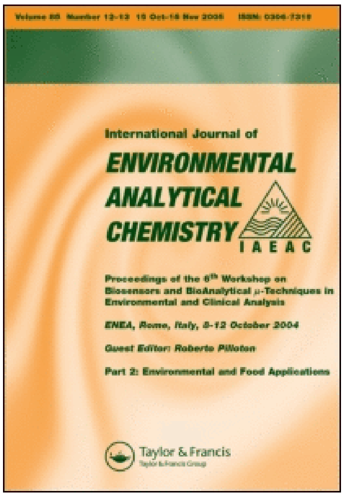

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RAPID QUANTITATION OF TEN POLYCYCLIC AROMATIC HYDROCARBONS IN ATMOSPHERIC AEROSOLS BY DIRECT HPLC SEPARATION AFTER ULTRASONIC ACETONITRILE EXTRACTION

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Ultrasonic extraction followed by reverse phase HPLC separation and fluorescence detection were used in rapid analysis of ten polycyclic aromatic hydrocarbons (PAHs) in very small samples (50–100 mg) of ambient aerosols extracted for 10 min with 8 ml of acetonitrile. Filtered extracts were injected directly into the HPLC system without further fractionation. Fluorescence excitation and emission wavelengths were fixed at 250 nm and 370 nm, respectively. Gradient elution was carried out with acetonitrile (MeCN):water (40% to 100% MeCN in 20 min, held at 100% MeCN for another 5 min) at 0.9 ml/min. Precision and accuracy were determined by analysis of the NBS standard reference material no. 1649 (Urban Dust/Organic). The method was used in the analysis of PAHs in tunnel and atmospheric aerosols. The detection limit is 20 pg for benzo(a)pyrene. For the five NBS certified PAHs (fluoranthene, benzo(a)anthracene, benzo(a)pyrene, benzo(ghi)perylene and indeno(1,2,3-cd)pyrene), measurement accuracy ranges from 1 to 15%. Precision was under 10% for all ten PAHs studied.

KEY WORDS: Polycyclic aromatic hydrocarbons, PAHs in atmospheric aerosols, PAH extraction, HPLC, benzo(a)pyrene.

INTRODUCTION

PAHs are ubiquitous environmental pollutants, usually formed in combustion processes.[1] They constitute an important class of compounds because several are known carcinogens. Data on the concentration of benzo(a)pyrene (BAP, a prototype carcinogenic PAH) as a function of particle size revealed that the largest concentration was found in urban atmospheric aerosols with aerodynamic dia-

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meters between 0.075 and 0.12 μm.[2,3] Clearly, most of the mass of this carcinogen is in the respirable size range[4] which has a long atmospheric residence time. Knowledge of the exact environmental concentration of this, and other PAHs, is important for toxicologic studies, for use in source apportionment models and for the determination of PAH losses resulting from filter artifacts.[5]

The most common analytical procedure employed in the determination of particulate atmospheric PAHs involves collection on glass or quartz fiber substrates, soxhlet extraction with organic solvents such as benzene, cyclohexane, methanol or dichloromethane, followed by separation and quantitation by high performance liquid chromatography (HPLC), gas chromatography or gas chromatography–mass spectrometry. Usually, soxhlet extraction[6,7,8,9,10,11] requires long periods (6–48 h) and makes use of large volumes (100–450 ml) of expensive organic solvents. The use of ultrasonication in the extraction of PAHs from particulate matter has been reported for the determination of total PAHs,[12] benzo(a)pyrene[13,14] and groups containing four[15] or five PAHs.[16,17] A combination of ultrasonication for 1 hr and mechanical stirring for 2 hrs was used in the determination of 13 PAHs by HPLC.[18]

Simultaneous quantitation of several PAHs by HPLC may involve gradient solvent elution for about 1 hr and the use of two detectors in series[6,18] or several aliquot injections with wavelength programming.[6,9] The time demand in the extraction and quantitation of PAHs (8–52 hrs) using these protocols is too large for routine monitoring, limiting the number of samples analyzed. In this study we report the results of a rapid analytical protocol applied in the simultaneous determination of ten priority PAHs present in atmospheric particulate matter.

EXPERIMENTAL SECTION

Reagents

All organic solvents used were chromatography grade (Grupo Quimica Indl. Ltda., R.J.). NBS Standard Reference Material (SRM) No. 1647 was used for instrument calibration and SRM No. 1649 as positive control to determine analysis accuracy.

Apparatus

PAHs were analysed using a Spectra Physics liquid chromatograph model SP 6700 equipped with a Rheodyne injector (20 μL loop) model 8750, a Waters and Associates electronic integrator Data Module model M 730, and a Spectra Physics fluorescence detector model FS 970 set at 250 nm and 370 nm, respectively, for excitation and emission. A Supelcosil LC-PAH (Supelco Inc.) C18, 5 μm, 15 cm × 4.6 mm i.d. analytical column was used at room temperature. Ultrasonic PAH extractions were carried out using a Brasonic 12 ultrasonic bath.

Sample extraction

Aliquots between 0.0499 g and 0.1026 g of NBS SRM No. 1649 or samples collected on quartz fiber filters were extracted ultrasonically in a 25 ml erlenmeyer flask (stoppered with a piece of aluminium foil) using 8 ml of MeCN during 10 min. The extracts were then filtered using a double sheet of Whatman No. 40 filter paper. The sample filter (or the standard powder) which remained in the erlenmeyer was washed twice with new portions of MeCN. The volume of the extracts was then reduced to about 7–8 ml by passage of a gentle stream of nitrogen gas at room temperature. The extracts were transferred to a 10 ml volumetric flask and taken up with MeCN for direct HPLC analysis.

Quantitation

The HPLC system was calibrated using SRM No. 1647 diluted 200, 400 and 500 fold with MeCN. PAH separation was obtained using a solvent gradient consisting of MeCN and water (40% to 100% MeCN in 20 min, held at 100% MeCN for another 5 min) at 0.9 ml/min. Fluorescence sensitivity was 0.5 μA. Average retention times (in min) were: phenanthrene (PHE), 13.6; fluoranthene (FLT), 15.7; pyrene (PYR), 16.4; benzo(a)anthracene (BAA), 18.7; crysene (CRY), 19.0; benzo(b)-fluoranthene (BBF), 21.0; benzo(k)fluoranthene (BKF), 21.80; benzo(a)pyrene (BAP), 22.5; benzo(ghi)perylene (BGP), 24.6; and indeno(1,2,3-cd)pyrene (IND), 25.0. Our HPLC solvent system takes about an hour to stabilize. To obtain the accuracy reported, prior to the actual quantitation, it is necessary to make three or four injections of the liquid standard (or of a sample extracted with acetonitrile) into the column. After this conditioning period, the chromatograms are very reproducible.

Ambient sample collection

Total suspended particulate matter (TSP) samples were collected with a General Metal Works hi-vol sampler, at a flow rate of 1.12 m3/min (40 CFM), on 20.3 cm × 25.4 cm (8″ × 10″) quartz fiber filters from Pallflex (Putnan, CT). Immediately after collection, the filters were stored in aluminium foil, were temperature- and humidity-equilibrated for about a day, weighed and stored in a freezer before analyses. A sample of automotive emission was collected during a 1-hr period inside the Santa Barbara Tunnel, in the city of Rio de Janeiro. The tunnel is 1.3 km long and carries four lanes of traffic, two in each direction. The sampler was located about 340 m from the south exit of the tunnel approximately 1 m above the ground. Sample collection time was 60–75 min. Temperature during collection was 31 ± 1 °C. An ambient TSP sample was collected during a 12-hr period (7.00 a.m. to 7.00 p.m.) in a mixed residential-commercial section of Vila Isabel, in the city of Rio de Janeiro. During the collection period the temperature varied between 19.0 and 22.0 °C.

RESULTS AND DISCUSSION

Typical chromatograms obtained for the NBS liquid and dust standards and from an atmospheric aerosol sample are shown in Figure 1a–e. Dichloromethane extraction of SRM 1649 followed by direct injection in the HPLC system gave chromatograms with several poorly resolved peaks (Figure 1c). However, dichloromethane extraction followed by evaporation under a gentle stream of nitrogen gas and take up in a solvent mixture consisting of methyl formamide/chloroform gave well resolved peaks which allowed accurate quantitation of all ten PAHs (Figure 1a). The peaks of all ten PAHs were resolved in 25 min, with a single fluorescence detector under only one set of excitation and emission conditions when the acetonitrile extracts were chromatographed without further sample treatment or clean up (Figure 1b and 1e).

Precision, accuracy, detection limits and linearity Table 1 compares the results obtained with the present method with those reported in the NBS certificate for the concentrations of the ten PAHs studied. For the five certified and two of the non-certified PAHs no statistical differences were found in the results. The overall accuracy was within 10% for the five certified PAHs and between 11 and 16% for the others (Table 1). In fact, considering the reported standard deviations, except for phenanthrene, pyrene and benzo(k)fluoranthene whose concentrations were slightly lower, all the results are statistically identical. The detection limits are in the range of 10 to 50 picogram. Fluorescence responses are linear between 5 and 100 picogram.

Reanalyses of the MeCN extracts of both SRM 1649 and the ambient samples after a one-week storage period in a refrigerator showed no differences in the results.

The results for samples collected inside the urban tunnel and at the residential site showed that the concentrations for all ten PAHs were determined with an average standard deviation of less than 10% (Table 2). Analyses of samples extracted with MeCN for up to 60 min, or extracted twice for 50 min, produced no statistical differences when compared with the results reported in Table 2.

CONCLUSIONS

The results presented above show that extraction of samples with acetonitrile and injection into the HPLC system without pretreatment allows four determinations (in duplicate) of the ten PAHs, with high accuracy and precision, during a regular eight-hour day, after stabilization of the HPLC solvent system and column.

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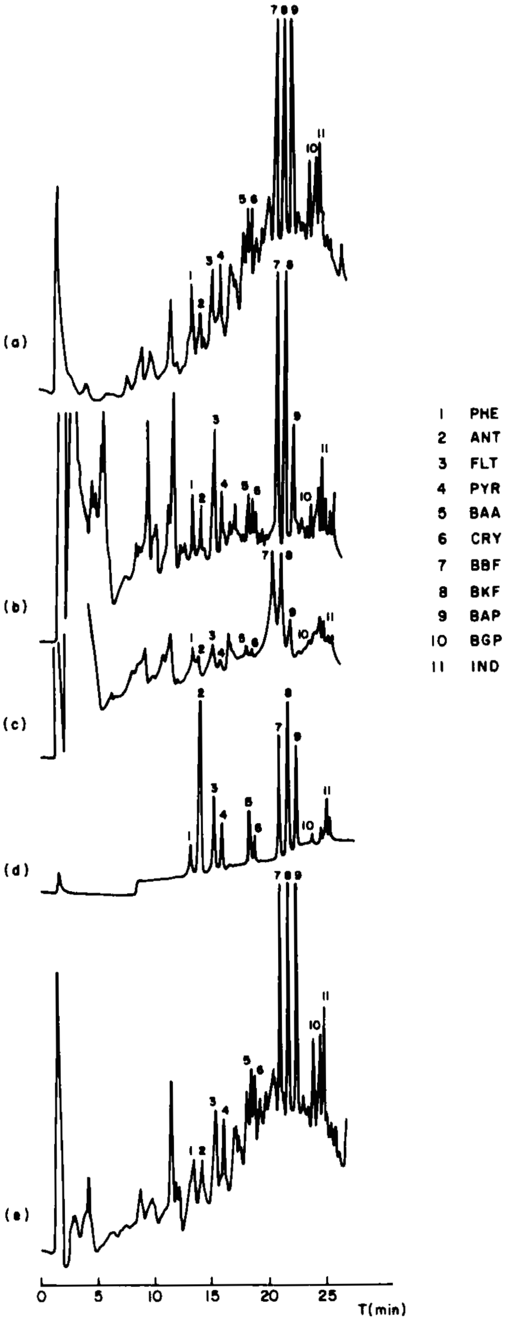

Figure 1 Typical chromatograms obtained for NBS standards and an atmospheric sample: (a) dichloromethane extraction of NBS 1649 followed by solvent exchange to dimethyl formamide/chloroform (4:1 v.v.); (b) acetonitrile extraction of NBS 1649; (c) dichloromethane extraction of NBS 1649; (d) NBS SRM 1647 in acetonitrile; and (e) residential area sample extracted with acetonitrile. Chromatograms of the tunnel sample were similar to (e).

Table 1 Accuracy and precision determined with standard reference material NBS 1649 (concentrations are given in ng/g)

NBS results				*Difference (%)*			
PAH	*LC-I*	*LC-II*	*Certified*	*This study*	*Cert.*	*LC-I*	*LC-II*
PHE		4.5±0.3		3.6±0.3			−20
FLT	7.0±0.5	6.8±0.4	7.1+0.5	7.0±0.2	−1.4		
PYR	6.3±0.4	6.2±0.2		5.3±0.4		−16	−15
BAA	2.8±0.3	2.4±0.1	2.6+0.3	2.2±0.1	−15		
CRY	3.5+0.1	3.7±0.2		3.3±0.1		−5.7	−11
BBF	6.2±0.3			5.8±0.4		−6.5	
BKF	2.0±0.1	2.1±0.1		1.7±0.1		−15	−19
BAP	2.6±0.4	2.6±0.1	2.9+0.5	2.5±0.1	−14		
BGP	3.9±0.8	5.2±0.6	4.5+1.1	4.3±0.2	−4.4		
IND	3.4±0.4	3.6±0.2	3.3+0.5	2.9±0.1	−12		
n	18	9		6			
Average of differences for the group (%)					−9.4	−11	−16

LC-I and LC-II refer to the information values (non-certified) reported by NBS. Standard deviations refer to 1 sigma. *n* = number of powder or filter aliquots analysed in duplicate.

PHE = phenanthrene; FLP = fluoranthene; PYR = pyrene; BAA = benzo(a)anthracene; CRY = crysene; BBF = benzo(b)fluoranthene; BKF = benzo(k)fluoranthene; BAP = benzo(a)pyrene; BGP = benzo(ghi)perylene; IND = indeno(1,2,3-cd)pyrene.

Table 2 PAH concentrations (ng/m3) of ambient samples and precision of the method[a]

	Collection site	
PAH	*Residential area*	*Tunnel*
PHE	15.0 ±0.74 (5.0)	96.9 ±0.75 (1.8)
ANT	0.49±0.04 (8.6)	4.19±0.36 (8.6)
FLT	7.90±0.30 (3.8)	69.6 ±4.67 (6.7)
PYR	7.92±0.30 (3.8)	76.3 ±5.85 (7.7)
BAA	8.08±0.14 (1.7)	51.3 ±3.34 (6.5)
CRY	9.87±0.63 (6.3)	69.5 ±4.77 (6.8)
BBF	14.6 ±0.46 (3.2)	88.2 ±3.97 (4.5)
BKF	3.77±0.22 (6.0)	36.7 ±2.32 (6.3)
BAP	17.6 ±0.79 (4.5)	90.7 ±4.53 (5.0)
BGP	19.9 ±1.06 (5.3)	162.0 ±6.49 (4.0)
IND	16.1 ±1.55 (9.6)	84.2 ±3.24 (3.8)

[a] Two samples each determined in triplicate. Percentage standard deviations are in parentheses.

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