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Water analysis of the sixteen environmental protection agency—polycyclic aromatic hydrocarbons via solid-phase nanoextraction-gas chromatography/mass spectrometry

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ABSTRACT

The growing concern with a sustainable environment poses a new challenge to analytical chemists facing the routine monitoring of polycyclic aromatic hydrocarbons (PAHs) in water samples. The new method presented here meets several features of green analytical chemistry. PAHs are extracted from 500 μL of water sample with 1 mL of a gold nanoparticles aqueous solution and released with 100 μL of organic solvents for subsequent analysis via gas chromatography/mass spectrometry. The relative standard deviations of the overall procedure ranged from 2.4 (acenaphthene) to 7.8% (dibenz[*a,h*]anthracene). The limits of detection were excellent as well and varied from 4.94 (fluoranthene) to 65.5 ng L^{-1} (fluorene). The excellent analytical figures of merit, the simplicity of the experimental procedure, the short analysis time and the reduced solvent consumption demonstrate the potential of this approach for the routine monitoring of the sixteen priority pollutants via and environmentally friendly methodology.

1. Introduction

The fact that polycyclic aromatic hydrocarbons (PAHs), which originate from many natural and anthropogenic sources, can induce cancer has been documented in numerous epidemiological studies [1–6]. The US Environmental Protection Agency (EPA) includes sixteen PAHs in its priority pollutants list, namely benz[*a*]anthracene (B[*a*]A), benzo[*b*]fluoranthene (B[b]F), benzo[*k*]fluoranthene (B[*k*]F), benzo[*a*]pyrene (B[*a*]P), dibenz[*a,h*]anthracene (DB[*a,h*]A), indeno[*1,2,3-cd*]pyrene (I[*1,2,3-cd*]P), naphthalene (Nap), acenaphthylene (Aceny), acenaphthene (Acen), fluorene (Flu), phenanthrene (Phen), anthracene (Ant), fluoranthene (Fluo), pyrene (Pyr), chrysene (Chr), and benzo[*ghi*]perylene (B[*ghi*]P) [7]. Since a primary route of human exposure to PAHs is contaminated water, the routine monitoring of the sixteen EPA-PAHs is recommended in water samples taken from municipal wells and agricultural irrigation sources such as ponds, lakes and rivers [8–21].

Maximum contaminant levels (MCL) of regulated PAHs range from 10 to 200 ng L^{-1} [7,22]. The EPA recommends MCL not to exceed 200 ng L^{-1}. The European Union and the World Health Organization (WHO) have set a 10 ng L^{-1} MCL value for the highly toxic B[*a*]P and 200 ng L^{-1} MCL values for Fluo, B[*b*]F, B[*k*]F, B[*ghi*]P, and I[*1,2,3-cd*]P. These rather low concentration levels make water analysis a particularly challenging task. The classic approach follows the sequence of sample preparation and chromatographic analysis. By removing PAHs from the water sample into an organic solvent suitable for chromatographic analysis, sample preparation pre-concentrates PAHs, simplifies matrix composition and facilitates analytical resolution in the chromatographic column. Solid-phase extraction (SPE) is nowadays the recommended method for water samples [23]. When compared to liquid–liquid extraction, SPE reduces solvent consumption, prevents emulsions and provides better extraction efficiency. The main disadvantage of SPE is its long processing time. The extraction of 1 L of water – which is the recommended volume to reach detectable PAHs concentrations by classic chromatographic approaches [23] – adds approximately 1 h to the total analysis time.

High-performance liquid chromatography (HPLC) and gas chromatography/mass spectrometry (GC/MS) are the basis of EPA methodology. Ultraviolet absorption (254 nm) and room temperature fluorescence detection are widely used in HPLC, but the selectivity of these detectors is modest. Since PAHs identification is solely based on retention times, unambiguous PAH identification requires complete chromatographic resolution in the separation column. When HPLC is applied to "unfamiliar" samples, a supporting analytical technique such as GC/MS is recommended to verify

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compound identification and to check peak-purity of HPLC fractions [23].

Research efforts in our lab have focused on the development of analytical methodology for a sustainable environment [24–26]. Within the concept of green analytical chemistry [27–29], HPLC presents a distinct disadvantage over GC/MS, which is the need of organic solvents for PAHs separation. Under classic EPA methodology [23], the HPLC analysis of the sixteen priority pollutants consumes approximately 75 mL of mobile phase (methanol-water) per sample. Considering the gradient elution of the chromatographic separation, this mobile phase volume is equivalent to 66 mL of methanol. Adding the volumes of eluting solvents from the SPE procedure – i.e., 5 mL of ethyl acetate and 5 mL of methyl chloride – the total volume of organic solvents is approximately 76 mL per sample.

The new method we present here requires only 100 μL of organic solvent per sample. EPA-PAHs are extracted from water samples with the aid of an experimental procedure previously developed for the analysis of high-molecular weight PAHs [30,31]. This procedure – which we have named solid-phase nanoextraction (SPNE) – takes advantage of the strong affinity that PAHs have for the surface of gold nanoparticles (Au NPs). Separation and determination of the sixteen EPA-PAHs is accomplished in 22 min via an optimized GC/MS method. The entire analysis – i.e., SPNE and GC/MS – takes less than 25 min per sample. The excellent analytical figures of merit (AFOM) – associated to the simplicity, short analysis time and reduced solvent consumption – demonstrate the potential of SPNE-GC/MS for the routine monitoring of EPA-PAHs via environmentally friendly methodology.

2. Experimental

2.1. Chemicals

Nanopure water from a Barnstead Nanopure Infinity water system was used throughout. 20 nm average diameter Au NPs in aqueous solutions (7×10^{11} particles mL^{-1}) were purchased from Ted Pella, Inc. (Redding, CA). HPLC grade methanol was purchased from Fischer Scientific (Pittsburg, PA). Analytical grade 1-pentanethiol and n-octane were from Acros Organics (Atlanta, GA). B[*a*]A, B[*b*]F, B[*k*]F, B[*a*]P, DB[*a,h*]A, I[*1,2,3-cd*]P, Nap, Aceny, Acen, Flu, Phen, Ant, Fluo, Pyr, Chr and B[*ghi*]P were purchased form Sigma-Aldrich (Milwaukee, WI) at their highest available purity (≥98%).

Note: use extreme caution when handling PAHs that are known to be extremely toxic.

2.2. Solution preparation

Stock PAH solutions were prepared in either HPLC grade methanol or n-octane and kept in the dark at 4 °C. Possible PAH degradation was monitored via room-temperature fluorescence spectroscopy. Working solutions of PAHs were prepared by serial dilution of stock solutions with the appropriate solvent. Commercial solutions of Au NPs were kept in the dark at 4 °C. The physical integrity of Au NPs was monitored periodically via ultraviolet-visible absorption spectroscopy.

2.3. Extraction of EPA-PAH with Au NPs

A 500 μL aliquot of the water sample was mixed with 1 mL of 20 nm Au NPs. The mixture was shaken for 5 min at 1400 rpm and centrifuged for 10 min at 13,400 rpm. The supernatant was separated from the precipitate with a micro-pipette. 2 μL of 1-pentanethiol, 48 μL of methanol, and 50 μL of n-octane were added to the precipitate. The new mixture was shaken for 5 min at 1400 rpm. All mixing and shaking times were previously optimized for best PAH recovery.

2.4. Absorption spectroscopy

Absorbance measurements were carried out with a single-beam spectrophotometer (model Cary 50, Varian) equipped with a 75-W pulsed xenon lamp, 20-nm fixed band-pass, and 24,000 nm min^{-1} maximum scan rate.

2.5. Sample mixing and centrifugation for PAHs extraction with gold colloids

Sample mixing and centrifugation were performed in 2-mL Microplain glass tubes. Sample mixing was done with a Maxi Mix III Rotary Shaker (Type M65800, Barnstead-Thermolyne) equipped with a PT500X6A Vortex Mixer accessory. Centrifugation was performed with a MiniSpin centrifuge (Eppendorf) at the maximum rotational speed (13,400 rotations per minute) of the centrifuge.

2.6. Gas chromatography/mass spectrometry

GC/MS was carried out with the aid of a gas chromatograph (6850 GC, Agilent, Avondale PA) coupled to a quadruple mass spectrometer with electron impact (EI) ionization at 70 eV (5975 VL, Agilent). The gas chromatograph was equipped with an auto sampler using 5 μL syringes. Pulsed, 2 μL splitless injections were performed at 275 °C and purged for 100 mL min^{-1} at 0.25 min. Separations were carried out on a 5% phenyl methyl siloxane (DB-5ms) column (30 m × 0.25 mm i.d. × 0.25 μm film thickness). The temperatures of transfer line, manifold and source of ionization were set at 280 °C, 280 °C and 230 °C, respectively.

The oven temperature program for "slow" separation conditions were 50 °C for 0.8 min followed by temperature increases to 200 °C at 10 °C min^{-1}, 225 °C at 2.0 °C min^{-1}, 266 °C at 2.0 °C min^{-1}, and 285 °C at 2.0 °C min^{-1}. The solvent delay time was 6.0 min and the total run time was 60 min. The oven temperature program for "fast" separation conditions were 80 °C for 1.0 min, temperature increase to 250 °C at 25 °C min^{-1} and held constant for 6.0 min, and an additional temperature increase to 300 °C at 10.0 °C min^{-1} and held constant for 2.0 min. The solvent delay time was 3.5 min and the total run time was 22 min. In all cases, the carrier gas was ultrapure helium at constant flow rates of 0.8 mL min^{-1} (slow) and 1.8 mL min^{-1} (fast).

PAH peak identification was based on the retention times and full scan spectra of the standards. A mass range of m/z 50–300 was recorded in the full-scan mode. AFOM in the selective ion monitoring (SIM) mode were obtained at the main molecular ion peaks of individual PAHs, namely m/z = 128 (Nap), m/z = 152 (Aceny), m/z = 154 (acen), m/z = 166 (Flu), m/z = 178 (Phen and Ant), m/z = 202 (Fluo and Pyr), m/z = 228 (B[*a*]A and Chr), m/z = 252 (B[*b*]F, B[*k*]F and B[*a*]P), m/z = 276 (I[*1,2,3-cd*]P and B[*ghi*]P) and m/z = 278 (DB[*a,h*]A).

3. Results and discussion

3.1. GC separation of the sixteen EPA-PAHs

One of the challenges facing GC/MS for the analysis EPA-PAHs is the separation of priority pollutants with the same molecular weight and virtually identical fragmentation patterns [32,33]. The most popular GC column for the separation of EPA-PAHs utilizes a stationary phase composed of 5% phenyl and 95% methylpolysiloxane (DB-5ms) [32–44]. Depending on the complexity of the sample matrix, the length of the column may vary between 15 and 60 m. In highly complex environmental matrixes, the individual resolution