanthrene-d_{10}, chrysene-d_{12}, and perylene-d_{12}) and surrogate standard (*p*-terphenyl-d_{14}) were also purchased from Accustandard.

A certified reference material for 16 priority PAHs (HS-6 Marine sediment) was supplied by the National Research Council of Canada and was used to test the validity of the entire method.

Reagents and solvents were of analytical and chromatographic grade. Acetone, *n*-hexane, and methylene chlorine purchased from J.T. Baker (Phillipsburg, NJ) were used throughout the work.

Anhydrous sodium sulfate, obtained from Merck (Germany), was heated for 4 h at 400°C, cooled, and then stored in a drier. Silica gel (60–230 mesh, J.T. Baker) and alumina (J.T. Baker) were activated for at least 16 h at 130°C and 400°C, respectively, before their use.

Apparatus

A Shimadzu QP 2010 GC–MS (Kyoto, Japan) GC coupled to a quadrupole MS was used to analyze the sediment samples. Ultrasonic extractions were performed with an Ultra Cleaner 4800–40 kHz and 220 W, from Unique (Brazil), while the microfiltration apparatus employed was a Kontes Ultra-Ware microfilter (Grace, Deerfield, IL).

Sample collection

The sediment samples were collected at three sampling points of the Ibirité Reservoir located in the vicinities of Betim-MG, Southeast Brazil. The water body receives treated effluents from a petroleum refinery, as well as untreated domestic sewage from surrounding cities, as shown elsewhere (later), which are the main source of nutrients and the main cause of eutrophication. The collected samples were fully homogenized, stored in amber glass bottles, and cooled at 4°C until the laboratory analyses were performed.

Preparation of spiked sample

The sediment samples used in the optimization step of the PAHs extraction process were collected in the upmost part of the Taboões stream located in the metropolitan region of Belo Horizonte (MG, Brazil). This site is considered a pristine ecosystem, although it is relatively close to a metropolitan area and is, therefore, used as a reference site in studies carried out in the Ibirité Reservoir.

These samples presented grain size distribution predominantly of fine fractions, 68% silt-clay and 32% sand, with an organic carbon content of 3%. The collected samples were homogenized, dried at 40°C, and stored in amber glass bottles.

Immediately prior to extraction, sediment samples were spiked with the mixture standard solution of 16 PAHs at a concentration of 100 µg/kg and also with the surrogate standard. The samples were extracted and subjected to a cleanup process. Spiked and non-spiked samples were systematically compared.

Sediment extraction and clean-up

PAHs extraction were based on the U.S. EPA methods 3550C (34) and on the study of Banjoo (21). Aliquots of 10 g (weighted to ± 0.0001 g) of the sediment sample were treated with anhydrous Na_2SO_4 in a constructed extraction flask adapted to the ultrasonic bath, which consisted of an Erlenmeyer with screw cap and teflon-silicone septa. Before the extraction, 100 ng of standard *p*-terphenyl-d_{14} were added as surrogate. Ultrasonic extraction was performed with 50 mL of hexane–acetone (1:1) in an ultrasonic bath for 15 min. The extract was then filtered through Whatman 540 filter paper, under vacuum, using the aforementioned Kontes microfilter. The use of an ice bath during the filtration step was also included. The last two steps were repeated two more times. The sonicated extracts were evaporated in a rotary evaporator and concentrated to ~ 1 mL under a gentle stream of purified N_2 gas for further cleanup.

Extracts were purified following a cleanup procedure using a glass column (1 cm i.d. and 30 cm height) packed at the top with copper for sulfur removal, followed by 1 g of anhydrous Na_2SO_4, 1 g of water-deactivated alumina 2%, and 8 g of activated silica gel. The elution solvents used were based on the U.S. EPA method

3630C (29), only substituting pentane with hexane. The solvent mixture used in this study was 50 mL of 3:2 hexane–dichloromethane, the extract was then evaporated in a rotary evaporator and concentrated to 1 mL under a stream of nitrogen gas, after which 100 ng of an internal standard mixture were added.

Equipment parameters

The chromatographic analysis was based on a previously reported GC–MS methodology, U.S. EPA methods 8270D (35). PAHs were analyzed in a GC coupled to a quadrupole MS (Shimadzu QP-2010, Japan) operating in the electron impact mode (70 eV). The separation was carried out in a 30 m × 0.25 mm i.d. DB-5 MS column (J&W Scientific, Folsom, CA) coated with a 0.25-µm thick film of 5% diphenyl–polydimethylsiloxane. The heating schedule started at 45°C (held for 1 min), increased at 45°C/min to 130°C, then 10°C/min to 180°C, 6°C/min to 240°C, then finally 13°C/min to 310°C (held for 10 min). Injection was performed in splitless mode for 1 min. The carrier gas was helium (purity > 99.999 %), used at a flow of 1.2 mL/min. Injector, interface, and ion source temperature were 250°C, 250°C, and 200°C, respectively.

To increase the sensitivity and specificity, the analyses were performed in selected ion monitoring (SIM) mode using three ions for each PAH compound. The ion mass program used for quantification is detailed in Table I. Total runtime was 28.26 min.

The calibration technique is the internal standard multipoint calibration using five standard solutions (10 to 5000 µg/L). The compounds are quantified using the ratio of the analyte and internal standard response (36). The internal standard was added to the sample extract just prior to the instrumental analysis. The analytes were identified by matching the retention time of each compound with the retention times listed in the calibration standards and mass spectral libraries (NIST 27 and NIST 147).

Table I. GC–MS Conditions: Time Frame, Retention Time of Each Analyte and Deuterated Standards and Specific Ion of Each Compound

Time Frame (min)	Compounds	Retention Time (min)	Ions
4.00–6.50	*Naphthalene-d_8*	5.22	136
	Naphthalene	5.25	128, 127, 129
6.50–10.00	Acenaphthylene	7.62	152, 151, 150
	Acenaphthene-d_{10}	7.88	164
	Acenaphthene	7.95	154, 153, 152
	Fluorene	9.02	166,165,163
10.00–15.80	*Phenanthrene-d_{10}*	11.42	188
	Phenanthrene	11.49	178, 179, 176
	Anthracene	11.64	178, 176 179
	Fluoranthene	15.29	202, 101, 203
	Pyrene	16.05	202, 200, 203
	p-terphenyl-d_{14}	16.87	244
15.80–21.50	Benzo[a]anthracene	20.14	228, 229, 226
	Chrysene-d_{12}	20.17	240, 120, 236
	Chrysene	20.23	228, 226, 229
21.50–28.26	Benzo[b]fluoranthene	22.67	252,253, 125
	Benzo[k]fluoranthene	22.73	252,253, 125
	Benzo[a]pyrene	23.29	252,253, 125
	Perylene-d_{12}	23.39	264
	Indeno[1,2,3-cd]pyrene	25.61	276, 18, 227
	Dibenzo[a,h]anthracene	25.69	278, 138, 279
	Benzo[ghi]perylene	26.22	276, 138, 277

Quality assurance and quality control

The accuracy and precision of the optimized analytical method was determined by using a HS-6 certified reference material and sediment sample spiked with all 16 PAHs.

A standard solution was injected daily into the GC–MS to calibrate the instrument. To check for contamination problems, a procedural blank was analyzed periodically for each batch of 10 samples. This blank was prepared following the entire analytical procedure and using the same reagents and solvents as those used for the samples.

To determine the concentration of PAHs in the sediment, which is considered a complex matrix, it is common to use surrogates to rectify losses produced in the sample preparation step (12) and internal standards to account for routine variations in the response of chromatographic system (36). Table I shows the five deuterated PAHs used as internal standards, one in each chromatographic window, used to quantify all the target compounds.

Results and Discussion

The sample pretreatment before the chromatographic analysis is generally long, and therefore extraction of the PAHs, purification due to the complexity of these environmental matrices, and pre-concentration steps can lead to total or partial losses of the target analytes (37). It is, therefore, necessary to validate the used method. The first step to evaluate the extraction efficiency of PAHs was the use of a spiked sediment sample with standard mixture of 16 PAHs at concentration of 100 µg/kg.

The choice of a classical extraction method in this study was based on parameters discussed in the literature, such as relative capital cost, organic extraction solvent volume, extraction time, as well U.S. EPA standardization (20,23). Moreover, many studies have shown that the ultrasonic extraction in environmental samples presents good extraction efficiency for less volatile PAHs, resulting in high recovery values, between 60% and 114% (12,21,25). However, in ultrasonic extraction, volatile PAHs present low recoveries due to evaporation during the extraction processes (12,21,24). It must be pointed out that in the literature many studies present very low recoveries to naphthalene, ranging between 23% and 65% when ultrasonic extraction is employed (13,25,24). To overcome this problem, the ultrasonic extraction technique used with some important modifications resulted in increased extraction efficiencies, especially for very volatile compounds, such as naphthalene. Therefore, to avoid losses of volatile compounds, an extraction flask was constructed and adapted to the ultrasonic bath consisting of an Erlenmeyer with screw cap and teflon–silicone septa. The use of an ice bath during the filtration step was also included. These relevant modifications significantly increased the recovery rate of this compound in spiked sediment samples, which was as low as 33% to 86%; however, improvements were also made with respect to acenaphthylene and acenaphthene to a lesser degree.

Another alteration introduced in this work, in comparison with similar works found in the literature, refers to the cleanup procedure, which is in fact based on the U.S. EPA method 3630C (29). Many studies (24) show that the choice of the elution solvent is a determinative factor in the efficiency of the cleanup procedure, thus the polarity index of the solvent mixture used was

changed, becoming more non-polar when substituting pentane for hexane, as suggested by the US EPA method. This modification helped to elute polar compounds to a lesser degree, reducing the co-elution problems in chromatographic analysis.

The developed method permitted, as shown in Table II, to obtain recovery rates to the 16 priority U.S. EPA PAHs varying between 71% and 108%, which are values that fall within the recovery range of 70% to 130% established in the literature as a validated range (32,36). In our work, the only exceptions are the compounds acenaphthylene and benzo[a]pyrene, the least recovered ones (recovery rates of 68). It must be emphasized that the range of the recovery rate for the compounds found in the work are similar to what can be found in the literature (21,24,25), except for the most volatile ones, naphthalene, acenaphthylene, and acenaphthene, especially for the first compound.

For surrogate standard *p*-terphenyl-d_{14}, the average recovery rate was 106 ± 11%. Following the recommendations of the US EPA method, the surrogate recovery was not used to adjust analyte concentrations.

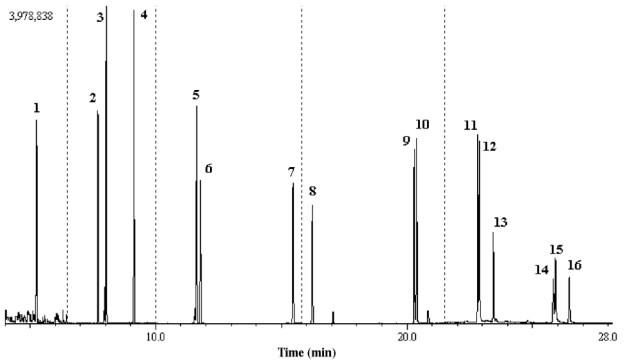

Figure 1. Chromatogram (SIM mode) of a spiked sediment sample and chromatogram (SIM mode) of a non-spiked sediment sample. Identification number: 1, naphthalene; 2, acenaphthylene; 3, acenaphthene; 4, fluorine; 5, phenanthrene; 6, anthracene; 7, fluoranthene; 8, pyrene; 9, benzo[a]anthracene; 10, chrysene; 11, benzo[b]fluoranthene; 12, benzo[k]fluoranthene; 13, benzo[a]pyrene; 14, indeno[1.2.3-cd]pyrene; 15, dibenzo[a.h]anthracene; and 16, benzo[ghi]perylene.

Table II. Validation Parameters Obtained from Spiked Sediments for the 16 PAHs Priority Pollutants by the U.S. EPA

Compounds	r	LOD (µg/kg)	LOQ (µg/kg)	Recovery Rate (%)	RSD (%)	
					Repeatability	Reproducibility
Naphthalene	0.9999	1.54	5.14	86	5	9
Acenaphthylene	0.9999	1.49	4.96	68	5	10
Acenaphthene	0.9999	1.41	4.71	81	4	2
Fluorene	0.9999	1.89	6.30	90	5	2
Phenanthrene	0.9999	1.27	4.25	102	8	5
Anthracene	0.9998	1.80	6.00	71	15	19
Fluoranthene	0.9998	2.97	9.91	106	10	14
Pyrene	0.9989	2.03	6.78	88	12	16
Benzo[a]anthracene	0.9999	1.40	4.68	103	10	8
Chrysene	0.9999	0.53	1.78	108	8	2
Benzo[b]fluoranthene	0.9999	3.56	11.86	104	9	6
Benzo[k]fluoranthene	0.9999	1.69	5.64	100	11	13
Benzo[a]pyrene	0.9998	0.41	1.36	68	15	20
Indeno[1.2.3-cd]pyrene	0.9987	1.35	4.51	83	11	13
Dibenzo[a.h]anthracene	0.9992	1.14	3.81	93	10	14
Benzo[ghi]perylene	0.9996	2.24	7.47	93	11	7

Validation Study

To confirm that the method is suitable for its intended use, a validation process was carried out by establishing the basic analytical requirements of the performance to be appropriate for quantitation of PAHs in sediment samples.

Selectivity/specificity is the first step in the development and validation of an instrumental method of separation (32). By definition, the selectivity refers to the extent to which a method can determine a particular analyte in a complex mixture without interference from other components in the mixture (38), and specificity is considered to be the ultimate in selectivity; it means that no interferences are supposed to occur (39,40). The use of mass spectrometer as detector minimizes interferences from coeluting compounds (41) by the selective nature of this detector. The specificity of the analytical method in this study was determined by comparing the results from sediment samples with and without the spiked analytes (40). Figure 1 shows the chromatograms of these samples. The analytes of interest were well separated from other components present in the samples.

To determine the linear range of the detector, several standard solutions were prepared in different concentrations and injected into the GC–MS. A linear correlation coefficient of > 0.999 was obtained for almost all calibration curves (see Table II).

Precision of an analytical method is the degree of agreement among individual test results when the procedure is applied repeatedly to multiple samplings of a homogeneous sample or to artificially prepared samples (39,42); it is usually stated in terms of standard deviation or relative standard deviation (38). The two most common precision measures are repeatability and reproducibility. The repeatability of an analytical method refers to the use of the procedure in a laboratory over a short period of time, carried out by the same analyst with the same equipment (43). Thus, repeatability was studied using seven replicates at concentration of 100 µg/kg. The intra-laboratory reproducibility of an analytical method is the degree of agreement of the test results obtained by analysis of the same sample under various conditions: different analysts, over extended time scales, within a single laboratory (38). Reproducibility was evaluated at the same concentration level, and spiked samples were analyzed at three different days. It can be observed that precision values, expressed as RSD, were lower than 20% for all analytes (see Table II).

The limit of detection (LOD) of the entire procedure is defined as "the minimum concentration of a substance that can be measured and reported with 99% confidence…" (44). The determination of the detection limit method requires the analyses of at least 7 replicate samples of a single matrix that have been spiked with standard analytes at a known concentration. A standard deviation was obtained for each analyte multiplied by the appropriate Student's *t* value that represents the LOD. As shown in Table II, LODs ranged from 0.41 to 3.56 µg/kg, with benzo[a]pyrene as the lowest value of LOD, and the limit of quantitation (LOQ) ranged from 1.36 to 11.86 µg/kg.

Accuracy of an analytical method is the

closeness of test results obtained by that method to the true value, and is usually expressed as percent recovery by the assay of known amounts of analyte, and it is usually determined by the study of relevant reference materials or by spiking studies (38,39). The accuracy was checked by analyzing the HS-6 certified sediment. Three replicates were analyzed, and the whole analytical procedure was tested in real situations. The resulting values were compared with data given for these certified materials falling within the expected range (considering the standard deviation for each certified concentration) for all certified compounds except for naphthalene, acenaphthene, and fluorene (see Figure 2).

Application of the method to sediment samples from a field case

In our laboratory, among a quite large number of applications, the optimized procedure has been used for the determination of PAHs in sediment samples from different study sites across Southeast Brazil as the study carried out in the Ibirité reservoir (45), an artificial water body found in the metropolitan area of Belo Horizonte (MG, Brazil), which receives treated effluents from a petroleum refinery and, predominantly, in natura domestic sewage. A summary of results from this case study is shown in Table III.

Table III shows that the compounds acenaphthylene, acenaphthene, fluoranthene, and benzo[k]fluor-anthene were the only undetected ones in the sediment samples collected in this reservoir. The total concentration of PAHs of the 16 analyzed hydrocarbons in the sediment samples varied between 103.96 and 180.87 µg/kg on a dry weight basis. The highest total concentration of PAHs was found in the sampling point next to the dam, which may be explained by the high fine-particle sedimentation rates detected in this specific sampling point (45). The obtained results were also compared to the Canadian Sediment Quality Guidelines (SQG) for organic compounds (46). For each contaminant two SQGs were used, TEL (Treshold Effect Level) (i.e., adverse biological effects are never or almost never observed below the TEL) and PEL (Probable Effect Level) (i.e., adverse biological effects are expected to occur more often than not above PEL). It was found that none of the sediment samples presented concentrations higher than TEL or PEL for any of the 16 analyzed compounds (see Table III). Thus, these sediment samples may not show toxicity to benthic organisms as far as PAHs compounds are concerned (45). However, acute toxicity to two different benthic test-organisms were detected in whole sediments, and its pore water must be a consequence of high concentrations of ammonia found in the pore water (up to 38 mg/L), as well as, due to the presence of relatively high concentrations of copper and nickel (up to 0.01 and 0.03 mg/L, respectively) according to TIE (toxicity identification evaluation) procedures (45).

Conclusions

The literature describes several methods that have been proposed and optimized to extract the 16 priority U.S. EPA PAHs from sediment samples. The method proposed in this paper in order to extract and analyze PAHs in sediment samples uses ultrasonic extraction and GC–MS determinations. These determinations require a cleanup procedure to remove interferences from the samples, using a surrogate standard containing *p*-terphenyl-d_{14} to evaluate the performance of the method based on an analysis in a GC–MS equipment and evaluation of the PAHs concentration based on the quantification of an internal standard.

Alterations in the extraction techniques introduced in this work, namely the construction of a special extraction flask adapted to the ultrasonic bath consisting of an Erlenmeyer with screw cap and teflon-silicone septa, greatly reduced losses and increased the extraction efficiency of most volatile compounds, especially of naphthalene. The use of an ice bath during the filtration as an extra step was also included, which helped to improve this extraction efficiency. Another important modification introduced in this work refers to the cleanup procedure, in which the used solvent mixture pentane was changed to hexane, a less polar solvent. This modification helped to elute polar com-

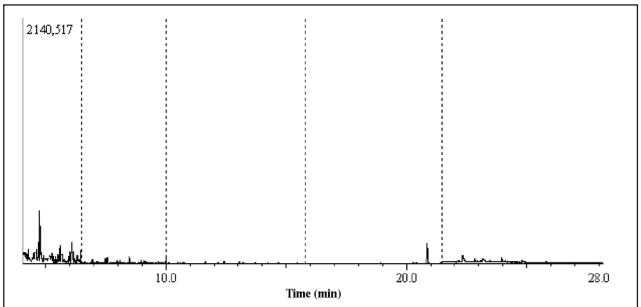

Figure 2. Certified and measured concentrations and standard deviation (SD) of PAHs in the HS-6 reference material. Identification number: (1) naphthalene; (2) acenaphthylene; (3) acenaphthene; (4) fluorine; (5) phenanthrene; (6) anthracene; (7) fluoranthene; (8) pyrene; (9) benzo[a]anthracene; (10) chrysene; (11) benzo[b]fluoranthene; (12) benzo[k]fluoranthene; (13) benzo[a]pyrene; (14) indeno[1.2.3-cd]pyrene; (15) dibenzo[a.h]anthracene; and (16) benzo[ghi]perylene.

Table III. PAHs Concentration Range in Sediment Samples Collected in Three Sampling Points in the Ibirité Reservoir (Belo Horizonte, MG-Brazil) and the TEL and PEL, for Each Analyzed Organic Compound*

Compound	Conc. range (µg/kg)	TEL	PEL
Naphthalene	9.10–18.92	34.6	391
Acenaphthylene	< 4.96†	5.87	128
Acenaphthene	< 4.71†	6.71	88.9
Fluorene	< 6.30–10.79	21.2	144
Phenanthrene	9.08–15.15	41.9	515
Anthracene	< 6–10.03	46.9	245
Fluoranthene	< 9.91†	111	2355
Pyrene	< 6.78–15.02	53	875
Benzo[a]anthracene	13.80–22.85	31.7	385
Chrysene	4.08–9.05	57.1	862
Benzo[b]fluoranthene	< 11.86–14.75	–	–
Benzo[k]fluoranthene	< 5.64†	–	–
Benzo[a]pyrene	15.65–23.29	31.9 782	
Indeno[1.2.3-cd]pyrene	4.93–9.80	–	–
Dibenzo[a.h]anthracene	6.01–9.15	–	–
Benzo[ghi]perylene	< 7.47–12.73	–	–
∑PAH	75.47–171.53	–	–

* TEL = Treshold Effect Level and PEL = Probable Effect Level, both are Canadian Sediment Quality Guidelines.
† This compound was not detected in any of the three sediment samples collected in the Ibirité Reservoir.

pounds to a lesser degree, reducing the co-elution problems in chromatographic analyses.

The proposed method was validated and yields recovery rates of 68% to 108% using spiked sediment samples for the 16 priority PAHs by U.S. EPA. The accuracy was checked by analyzing the sediment reference material, and the results fell within the expected range for most of the certified compounds. The optimized method was also applied to sediment samples collected in the Ibirité reservoir, Southeast Brazil. The results have shown that this eutrophic water body has not been significantly contaminated by PAHs and that the sediments do not present toxic potential (acute toxicity) to the benthic organisms due to the presence of this class of compounds but rather due to high concentrations of ammonia, copper and nickel found in sediment and its pore water.

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