

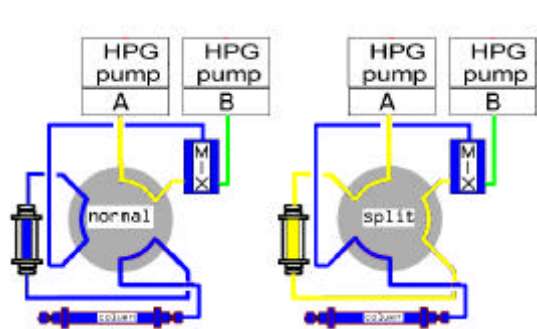
AUTOMATED SAMPLE PREPARATION AND HPLC ANALYSIS OF PAHs IN WATER SAMPLES

Introduction

Hydrocarbons with multiple ring structures are collectively referred to as polynuclear aromatic hydrocarbons, commonly abbreviated as PAHs. This class of compounds are believed to be mutagenic and contain toxic chemicals. These chemicals contain carcinogenic properties which have led to legislative restrictions on their release in the environment. Therefore, suitable monitoring methods are extremely important. In general, the amount of PAHs in water is approximately 10 ppt for each component, depending on the type of water inspected. This application describes the automated sample preparation and analysis of PAHs in water using the UNEXAS system. This system uses high performance solid phase extraction, introduces the analytes directly into the HPLC-system, and is combined with an UV and fluorescence detector.

Experiment

The chromatographic separation is carried out with a binary High Pressure Gradient (HPG) system, implemented in the UNEXAS system, combined with a Shimadzu fluorescence detector and WellChrom Spectro-Photometer K-2600. Online SPE is carried out with an UNEXAS system which controls the Autosampler Triathlon. The SPE pump pushes the water sample into the system. To ensure rapid desorption with 100% acn, a split gradient is programmed. Water is added to the mixing chamber after desorption to form the gradient.



Chromatographic Conditions

Anal. Column:	C ₁₈ ULTRASEP ES PAH, 250 x 2 mm ID
Cartridge:	HySphere C-8, 8 µm, 10 x 2 mm ID
Mobile Phase:	Gradient acetonitrile/water (60:40 v/v) 60 – 100% acn in 28 min
Flow Rate:	0.3 ml/min
UV Detector:	254 nm
FL Detector:	excitation 254 nm, emission 320 nm

Figure 1: Normal or split gradient elution cartridge flow scheme

Sample Preparation

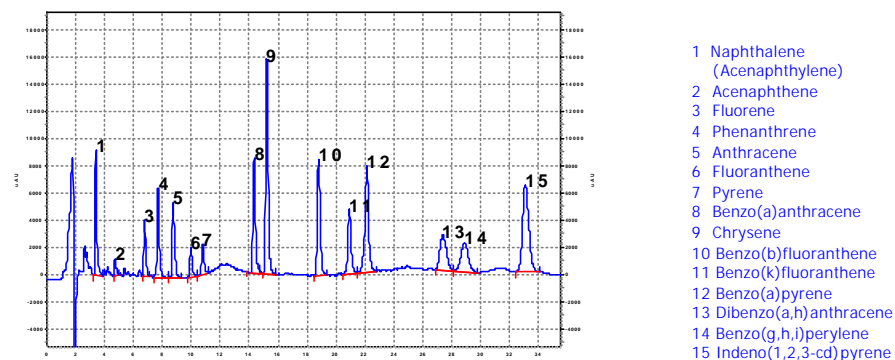
Prior to solid phase extraction rinse the glassware with isopropanol and 20% nitric acid to minimize PAH adsorption.

1. Dilute the water sample with isopropanol (50 ml isopropanol and 150 ml water).
2. Activate the cartridge for 2.0 min with 1.0 ml/min tetrahydrofuran.
3. Condition the cartridge for 2.0 min with 1.0 ml/min 20% acn 80%water.
4. Load the 100 ml sample on the cartridge with 2.5 ml/min.
5. While loading, wash the cartridge for 2 min with 20% acn at 1 ml/min.
6. Elute the clean sample to analytical column for 5.0 min with acn (split gradient mode) at 0.3 ml/min and run the sample analysis. In the meantime, clean the SPE unit and reactivate the cartridge.

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Results

Figure 2 shows a chromatogram of a groundwater sample spiked with 50 ppt PAH.



Conclusion

The hydrophobic PAHs are difficult to analyze, especially when they are present in watersamples. With the use of 25% isopropanol as final modifier an automated on-line SPE-HPLC application has been developed with good recoveries and a high reproducibility. The unique switching diagram to preconcentrate and analyze PAHs allows the elution of the cartridge with 100% acn. Investigations showed that the normal gradient elution is too weak for On-Line desorption. The preconcentration of 100 ml water sample enables the measurement of analyte concentrations in the range between 3 and 20 ppt with fluorescence detection. So the developed method has proven to be an excellent alternative for liquid-liquid extraction.

Component	Recovery (%)	RSD (%) n = 5	LOD (ppt)
Naphthalene	96	6.9	20
Acenaphthylene	-	-	10 UV
Acenaphthene	78	4.5	8 UV
Fluorene	80	3.5	5
Phenanthrene	97	2.8	3
Anthracene	95	3.2	5
Fluoranthene	85	2.8	10
Pyrene	98	3.5	8
Benzo(a)anthracene	91	2.3	3
Chrysene	92	3.1	3
Benzo(b)fluoranthene	80	1.9	5
Benzo(k)fluoranthene	82	1.8	8
Benzo(a)pyrene	78	1.8	5
Dibenzo(a,h)anthracene	95	5.3	10
Benzo(g,h,i)perylene	108	2.3	10
Indeno(1,2,3-cd)pyrene	82	4.8	10