Article

Determination of Polycyclic Aromatic Hydrocarbons in Groundwater Samples by Gas Chromatography-Mass Spectrometry After Pre-Concentration Using Cloud-Point Extraction with Surfactant Derivatization

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A cloud-point extraction (CPE) method using the surfactant (30)*p-tert*-octylphenol polyoxyethylene (OPEO30) was proposed as the preceding step for the determination of polycyclic aromatic hydrocarbons (PAHs) by gas chromatography-mass spectrometry (GC-MS). Given the need for surfactant derivatization before the chromatographic analysis, the reaction conditions of coacervate derivatization were studied. The extraction process was also optimized, where surfactant concentration, temperature and time were analyzed as variables. The limits of detection obtained were between 0.02 and 0.05 µg L^{-1}, and the recoveries of analytes were between 70 and 98%, with coefficient of variation better than 10.3%. The analytical method developed provides an efficient, precise and accurate method for the determination of the 16 priority PAHs, generating results in accordance with the USEPA 3510C method. The method was applied to the analysis of groundwater samples collected from artesian wells located at retail fuel stations.

Keywords: polycyclic aromatic hydrocarbons, cloud-point extraction, GC-MS, groundwater

Introduction

Cloud-point extraction (CPE) has been employed as a preceding step in the separation and pre-concentration of different species, mainly because it is in accordance with the principles of green chemistry: (*i*) diluted solutions of surfactants are used as the extracting medium, resulting in reagent economy and the generation of low amounts of residues; (*ii*) the surfactants employed in CPE exhibit low toxicity, are not volatile and are not highly flammable. In CPE, aqueous surfactant solutions can undergo separation with the manipulation of temperature or the inclusion of additives, like sodium sulfate, resulting in two phases: one surfactant-rich phase and one aqueous phase with a surfactant concentration close to the critical micelle concentration.[1-4] In the surfactant-rich phase, hydrophobic species can be extracted and pre-concentrated from aqueous systems, including polycyclic aromatic hydrocarbons (PAHs).[5,6] To determine the analytes extracted, CPE can be combined with different analytical techniques, such as spectrometric techniques for the determination of inorganic species[7-9] or chromatographic techniques in the case of organic analytes.[5,10]

However, the combination of CPE with gas chromatography (GC) for the determination of organic compounds is difficult.[10,11] Usually, the surfactant-rich phase containing the organic analyte cannot be directly introduced into the chromatograph because of problems related to the injection of the surfactant into the column.[12] To quantify the organic compounds after CPE by GC, the surfactant must be eliminated before injection because of issues related to its viscosity and the possibility of adsorption in the stationary phase, which results in low repeatability of analyte retention times.[10] In addition, the injector liner can become contaminated. Hence, a clean-up step or re-extraction of the analyte in the coacervate is generally necessary.[2,5,11,12] Alternatively, the surfactant present in the coacervate can be derivatized, such as in the case of the surfactant OPEO7.5, in a step after the CPE and before the determination of PAHs by GC; this approach results in chromatograms that are free of surfactant peaks and exhibit repetitive retention times, with accurate quantitative results.[10]

Some surfactant characteristics are desirable for their use in CPE, such as high density, commercial availability,

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low cost, low toxicity, and low cloud-point.[13,14] Nonionic surfactants of the OPE type are the most used, especially because of their low cloud-point and availability. Some of the surfactants most commonly employed in CPE include OPEO7.5 (Triton X-114) and OPEO9.5 (Triton X-100). In contrast, the surfactant OPEO30 (Triton X-305) exhibits a cloud-point greater than 100 °C, making it difficult to be used in CPE. However, the presence of additives may enable its use in procedures involving CPE, which makes OPEO30 an interesting surfactant for extraction purposes, increasing the utilization possibilities of surfactants in CPE.[15]

In the present study, the use of non-ionic OPEO30 surfactant is proposed for the CPE of PAHs in natural waters, with surfactant derivatization for subsequent determination of PAHs by gas chromatography-mass spectrometry (GC-MS). The conditions of the coacervate derivatization reaction were optimized using simultaneous experimental design. The proposed procedure enables the use of an alternative surfactant for the pre-concentration of PAH using CPE, thereby avoiding treatment of the coacervate with pre-columns or analyte re-extraction prior to chromatographic analysis.

Experimental

Instrumentation

CPE and the derivatization procedure were conducted in a water bath with controlled heating and adjustable temperature with a precision of ± 0.1 °C (Tecnal, São Paulo, Brazil). The samples were centrifuged in a centrifuge (Quimis, São Paulo, Brazil). The groundwater samples were collected with a Solinst low-flow peristaltic pump (Ontario, Canada) coupled to a MicroPurge Basics flow cell (Clean Environment Brasil, Campinas, Brazil) for low-flow sampling. Samples were analyzed by gas chromatography-mass spectrometry using a Shimadzu GC2010 gas chromatograph (Shimadzu, Kyoto, Japan) linked to a Shimadzu QP2010 Plus mass spectrometer.

Reagents and solutions

The nonionic surfactant Triton X-305 [(30)*p-tert*-octylphenol-polyoxyethylene, general formula $C_{14}H_{22}O(C_2H_4O)_n$ (n = 30), OPEO30], that has an aromatic hydrophobic group and a hydrophilic polyethylene oxide chain, was of analytical grade and were obtained from Sigma-Aldrich (St. Louis, MO, USA). Pyridine and the derivatization agent *N,O*-bis(trimethylsilyl)trifluoroacetamide (BSTFA) were also of analytical grade and were obtained from Sigma-Aldrich. The standard containing the 16 priority

PAHs (naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo (a) anthracene, chrysene, benzo (k) fluoranthene, benzo (b) fluoranthene, benzo (a) pyrene, benzo (g,h,i) perylene, indeno (1,2,3-cd) pyrene and dibenzo (a,h) anthracene) according to the U.S. Environmental Protection Agency (USEPA) were also obtained from Sigma-Aldrich (2000 μg mL^{-1} each component). The structure, formula and aqueous solubility for each PAH can be found in Table S1, in the Supplementary Information (SI) section. From this solution, a 10.00 mg L^{-1} intermediate solution with dichloromethane or methanol was prepared for the subsequent preparation of calibration solutions. The silylating reagents, stock solutions and calibration solutions containing the analytes were stored in the absence of light and under refrigeration at 5 °C.

The analytical grade sodium sulfate used for reduction of the cloud-point of OPEO30 was obtained from Merck (São Paulo, Brazil). This salt was previously tested with success in reducing the cloud point of the TX-305.[15] The ultrapure water used to prepare the solutions was distilled twice in a quartz biodistiller and subjected to a MilliQ® ultra purification system (Bedford, MA, USA).

Recommended procedures

The CPE was performed by adding 1000 μL of a 10% (m v^{-1}) surfactant solution to a conical glass test tube with a lid containing 10.00 mL of standard solution or sample and 1.25 g of anhydrous sodium sulfate. Next, the test tube was manually agitated to completely dissolve the salt and mix the reagents. The tube was then placed in a water bath at 70 °C for 10 min. After being heated, the solutions were centrifuged at 3000 rpm for 5 min. The aqueous phase was removed with a Pasteur pipette. This heating, centrifugation and water removal process was repeated two additional times, until two phases formation was no longer observed.

Derivatization was carried out with the addition of 125 μL of BSTFA and 100 μL of pyridine to 30 μL of the surfactant-rich phase obtained after the CPE procedure. The system was then heated in a water bath at 70 °C for 45 min. Two microliters of each derivatized sample was injected into a gas chromatograph fitted with a 30 m HP-5 fused silica capillary column (0.32 mm × 0.25 μm film thickness) and connected to a mass selective detector. The carrier gas, helium, was maintained at a flow rate of 1.91 mL min^{-1} by electronic pneumatic control. The injection port temperature was 250 °C and split ratio 10:1. The source temperature was 260 °C. The oven program for standards and samples was as follows: 45 °C increased to 130 °C at 20 °C min^{-1}, increased to 180 °C at 10 °C min^{-1},

increased to 240 °C at 6 °C min^{-1}, after 1 min increased to 310 °C at 10 °C min^{-1}, held for 3 min. Quantification confirmation ions (*m/z*) of the 16 PAHs monitored have been described in literature.[16,17]

The detector was also operated in the scan mode to allow evaluation of the derivatization reaction by the generated chromatographic profile. In the scan mode, the temperature of injector was 280 °C. The oven temperature program was: 45 °C for 1 min, increased to 280 °C at 6 °C min^{-1}, increased to 320 °C at 8 °C min^{-1}, after 20 min, increased to 325 °C at 10 °C min^{-1} and isotherm 1.33 min. A volume of 2 µL of sample was then injected with a split ratio of 100:1. Helium was used as the carrier gas with a flow rate of 1.91 mL min^{-1}. The interface was maintained at 300 °C, and the scan was carried out at a mass ratio (*m/z*) of 40 to 699. Integration was performed with the software GCMSSolution (Shimadzu, Kyoto, Japan). All qualitative data were based on the measurement of the peak area of the analytes studied.

The groundwater samples were collected from artesian wells installed in fuel stations in the city of Salvador, Brazil, using a low-flow peristaltic pump. The samples were placed in 1.0 L amber flasks and refrigerated until arrival at the laboratory, where they were analyzed.

Experimental design

To obtain the conditions under which the derivatization reaction is performed with adequate efficiency, 2^3 full factorial design was applied, with triplicate of the center point,[18,19] to evaluate the influence of the factors on the response of the cloud-point extraction of PAHs. The response was evaluated according to the area under the peak of each of the PAHs. The variables analyzed were the derivatization reagent volume (100-150 µL), the temperature (60-80 °C) and the reaction time (30-60 min) (Table S2). The experiments were performed in random order, and the replicates of the center points were used to estimate the experimental error for a confidence level of 95%. The experimental data were processed using the software Statistica®.

The response of the experiments was evaluated in terms of the normalized responses sum of the ratio of each analyte area by maximum area measured, i.e., by the application of the multiple response concept.[20] The multiple response was calculated using the following equation:

$$\text{Multiple response} = \sum \left(\frac{\text{PAH area}}{\text{Maximum PAH area obtained in design}} \right)$$

A dimensionless scale was created for the response of each analyte, and then, all the responses were added. Hence,

the simultaneous optimization of the numerous responses included the optimum conditions under which recovery of the analytes studied tended toward the maximum.

Results and Discussion

Optimization of the derivatization reaction

The peak areas obtained for each PAH and the multiple response of each experiment are presented in Table S3. From the multiple responses obtained, a Pareto chart (Figure 1) was created. The graph shows that the three variables studied are statistically significant for the determination of the PAHs extracted and pre-concentrated by CPE. In addition, the three variables have a positive effect on the areas of the 16 PAHs, i.e., the response was maximized as the three variables tend towards the higher design level (reaction time > volume of BSTFA > reaction temperature). The interactions between the volume of BSTFA and reaction temperature were also significant for the multiple response. As the variables tend towards the maximum, a greater amount of surfactant is derivatized, thereby making the PAH in the micelle nucleus more easily available and maximizing the analytical signal.

A curvature test was applied to evaluate the presence of curvature in the mathematical model. The negative curvature indicates the existence of a maximum condition at the region of the center point of the experimental range established by the proposed design.[21] This result indicates that by employing the experimental conditions of the center point, i.e., 125 µL of BSTFA, a water bath temperature of 70 °C and 45 min of reaction time, the responses for the PAHs were close to the maximum.

Figure 2 displays the GC-MS chromatograms generated in scan mode for three different coacervate conditions, in the absence of PAHs. The peaks numbered from 1 to 10 are
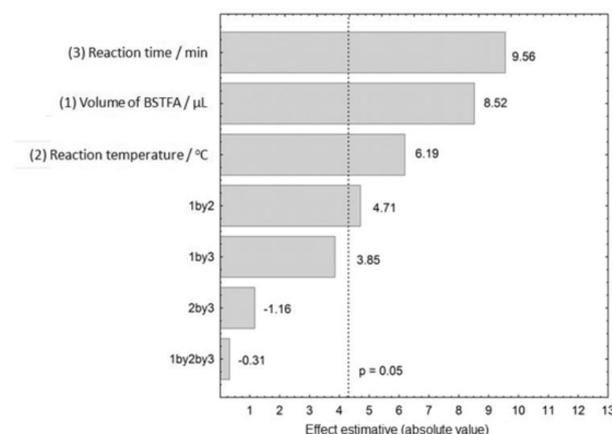

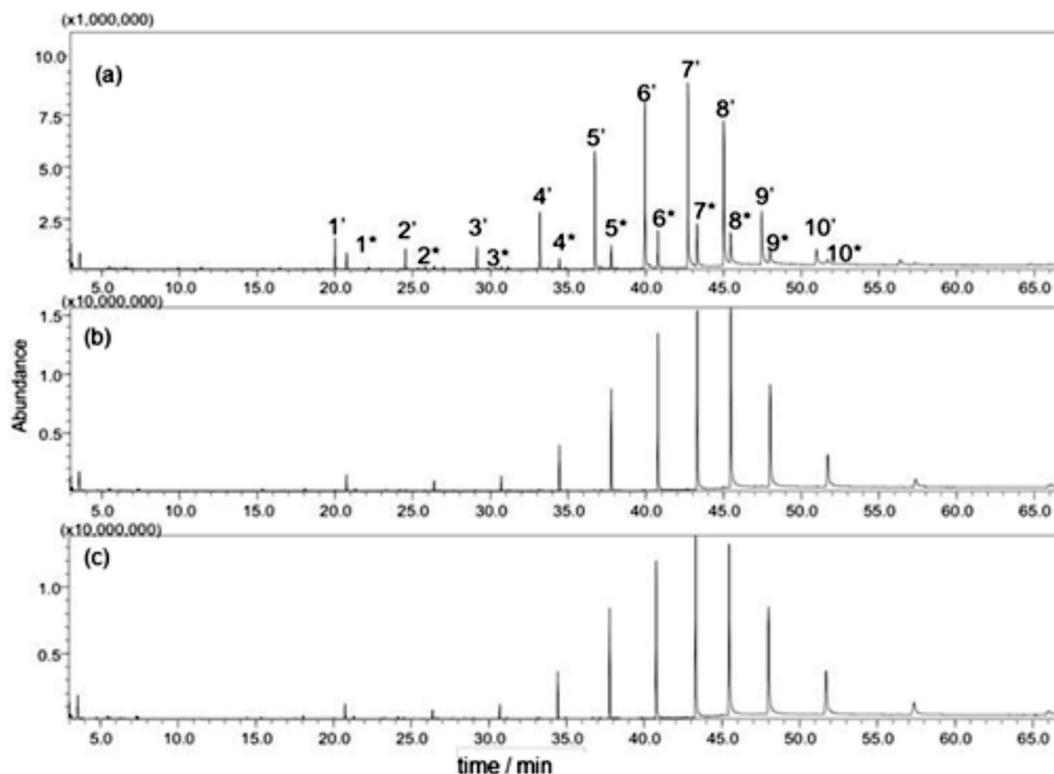**Figure 1.** Pareto chart of the complete 2^3 factorial design for the derivatization reaction.

Figure 2. Chromatograms of the surfactant-rich phase after derivatization with BSTFA (a) before optimization (' non-derivatized surfactant peaks and * derivatized surfactant peaks), (b) under the experimental conditions of experiment 1 and (c) under the experimental conditions of the center point.

related to the number of eluted ethylene oxide units present in the OPEO30 structure.

Figure 2a presents a chromatogram of an incomplete derivatization reaction, obtained before simultaneous experimental design. Figures 2b and 2c display the chromatograms obtained with the injection of coacervates obtained under the conditions of experiment 1 and under the conditions of the center point (Table S3), respectively. The chromatograms reveal that the peaks with greater intensity are related to the derivatized surfactant, whereas the peaks corresponding to the non-derivatized surfactant are absent, indicating efficiency in the derivatization reaction under the conditions of experiment 1 and under those of the center point.

In regard to the efficiency of the derivatization reaction, both the conditions of experiment 1 (Figure 2b), where all variables are at their maximum level, and the conditions of the experiment at the center point (Figure 2c) can be used. Under both conditions, non-derivatized surfactant peaks were not observed. However, under the center-point experiment conditions, a lower amount of reagent is used and the reaction time is shorter in comparison to the conditions of experiment 1. Furthermore, the temperature used in the center-point experiment is lower, which diminishes the risk of analyte loss by evaporation.

During the derivatization reaction using BSTFA as a silylating reagent, the hydrogen from the hydroxyl present in the non-ionic surfactant molecule is replaced by the trimethylsilyl (TMS) group, increasing the surfactant's volatility. Figure 3 shows the mass spectrum of the chromatographic peak of Figure 2c at the retention time of 40.74 min for TMS-OPEO30. The fragments at m/z 117, 161, 205, 249 and 293 result from the TMS-polyoxyethylene species, which differ in number of ethylene oxide units present; the molecular mass of the ethylene oxide units is 44. The peaks at m/z 57 and 73 indicate the presence of *tert*-butyl and TMS fragments, respectively. The peak at m/z 427 corresponds to the fragment remaining after the dissociation of TMS from the OPEO30 molecules.

Observation of all ions related to the silylation of OPEO30, such as the peak of the molecular ion and the ethylene oxide units larger than 10, was not possible. OPEO30 has an average of 30 ethylene oxide units, with the peak of the molecular ion at $m/z > 700$, which is a band unreached by the mass detector used. However, the results obtained from the chromatogram, as well as those from the mass spectrum, indicate that the reaction between the OPEO30 surfactant and the BSTFA was essentially completed. This statement is reinforced by the presence of the peak at m/z 73, which corresponds to the excess of the derivatization reagent.
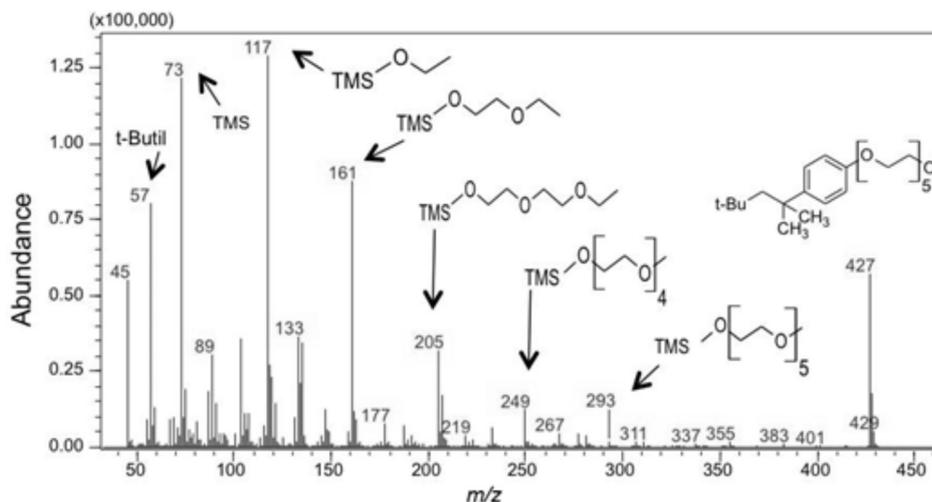
Figure 3. Mass spectrum of the peak at 40.74 min for derivatized OPEO30, corresponding to the chromatogram in Figure 2c, for six ethylene oxide units (n = 6), with the instrument operated in scan mode.

Based on multiple response, Pareto chart, curvature test and chromatographic data analysis, one can conclude that although the factors studied influence the response, with the levels studied tending to the maximum, the proposed experimental conditions at the center point represented a situation where the analytical response tends to be maximized. Thus, a compromise was maintained between the determination of the PAHs and the use of more convenient experimental conditions. Hence, the center point experimental conditions were used in the derivatization procedure, where 30 µL of the rich phase from the CPE was used, in addition to 125 µL of BSTFA, 100 µL of pyridine and a water bath at 70 °C for 45 min, with subsequent determination by GC-MS.

Optimization of the CPE pre-concentration procedure

After the conditions for the surfactant derivatization reaction were established, some CPE aspects were evaluated to obtain better performance in the recovery of the 16 PAHs. The surfactant concentration, temperature and water bath time were assessed.

To evaluate the effect of surfactant concentration, 10.00 mL of sample was used and the OPEO30 solution volume was kept constant at 1000 µL; its final concentration varied between 0.5 and 1.7% (v v^{-1}). The final volume of the surfactant-rich phase (Vr) after the CPE procedure was observed to be proportional to its concentration. For the surfactant concentrations of 0.5% and 1.7%, the Vr values obtained were 30 µL and 160 µL, respectively. For selection of the surfactant concentration, the minimum volume of the surfactant-rich solution after the CPE that allowed sufficient quantity for proper manipulation at the derivatization reaction step was 70 µL. This volume was obtained when

a 0.9% OPEO30 solution was used. Because a compromise condition should be reached to obtain a maximum pre-concentration factor (Fc), while simultaneously providing a proper Vr for handling subsequent volumes and increasing the extraction efficiency, the concentration of 0.9% (v v^{-1}) was chosen. The Fc was calculated as the volume ratio of the sample before extraction (10.00 mL) to surfactant-rich phase after phase separation (70.0 µL),[22] which resulted in a Fc equal to 142.

The water bath temperature tests were carried out at temperatures starting at 60 °C, because below this temperature, elimination of the water in the surfactant-rich phase was not effective, which made the derivatization step more difficult. If the water is still present in the surfactant-rich phase, the trimethylsilylation reaction does not proceed to any significant extent.[10] Experiments at temperatures above 80 °C were not conducted because of risks of losing analytes by evaporation. Hence, the tests were conducted at 60, 70 and 80 °C.

The recovery (%R) was calculated as the percentage of PAH extracted from the sample into the surfactant-rich phase.[22] The recovery of the PAHs ranged between 44 and 76% when the water bath temperature was 80 °C, most likely because of the loss of analytes by evaporation. The recoveries were satisfactory at 60 or 70 °C. However, the water bath temperature selected was 70 °C (recoveries between 85 and 120%) because it corresponds to the temperature at which the derivatization reactions were conducted, thereby increasing the analytical throughput of the procedure. The influence of the water bath time on PAH extraction tested were 5, 10 and 20 min. With a water bath time of 5 min, the recoveries were between 74 and 99% and were lower than those obtained with the other times tested. The results obtained with 10 and 20 min were similar, and

the difference between the recoveries was not significant according to the t-paired test results (95% confidence level). Hence, the extraction time was maintained at 10 min, where the analyte recoveries were between 80 and 105%.

The centrifugation time and speed are not critical factors, but they cannot be very short or slow.[23,24] Therefore, the samples were centrifuged at 3000 rpm for 5 min, and this time and rotation were observed to be sufficient for the adequate separation of phases.

Method validation

Using the proposed procedure, a sample of natural water spiked with the 16 analytes studied was used to evaluate the effect of the matrix, the detection and quantification limits, the accuracy and precision.

The effect of the matrix in the determination of analytes, in relation to the presence of derivatized coacervate was assessed through preparation of two calibration curves.[25] The slopes of the calibration curves with and without the matrix differ substantially; this effect was observed for all 16 PAHs. Hence, preparation of the calibration curves in the presence of a matrix was necessary, with the standard analyte solutions being subjected to the CPE and derivatization procedures. Calibration by standard addition method was not required, although water samples can vary significantly in composition.

The developed method has good selectivity, verified by the excellent separation of the peaks of the analytes. Furthermore, no interference peaks were observed at the specific retention times of the analytes, thus indicating that no co-elution of the peaks corresponding to the derivatized surfactant occurs at retention times close to the PAH peaks determined in this study. Notably, no change was observed in the retention times of the analytes in the presence of the derivatized surfactant-rich phase.

The limits of detection (LOD) and quantification (LOQ) of the method were established on the basis of the signal/noise ratio (S/N).[26] Table 1 presents the LOD of the proposed method and other procedures for determination of PAH in water samples using GC. The LOD from the proposed method was, for example, forty eight times lower in relation to dispersive liquid-liquid procedure for the benzo (k) fluoranthenemicroextraction procedure (DLLME)[27] and comparable with LOD obtained by solid phase extraction (SPE).[28]

Addition and recovery tests were performed by comparing the concentration of each PAH added to the sample before the CPE procedure with the concentration determined after the proposed procedure. A spiked groundwater sample was prepared at three different concentrations, with six replicates *per* concentration. The results of the addition and recovery tests for each PAH at the three levels studied are presented in Table 2. Recoveries ranged between 71 and 90% for the low concentration level (100 ng L^{-1}); between 80 and 98% for the intermediate level (500 ng L^{-1}); and between 72 and 86% for the highest level (1000 ng L^{-1}). At the three concentration levels studied, the recovery intervals were acceptable for trace analysis (70-120%).[29] For all analytes, the coefficients of variation (CV) were between 1.3 and 10.3% (n = 6) and were therefore inside the limit considered acceptable (CV < 20%) for trace analysis.

Table 1. Limits of detection (LOD) obtained for the proposed method and other procedures for determination of PAH using GC

Analyte	LOD / (µg L^{-1})		
	DLLME[26]	SPE[27]	CPE, this study
Naphtalene	0.34	0.02	0.04
Acenaphthylene	0.39	0.03	0.05
Acenaphthrene	0.34	–	0.05
Fluorene	0.45	–	0.05
Phenantrene	0.36	0.052	0.01
Anthracene	0.44	–	0.02
Fluoranthene	0.56	0.025	0.02
Pyrene	0.38	0.021	0.03
Benzo (a) anthracene	0.42	–	0.03
Crysene	0.67	–	0.02
Benzo (b) fluoranthene	0.72	–	0.02
Benzo (k) fluoranthene	0.98	–	0.02
Benzo (a) pyrene	0.16	–	0.02
Benzo (g,h,i) perylene	0.18	–	0.02
Indeno (1,2,3-cd) pyrene	0.96	–	0.02
Dibenzo (a,h) anthracene	0.53	–	0.03

DLLME: dispersive liquid-liquid microextraction; SPE: solid phase extraction; CPE: cloud-point extraction.

The comparison of independent methods was also used to evaluate the accuracy of the proposed method. For the comparison, the method 3510C proposed by the USEPA was used, which employs liquid-liquid extraction and determination by GC-MS.[30] Table 2 displays the results for one of the spiked water sample. The proposed cloud-point extraction method provided good extraction efficiency compared to that of the reference method, especially in the cases of naphthalene, acenaphthylene, acenaphthene and fluorene, which are not satisfactorily recovered by the method of comparison. Additionally, when compared to liquid-liquid extraction (LLE), the proposed method has the main advantage of not involving the use of toxic solvents

Table 2. Recovery test results (%) using the proposed method in groundwater samples fortified with the PAHs at three concentration levels (n = 6) and the comparative method in a water sample fortified with 100 µg L^{-1} of each analyte (n = 3)[a]

Analyte	Amount added / (ng L^{-1})			Comparative method / (100 µg L^{-1})
	100	500	1000	
Naphtalene	90 ± 10	90 ± 2	86 ± 2	< 1
Acenaphtylene	87 ± 6	96 ± 5	81 ± 3	< 1
Acenaphthene	85 ± 7	96 ± 4	85 ± 7	< 1
Fluorene	80 ± 5	91 ± 8	79 ± 6	< 1
Phenanthrene	79 ± 3	92 ± 3	72 ± 2	101 ± 6
Anthracene	90 ± 3	98 ± 3	81 ± 7	98 ± 2
Fluoranthene	84 ± 1	95 ± 3	77 ± 9	93 ± 2
Pyrene	86 ± 2	95 ± 3	78 ± 9	95 ± 3
Benzo (a) anthracene	88 ± 2	97 ± 3	77 ± 7	83 ± 2
Chrysene	89 ± 2	97 ± 3	76 ± 6	96 ± 5
Benzo (k) fluoranthene	84 ± 2	97 ± 3	79 ± 8	95 ± 2
Benzo (b) fluoranthene	87 ± 2	96 ± 2	76 ± 6	92 ± 4
Benzo (a) pyrene	90 ± 2	91 ± 7	81 ± 9	97 ± 5
Benzo (g,h,i) perylene	76 ± 2	87 ± 7	72 ± 2	91 ± 3
Indeno (1,2,3-cd) pyrene	81 ± 2	92 ± 4	74 ± 3	101 ± 8
Dibenzo (a,h) anthracene	71 ± 1	80 ± 3	75 ± 5	91 ± 4

[a]Results expressed as mean ± standard deviation.

in large volumes, thus reducing the sample volume; the reference method used 500 mL of sample, and the proposed method required only 10 mL.

Analytical application

The analytical method developed for the determination of PAHs using CPE with OPEO30 surfactant-rich phase derivatization and detection by GC-MS was applied to ten groundwater samples collected from artesian wells at fuel stations in the city of Salvador, Brazil (Table S4).

The analysis results indicated the presence of some PAHs in samples from numerous collection points. In samples 1 through 6, 8 and 10, the PAHs were at concentrations below the method's LOD. In samples 7 and 9, at least one and a maximum of four out of the 16 PAHs studied were quantified.

Pyrene was quantified in two samples, with a minimum concentration of 0.15 µg L^{-1} and a maximum concentration of 0.71 µg L^{-1}; however, neither Resolution No. 396/2008 from the National Council of the Environment (CONAMA)[31] or Ordinance No. 2914/2011 from the Brazilian Ministry of Health (Ministério da Saúde do Brasil)[32] provide reference values for the this analyte.

Four compounds were quantified in sample 7, including fluoranthene and pyrene, which have mutagenic properties. This result can be explained by contamination by gasoline

and diesel oil because the well is open and car-washing activities were observed at the station without proper drainage of the effluent. None of the analyte concentrations in the collected samples exceeded the limits established by Brazilian law.

Conclusions

In the present study, the use of non-ionic OPEO30 surfactant was developed for the determination of aromatic organic compounds via GC-MS. The results demonstrate that it is possible via post-extraction derivatization of the surfactant of the surfactant-rich extractant phase to utilize the cloud-point extraction technique prior to GC or GC-MS analysis.

Addition of proper amounts of Na$_2$SO$_4$ to the micellar solutions of OPEO30 surfactant could suppress its cloud-point low enough, thus facilitating the CPE process. Heating was necessary to eliminate moisture (water) because trimethylsilylation reagent used in derivatization hydrolyze and becomes nonreactive. A pre-concentration factor equal to 142 was obtained when a 0.9% OPEO30 solution was used. The recoveries of the PAH from spiked water samples were between 71 and 98%.

In comparison to alternative methods involving CPE in association with GC available in literature, the proposed method does not require the elimination of the surfactant-

rich phase through re-extraction or clean-up because the surfactant-rich phase containing the analytes is injected into the chromatograph after derivatization. However, because of the relatively high inlet temperature requirement, the proposed approach will probably not be applicable for GC analysis of thermally labile analytes.

In comparison to LLE, the proposed analytical method provides the main advantage of using non-toxic solvents in reduced volumes and low-volume samples, consistent with the principles of green chemistry. Overall, this approach should serve to help expand the scope of CPE as an extraction procedure prior to the GC analysis.

Supplementary Information

Supplementary data are available free of charge at http://jbcs.sbq.org.br as PDF file.

Acknowledgments

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