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Chemometric-based determination of polycyclic aromatic hydrocarbons in aqueous samples using ultrasound-assisted emulsification microextraction combined to gas chromatography–mass spectrometry

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ABSTRACT

In the present research, ultrasonic-assisted emulsification-microextraction (USAEME) coupled with gas chromatography–mass spectrometry (GC–MS) has been proposed for analysis of thirteen environmental protection agency (EPA) polycyclic aromatic hydrocarbons (PAHs) in aqueous samples. Tetrachloroethylene was selected as extraction solvent. The main parameters of USAEME affecting the efficiency of the method were modeled and optimized using a central composite design (CCD). Under the optimum conditions (9 μL for extraction solvent, 1.15% (w/v) NaCl (salt concentration) and 10 min for ultrasonication time), preconcentration factor (PF) of the PAHs was in the range of 500–950. In order to have a comprehensive analysis, multivariate curve resolution-alternating least squares (MCR-ALS) as a second-order calibration algorithm was used for resolution, identification and quantification of the target PAHs in the presence of uncalibrated interferences. The regression coefficients and relative errors (REs, %) of calibration curves of the PAHs were in the satisfactory range of 0.9971–0.9999 and 1.17–6.59%, respectively. Furthermore, analytical figures of merit (AFOM) for univariate and second-order calibrations were obtained and compared. As an instance, the limit of detections (LODs) of target PAHs were in the range of 1.87–18.9 and 0.89–6.49 ng mL^{-1} for univariate and second-order calibration, respectively. Finally, the proposed strategy was used for determination of target PAHs in real water samples (tap and hookah waters). The relative recoveries (RR) and the relative standard deviations (RSDs) were 68.4–109.80% and 2.15–6.93%, respectively. It was concluded that combination of multivariate chemometric methods with USAEME-GC–MS can be considered as a new insight for the analysis of target analytes in complex sample matrices.

1. Introduction

PAHs are a large group of organic compounds with two or more fused aromatic rings consisting of only hydrogen and carbon. These compounds are known as ubiquitous environmental pollutants. They are generated during the incomplete combustion of fossil fuel, oil refinement, and industrial and municipal discharges. Also, tobacco and barbequed or smoked meat are potential matrices to find the PAHs [1,2]. PAHs have attracted attention of biochemists and analytical chemists because of their carcinogenicity, mutagenicity, toxicity and environmental persistence. They are also used as markers for fingerprinting and source identification of oils and oil spills [3,4].

Aqueous matrices should be continuously controlled for undeniably effects of PAHs on human and animal health. PAHs are present in environmental water samples at ng mL^{-1} (ppb) levels or lower due to their large hydrophobicity. On the other hand, identification and quantification of PAHs in many circumstances are faced with many problems due to the complexity of their matrices, low concentration levels and solubility in water and similarity in their properties [5]. Therefore, the development of sensitive and selective analytical methods including a sample preparation technique followed by a separation technique (e.g., GC and/or HPLC) is required for determination of PAHs in different sample matrices.

Great efforts have been made by different research groups to develop simple, low cost, selective and sensitive preconcentration techniques for the extraction of PAHs from different sample

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matrices. Among different methods, preconcentration techniques based on liquid and solid-phase microextraction [6–10] have attracted increasing attention due to their advantages of high recovery, simplicity, high speed, low cost and low consumption of organic solvents.

On the other side, during the last few years, there has been special attention to ultrasound irradiation in analytical chemistry. Ultrasound assisted extraction techniques have many advantages during the formation and implosion of very fine bubbles, such as speeding up the mass transfer between two immiscible phases, reducing the equilibrium time and increasing the preconcentration factor [11,12]. Ultrasound-assisted emulsification microextraction (USAEME), ultrasonic assisted extraction–dispersive liquid–liquid microextraction (UAE-DLLME), ultrasound-enhanced surfactant-assisted dispersive liquid–liquid microextraction (UESA-DLLME) and ultrasound-assisted dispersive liquid–liquid microextraction (USA-DLLME) are some of the examples of liquid-phase microextraction techniques assisted by ultrasonic irradiation [13–16]. In the past decade, dispersive liquid–liquid microextraction (DLLME) [6] has been frequently used as an appropriate preconcentration/extraction technique for the extraction of different target analytes from various sample matrices [17–19]. Briefly, DLLME is based on extraction of sought analytes into very fine droplets (organic phase) through the utilization of a mixture of a non-water-miscible extraction solvent (organic) and a water miscible polar dispersive solvent (e.g., methanol, acetonitrile or acetone). Compared to conventional DLLME, the USAEME does not need to disperser solvent. In fact, the extraction solvent disperses throughout the aqueous phase by ultrasonication. This procedure causes reduction of analyte partitioning in the aqueous phase and decreasing the solubility of the organic phase in the aqueous phase and therefore, increasing the enrichment factor [12].

As mentioned before, the presence of organic species in different matrices, such as natural waters and wastewaters, which are relatively at high concentration in contrast with very low concentration of PAHs, can interfere with PAHs quantification. Moreover, similarity in structure and physicochemical properties of PAHs themselves makes their simultaneous analysis difficult. Fortunately, these problems can be overcome by powerful chemometric techniques using the so-called second-order advantage [20] which means the calculation of analyte concentration in the presence of uncalibrated interferences. Over the past decades, different combinations of instrumental and chemometric techniques have been proposed for PAHs determination in aqueous matrices [21–29]. Excitation–emission matrix (EEM) fluorescence spectroscopy among instrumental techniques, and parallel factor analysis (PARAFAC) [30], multivariate curve resolution-alternating least squares (MCR-ALS) [31] and partial least squares (PLS)-based techniques from chemometric points of view are the most frequently used techniques in the reviewed works. EEM provides poor detection limit ($>$ng mL^{-1}) and suffers from lack of selectivity in complex matrices. On the other hand, most of the GC–MS analyses of PAHs were carried out by selected ion monitoring (SIM) mode for enhancing the sensitivity which causes loss of qualitative information. Surprisingly, combination of GC–MS and chemometric techniques for determination of PAHs in different sample matrices has been rarely studied. Nevertheless, by combining of full scan mode of GC–MS and chemometric techniques, possibility of comprehensive detection and sensitivity enhancement can be simultaneously provided. Furthermore, the full scan mode brings the capability of interference identification along with improvement of sensitivity and selectivity by second-order advantage.

In the present study, a chemometric-assisted strategy is proposed for optimization of USAEME-GC–MS procedure for extraction and preconcentration of thirteen PAHs. Then, MCR-ALS is used for resolution, identification and quantification of PAHs in water samples in the presence of fundamental chromatographic challenges (baseline/background contribution, elution time shifts, low S/N and peak overlap)[32]. Finally, the analytical figures of merit (AFOM) are obtained with the second-order calibration and compared with those of the traditional univariate method.

2. Experimental

2.1. Chemicals and reagents

A certified mixture of 13 PAHs (EPA 525 PAH Mix A) containing of 500 μg mL^{-1} of acenaphthylene, anthracene, benz[a]anthracene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[ghi]perylene, benzo[a]pyrene, chrysene, dibenz[a,h]anthracene, fluorene, indeno[1,2,3-cd]pyrene, phenanthrene, and pyrene in methylene chloride was provided by Supelco Analytical (Bellefonte, PA, USA). A stock standard solution (50 μg mL^{-1}) of PAHs was prepared by appropriate diluting of original standard in methanol and was stored at 4 °C. More diluted standards were daily prepared from the stock standard solution. Biphenyl, chloroform, carbon tetrachloride, trichloroethylene, tetrachloroethylene, chlorobenzene, methanol and sodium chloride with the purity higher than 99.0% were purchased from Merck Chemicals (Darmstadt, Germany). The tap water sample was collected from the cold-water tap of our laboratory. The hookah water sample was taken from a hookah water pipe that had been used for 30 min. The water samples were filtered through a 0.45 μm membrane and then stored in dark glass bottles at 4 °C.

2.2. The USAEME procedure

A 5.0 mL 1.15% NaCl in water (w/v) was placed into a conical bottom test tube. The solution was spiked with a standard mixture of PAHs (150 ng mL^{-1}), and then was subjected to ultrasonication in a water bath for 10 min. During ultrasonication, 9 μL of the extraction solvent (tetrachloroethylene) was slowly injected into the solution using a 10 μL microsyringe. Thereby, a cloudy solution consisting of tiny droplets of tetrachloroethylene dispersed through the aqueous sample solution was formed. The emulsification provides a very fast mass-transfer of PAHs from the sample solution to the extraction solvent. Then, the organic extraction phase was separated by centrifugation at 3500 rpm for 3 min. In our study, the height of sedimented layer was usually between 2 and 3 mm. By using 9 μL of tetrachloroethylene, approximately 3–5 μL of solvent (containing the extracted analytes) was remained after centrifugation that this volume was collected by 1 μL Hamilton syringe. Finally, 1 μL of the extract was injected into GC–MS for analysis.

2.3. GC–MS analysis

To obtain second-order data, a 6890 GC system coupled with a 5973 network mass selective detector (Agilent Technologies, Santa Clara, CA, USA) was used. Separation of PAHs was carried out on a HP5-MS capillary fused silica column (30 m length; 0.25 mm I.D.; 0.25 μm film thicknesses, (5% Phenyl)-methylpolysiloxane). The temperature program was started at 90 °C that fixed for 5 min, then increased with the rate of 50 °C min^{-1} to 270 °C, held for 15.4 min. The injection port temperature was set at 290 °C and operated in splitless mode for 1 min. Mass spectra were taken at 70 eV ionization energy and full scan mode. The scanned mass range was set at 50–350 m/z. The optimization of method was carried out using a Shimadzu-17AGC-FID (Tokyo, Japan) under the same operating conditions as used for GC–MS.