

Evaluation of Polycyclic Aromatic Hydrocarbons in Asphalt Binder Using Matrix Solid-Phase Dispersion and Gas Chromatography

Paulo R.N. Fernandes¹, Sandra de A. Soares¹, Ronaldo F. Nascimento², Jorge B. Soares³, and Rivelino M. Cavalcante^{4*}

¹Laboratório de Polímeros - Departamento de Química Orgânica e Inorgânica, Universidade Federal do Ceará, bloco 940. Av. Humberto Monte, s/n - Campus do Pici. CEP: 60455-760 - Fortaleza - CE, Brasil; ²Laboratório de Análise Traço - Departamento de Química Analítica e Físico Química, Universidade Federal do Ceará, bloco 939. Av. Humberto Monte, s/n - Campus do Pici. CEP: 60455-760 - Fortaleza - CE, Brasil; ³Laboratório de Mecânica dos Pavimentos - Departamento de Engenharia de Transportes, Universidade Federal do Ceará, bloco 703. Av. Humberto Monte, s/n - Campus do Pici. CEP: 60455-760 - Fortaleza - CE, Brasil; ⁴Laboratório de Biogeoquímica Costeira, Setor de Análise Orgânica, LBC-Org - Instituto de Ciências do Mar-LABOMAR - Universidade Federal do Ceará. Av. Abolição, 3207 - Meireles, CEP: 60165-081 - Fortaleza - CE, Brasil

Abstract

A method developed for the extraction and analysis of polycyclic aromatic hydrocarbons (PAHs) in the asphalt binder using a matrix solid-phase dispersion (MSPD) and gas chromatography is presented. The MSPD method was proposed as a rapid and easy approach to determining PAHs present in the maltenic phase of asphalt binder extracted through a mechanical shaking and sonication of the material. The recovery rates ranged from 62.77–89.92% (shaking) and from 56.54–93.6% (sonication) with relative standard deviations lower than 8.8%. The study shows that the recovery rates using shaking and sonication extractions are not significantly different at the $p < 0.05$ level. The limits of detection and quantification ranged from 0.7–1.8 mg/kg and 2.2–5.6 mg/kg, respectively. The proposed analytical method was applied to determine PAH levels in an asphalt binder from Brazil. The main PAHs found were BbF, BaP, Per, IncdP, DahA, and BghiP, with average concentrations of 10.2–20.7 mg/kg, but the PAHs Ace and Acy were not detected. However, Nap, Fl, Phen, Ant, Flr, Pyr, Chry, BaA, and BkF were present in average concentrations amounting to less than 10 mg/kg. The results showed that the MSPD method is potentially a valuable tool for the determination of PAHs in the asphalt binder.

Introduction

Asphalt binder is the product of the distillation of crude oil in petroleum refining. It ranges from a

dark brown to black cement-like thermoplastic material (1) with an extremely complex mixture containing a large number of high-molecular weight organic compounds (2). The asphalt binder constituents can be separated into two fractions: asphaltenes (polar fraction) and maltenes (apolar fraction). Chemical fractionation is the method most commonly used for the quantification of asphalt binder constituents (3). The SARA method separates the asphalt binder constituents into four fractions: saturates, aromatics, resins (fraction of maltenes soluble in apolar solvents) and asphaltenes (Figure 1), although the most important chemical family is the aromatic fraction (45.1–95.0%) (1,4).

The asphalt binder (or bitumen) is mostly used in paving operations. The remaining uses include waterproofing and insulation. Asphalt binders used for the construction of roads offer a variety of properties such as a good resistance to aging and

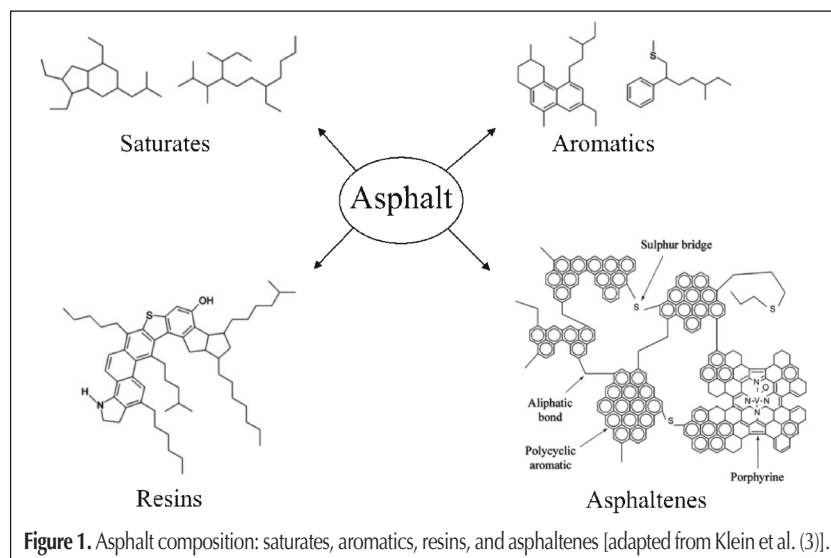


Figure 1. Asphalt composition: saturates, aromatics, resins, and asphaltenes [adapted from Klein et al. (3)].

* Author to whom correspondence should be sent: R.M. Cavalcante, Instituto de Ciências do Mar (LABOMAR), Universidade Federal do Ceará, Av. Abolição 3207-CEP 60165-081, Fortaleza, CE, Brasil, email rivelino@labomar.ufc.br.

high-performance traffic loading (5). However, the techniques used in the production and application of this material frequently involve a hot-mix asphalt production (6). The emissions generated during the production and application of asphalt binders contain a large number of substances, some of which are potentially harmful to the health of those involved (7,8). Exposure to compounds contained in the asphalt binder can occur through inhalation or even absorption through the skin during application to streets and roads (1,7). Another way in which the asphalt binder constituents can be released to the environment is through the degradation of the road surface, this being an important source of contamination of water bodies (9,10).

Polycyclic aromatic hydrocarbons (PAHs), which may be generated in various asphalt operations, are some such constituents that may be hazardous to workers' health (8). The PAHs are mainly released during the burning of petroleum and its derivatives (11). PAHs with 4–6 aromatic rings are highly mutagenic and carcinogenic, while those with 2–3 aromatic rings are highly toxic despite being less mutagenic (12). In addition, PAHs form part of the group of compounds known as persistent organic pollutants (POPs), which adversely affect the environment and are the focus of many research studies (9–11,13–17). Statistical data have revealed evidence of a risk of cancer, and there is a relation between carcinogenesis and the molecular structure of PAHs (18). This leads to a need for adequate procedures to detect PAHs in asphalt and the correct use of the material in order to avoid environmental and human contamination (18).

Few studies on asphalt binders have focused on the determination of the PAH content and, therefore, it is of great interest to develop an efficient method that can contribute to evaluating the real contribution of the asphalt industry to PAH contamination. In general, the specific determination of mono-, di-, and poly-aromatics (maltenes) involves the quantification of the total form (3), and a second separation stage is required to obtain these forms separately, which makes the procedure highly time-consuming and requires more materials (solvent and adsorbent).

The matrix solid-phase dispersion (MSPD) can be used as an alternative technique to the classical extraction methods because it allows the simultaneous extraction and clean-up of analytes from solid samples considered complex with a significant reduction in the solvent consumption and without requiring expensive instrumentation (19–21). MSPD has been mainly used for the extraction of organic environmental pollutants in food and biological matrices (21–23), but to our knowledge it has not been applied to the determination of PAHs in asphalt binder.

This study was performed in order to explore MSPD as an analytical method for the detection and the determination of 16 U.S. EPA (United States Environmental Protection Agency) PAH levels in an asphalt binder originating from the southeast of Brazil. The results could give a preliminary overview of the potential risk of contamination in the case of improper use. An investigation about the adequate procedures and the correct use of the product are required so as to avoid environmental and human contamination.

Experimental

Materials

The 50/70 asphaltic binder originating from Fazenda Campo Alegre (Espírito Santo, Brazil) was processed at Lubnor/Petrobrás. The solvents hexane, acetone, ethyl acetate, and also those used in cleaning, were purchased from Merck (Rio de Janeiro, Brazil) and Tedia (Rio de Janeiro, Brazil). The solvents were distilled twice before being employed in the analysis. The PAHs analyzed were the 16 priority compounds recommended by the US-EPA. The PAHs analyzed in this study were: naphthalene (Naph); acenaphthylene (Aci); acenaphthene (Ace); fluorene (Fl); phenanthrene (phen); anthracene (Ant); fluoranthene (Flr); pyrene (Pyr); benzo(a)anthracene (BaA); chrysene (Chry); benzo(b)fluoranthene (BbF); benzo(k)fluoranthene (BkF); benzo(a)pyrene (BaP); indene (1,2,3-cd)pyrene (IncdP); dizenbo(a,h)anthracene (DahA) and benzo(g,h,i)perylene (BghiP). The internal PAH standards and also 2-fluoro-biphenyl were obtained from Sigma Aldrich (St. Louis, MO) with a purity ranging from 99.5–99.9%. Silica gel (70–230 mesh), copper in powder form were purchased from Merck (Whitehouse Station, NJ), alumina from Riedel-de-Haën (Seelze, Germany), and anhydrous Na₂SO₄ from Vetec (Rio de Janeiro, Brazil). A bench shaker (Tecnal, São Paulo, Brazil) was employed to extract the PAHs. In the extraction stage an ultrasonic bath (130 W and 50 kHz) (Quimis, São Paulo, Brazil), rota-evaporator (Tecnal), and centrifuge (Quimis) were also utilized.

Optimization of the analytical method

Sample preparation and extraction

The extraction of the maltenic fraction of the asphalt binder was carried out using two different procedures: mechanical shaking and ultrasonication. In each case, 0.3 g of asphalt binder (in triplicate) were spiked with 10 µg/mL surrogate standards (acenaphthene-d10; phenanthrene-d10, chrysene-d12, and perylene-d12) in order to evaluate the recovery rates in the analysis including extraction, elution, pre-concentration, and gas chromatography (GC).

Mechanical shaking

To evaluate the recovery rates using mechanical shaking, 0.3 g of the asphalt binder in triplicate spiked with the surrogate standards, were dissolved in 12.0 mL of *n*-hexane. The mixture was then shaken for 12 h in a bench shaker. After shaking the mixture was vacuum filtered, the solution was collected (maltenic fraction) and then pre-concentrated to 2 mL using nitrogen for PAH determination by MSPD.

Ultrasonication

0.3 g of asphalt binder in triplicate spiked with the surrogate standards were dissolved in 12 mL of hexane, and the mixture was sonicated for 40 min in an ultrasonic bath. After sonication, the mixture was vacuum filtered, and the solution (maltenic fraction) was collected. It was then pre-concentrated to approximately 2.0 mL using nitrogen. The MSPD technique was then applied to the maltenic solution to determine the PAHs present in the asphalt binder.

MSPD

In order to extract the PAHs, 2 mL samples of the maltenic solution obtained by the use of the mechanical shaking and the ultrasonication methods were dispersed in 15.0 g of 60 mesh silica gel. After dispersion, the mixture was homogenized and transferred to a column (50.0 cm × 1.0 cm) containing 5.0 g of Al₂O₃ and 0.5 g of copper powder (activated to remove sulfur compounds) as the co-column. The column was rinsed with 50.0 mL of *n*-hexane to remove the aliphatic compounds present in the asphalt binder. After this stage, elution of the fraction containing the aromatic compounds (PAHs) was carried out using the solvent system described by Cavalcante et al (24). Solvents were selected using several testing procedures until the best solvent ratio was found, which would provide an efficient elution of the PAHs considering their different polarities. The elution of the aromatic fraction of the asphalt binder was carried out using different solvent ratios: first elution (36.0 mL hexane + 4.0 mL ethyl acetate), second elution (16.0 mL *n*-hexane + 4.0 mL ethyl acetate) and third elution (14.0 mL *n*-hexane + 6.0 mL ethyl acetate). The increase in the polarity of the fractions used for the elution of PAHs is due to the variation in the polarity of the PAHs of interest. The three fractions were combined, rota-evaporated, and pre-concentrated to 0.5 mL after which 10.0 µL of an internal standard (2-fluoro-biphenyl) was added. The samples were submitted to GC analysis.

Determination of 16 U.S. EPA PAHs in asphalt binder

The PAHs quantified in the Brazilian asphalt binder were the 16 PAHs, which are considered a priority by the U.S. EPA (6). After the extraction with ultrasound and MSPD, the concentrations of the 16 U.S. EPA PAHs were estimated based on the recovery ratio of the corresponding surrogate standards (acenaphthene-d10, anthracene-d10, chrysene-s12, and perylene-d12).

GC analysis

PAHs were determined on a Shimadzu 17A GC coupled to a flame ionization detector (Kyoto, Japan). The separation was performed in a J&W Scientific DB-5 column (30 m × 0.25 mm i.d., 0.25-µm film thickness) using split mode (1:20). The initial oven temperature was 60°C for 10 min, increasing to 120°C at 5°C/min, and then to 300°C at 3°C/min. The injector and detector temperatures were 280°C and 300°C, respectively. A 2 µL volume was injected, and hydrogen was used as the carrier gas at a flow rate of 1.0 mL/min. Concentrations of PAHs were measured using the response factors related to the internal standard (2-fluoro-biphenyl) added to the extract prior to injection. A calibration solution was prepared with the PAH standards (16 PAHs), the deuterated PAH solution (surrogate), and the internal standard (2-fluoro-biphenyl).

Results and Discussion

Optimization of the MSPD method

According to Barker (20), several factors should be evaluated when using MSPD, mainly the nature of the adsorbent, the best sample to the solid support (adsorbent) ratio, the choice of elution solvent, and the sequence of application in the column.

Thus, preliminary experiments using the asphalt binder spiked with the surrogate standards (data not shown) were carried out to optimize the main parameters that affect the MSPD, such as the nature of the solvent (silica gel and alumina), quantity of adsorbent (5 and 15 g of silica gel), and the polarity of the elution solvent (dichloromethane (DCM)-hexane and ethyl acetate-hexane, both 1:1, v/v).

There was no significant variation found between the PAH recovery rates using silica and alumina. However, owing to the cost, silica gel was selected as the solid support and alumina and copper powder as the co-column. Most studies that have employed MSPD applied a 1:4 ratio (0.5 g of sample to 2 g of solid support) (20,21). Experimentally, we found that 5 g of silica was not sufficient for the retention of interferences, and that 15 g was the quantity needed for the solid support. The passage of DCM-hexane and ethyl acetate-hexane was tested in the column containing silica gel as the solid support and alumina and copper powder as the co-column. However, interferences, such as aliphatic hydrocarbons, were observed in the extracts. Thus, 50 mL of hexane was passed through the column in order to elute the compounds which were not of interest (aliphatic hydrocarbons). No significant variation was found between the PAH recovery rates using DCM-hexane and ethyl acetate-hexane. Nevertheless, due to the greater risk of exposure to DCM (25,26), ethyl acetate-hexane was selected as the elution solvent.

Validation of the analytical method

Linearity, repeatability, and selectivity

A multipoint calibration with six standard solutions of dif-

Table I. Retention Times (t_R), Correlation Coefficient (R), and Limits of Detection and Quantification (LOD, LOQ) of the PAHs Studied

PAHs	t _R (min)	R	LOD (mg/kg)	LOQ (mg/kg)
Nap	14.38	0.997	0.7	2.2
PI	16.86	–	–	–
Ace-D	18.33	0.999	–	–
Acy + Ace	18.73	0.997	0.7	2.3
FL	20.36	0.997	0.7	2.2
Phen-D	23.48	0.999	–	–
Phen	23.88	0.995	0.8	2.4
Ant	24.06	0.995	0.8	2.4
Flr	28.91	0.995	0.7	2.2
Pyr	29.82	0.996	0.7	2.3
BaA	35.59	0.997	0.7	2.3
Chry-D	35.58	0.999	–	–
Chry	35.78	0.998	0.8	2.4
BbF	41.44	0.994	0.7	2.3
BkF	41.57	0.996	1.7	5.3
BaP	43.08	0.993	1.7	5.3
Per-D	43.28	0.999	–	–
Per	43.68	0.992	1.7	5.5
IncdP	48.98	0.987	1.8	5.6
DahA	49.25	0.986	1.8	5.6
BghiP	50.18	0.985	1.8	5.6

ferent concentration levels in the range of 0.5–20 µg/mL was used for the linearity verification. A good linearity of the calibration curves was obtained in the range 0.5–20 µg/mL. The correlation coefficient ranged from 0.985–0.999 for most of the PAHs analyzed (Table I).

The repeatability of the GC method was determined by analyzing a standard solution at 5 µg/mL, within-day and between-day. Three solutions were injected in the triplicate and the relative standard deviations (RSD) obtained for the retention times ranged from 0.019–0.036%. Concerning the relative peak areas, the values were lower than 4.8%. The repeatability of the analytical between-day procedure was determined and proved to be lower than 10% for all the PAHs studied. Therefore, the repeatability achieved with the chromatographic method under the study conditions was satisfactory and consistent with that of other studies (27).

The selectivity of the proposed MSPD procedure was assessed by analyzing control blanks of the reagents, adsorbents, and material extracts. The absence of background peaks at the retention times of the PAHs showed that no interferences occurred.

Detection and quantification limits

The limits of detection (LODs) were determined by considering a value three times the background noise obtained for the blank samples, whereas the limits of quantification (LOQs) were determined considering a value 10 times the background noise. The LODs and LOQs ranged from 0.7–1.8 mg/kg and 2.2–5.6 mg/kg, respectively (Table I).

Performance of the procedure

The recovery rates of the overall analysis, including extraction

Table II. Average Recoveries ($n = 6$) of the Overall Analysis for Asphalt Spiked with Deuterated PAHs

	Shaking Recovery (%)	RSD (%)	Sonication Recovery (%)	RSD (%)
Ace-D	62.77 ± 3.56	5.67	56.54 ± 3.99	7.06
Phen-D	65.05 ± 5.26	8.09	58.60 ± 2.81	4.80
Chry-D	89.92 ± 6.63	7.37	93.60 ± 4.11	4.39
Per-D	88.51 ± 7.78	8.79	88.32 ± 7.63	8.64

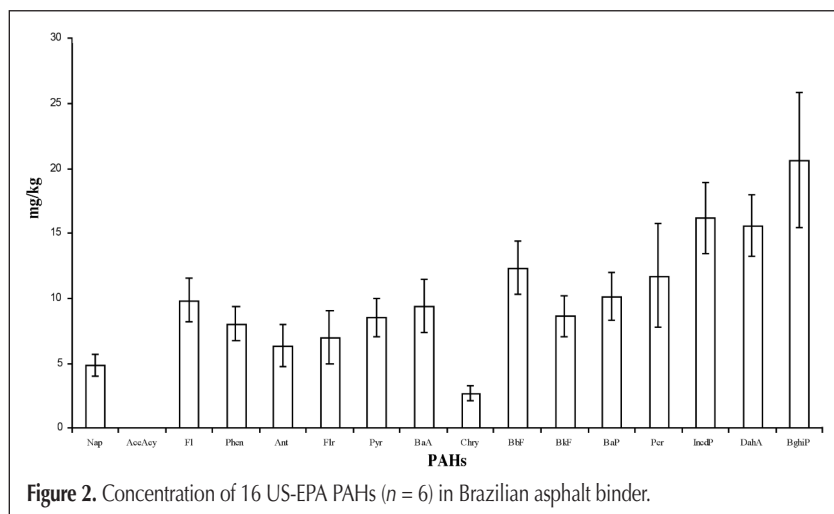


Figure 2. Concentration of 16 US-EPA PAHs ($n = 6$) in Brazilian asphalt binder.

followed by clean-up, were evaluated using samples of asphalt binder spiked with deuterated PAHs. The recovery rates ranged from 62.77–89.92% (shaking) and from 56.54–93.6% (sonication) with RSDs lower than 8.8% (Table II). The *F*-test, using STATISTIC 6 software, showed that the recovery rates are not significantly different at the $p < 0.05$ level using shaking and sonication extractions.

Unfortunately, there were no studies found in the literature to compare the results obtained in this study. Other studies comparing extraction by shaking and sonication also reported no significant differences in the PAH extraction efficiency of solid matrices (sediment and soil) (28,29).

Levels of PAHs in Brazilian asphalt binder

The validated method was applied to the determination of the 16 U.S. EPA PAHs in the asphalt binder produced at Fazenda Campo Alegre (Espírito Santo State, Brazil). The results of the analysis are given in Figure 2. The technique used was sonication because it involves more rapid procedures than shaking. As can be observed, Ace/Acy was not detected, and the PAHs: Nap, Fl, Phen, Ant, Flr, Pyr, Chry, BaA, and BkF were present in concentrations below 10 mg/kg. The PAHs found in greater quantities were BbF, BaP, Per, IncdP, DahA, and BghiP, with average concentrations of 10.2–20.7 mg/kg.

Due to the absence of individual quantification data for the 16 U.S. EPA PAHs in asphalt binder samples, we compared our results with those of similar matrices such as air emissions from paved layers, asphalt fumes, and aqueous leaching from bitumen and asphalt (3,8,10,30). Tang and Isacson (8) determined the chemical characterization of agents and emissions released from the asphalt by Fourier transform infrared spectroscopy-attenuated total reflectance (FTIR-ATR), gel permeation chromatography (GPC), and mass spectrometry (MS). The study reports that besides the presence of the 16 US-EPA PAHs found in our study, the presence of another 25 methyl-PAHs was also verified. PAHs (except BkF) varying from 1.15–140.21 ng/m³ were detected to originate from the emission of asphalt fumes (30). The PAHs of a higher molecular mass (4–6 rings) showed higher concentrations when compared with those of a lower molecular mass (2–3 rings). This behavior is similar to the one found for the asphalt binder analyzed in this study (Figure 2). In contrast,

Brandt and Groot (10) analyzed PAHs originating from aqueous leaching from bitumen and asphalt and reported only the release of PAHs with 1–4 rings (concentration varying between 0.1–400 ng/L). According to the study, Nap shows the highest concentration due to a greater solubility in water. On the other hand, the PAHs with 5–6 rings are absent because they have a low solubility and are not easily released from the matrix.

Conclusions

The results demonstrate that the accuracy, precision, and selectivity of the proposed procedure are satisfactory for the analysis of 16 U.S. EPA PAHs

considered a priority by the U.S. EPA. The Ace/Acy were not detected, and the PAHs Nap, Fl, Phen, Ant, Flr, Pyr, Chry, BaA, and BkF showed average concentrations lower than 10 mg/kg. Of the 16 U.S. EPA PAHs, the ones found in the greatest quantity were BbF, BaP, Per, IncdP, DahA, and BghiP with average concentrations of 10.2–20.7 mg/kg. The proposed procedure represents the first technical application of MSPD for the direct determination of PAHs contained in the asphalt binder. Extraction conditions were carefully selected to achieve a maximum recovery of the PAHs present in the asphalt samples while eliminating most of the interfering matrix components.

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