

## Comparison of extraction techniques on determination of PAHs in drinking water samples

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### Abstract

The purpose of this study is to provide some data about the extraction techniques and comparison of them for quantification of toxic compounds as polycyclic aromatic hydrocarbons in drinking water samples. It is very important detecting and analyzing polycyclic aromatic hydrocarbons (PAHs) because of their toxicity and carcinogenicity to human. There are some techniques of extracting PAHs from different water matrices such as drinking water. The classical technique is liquid-liquid extraction (LLE). Different extraction techniques as solid-phase extraction (SPE), LLE, Automated SPE, used to release PAHs from water samples have been overviewed in different studies. The method used in this study about extraction of SPE technique is Environment Protection Agency (EPA) 8310 method. Recoveries have been obtained using this SPE method, but not all parameters have significant value of recovery. Maybe these low values of recovery come from losing PAHs during the evaporation or from solvent of extraction. The recovery of PAHs is more significant in the case of the concentration 100 µg/L of stock standard (table 1), this means that in very low concentration SPE technique is not the right one. The accuracy of SPE technique is not on very high level depending on the PAHs results. The conclusion of this study is using LLE technique is more detectable in drinking water samples.

**Keywords:** Polycyclic aromatic hydrocarbons PAHs, extraction technique, LLE, SPE.

### Introduction

Polycyclic aromatic hydrocarbons (PAHs) are organic compounds that are mostly colorless, white, or pale yellow solids. PAHs can be formed both during biological processes and as products of incomplete combustion from either natural combustion sources (forest and brush fires) or man-made combustion sources (automobile emissions and cigarette smoke). The term "PAHs" refers to compounds consisting of only carbon and hydrogen atoms. PAHs are multiple organic ring structures and some are carcinogenic and mutagenic [5].

Different extraction techniques have been developed and applied for extracting PAHs from water samples. The selected extraction technique, not only influences the accuracy of the results, but also determines the total analysis time and costs. Solid-phase extraction (SPE) is an extraction and preconcentration technique that has been used successfully when trace levels of organic compounds were characterized [4, 6, 8]. SPE is a sequential method which includes adsorbent conditioning, adsorbent equilibration, sample loading, washing of adsorbent and the elution of analytes [2]. It is a quick, selective extraction and purification sample method, which allows small volume of samples to be analyzed without being pre-treated first as in liquid-liquid extraction (LLE) [2]. In contrast to the SPE, the LLE method despite its low cost

apparatus generates a lot of waste solvents and is time consuming [1]. The aim of this study is to improve the detectability of trace PAHs levels in drinking water samples by using SPE sample preparation method because you can analyze more samples at the same time and there are more advantages of using this preparation method.

### Materials and methods

Reagents: methanol (MeOH), acetonitrile (ACN), dichloromethane (DCM) of high purity, HPLC grade.

#### SPE procedure

- **Cartridge conditioning:**

Add 10 ml DCM to the SPE cartridge, let DCM wet and soak the SPE sorbent for 1 min before drawing to waste.

Add 10ml methanol to the SPE cartridge, let MeOH wet and soak the SPE sorbent for 2 min.

Add 20 ml reagent water to the SPE cartridge, pull water through leaving a water layer of about 1 cm above the frit.

- **Water Sample extraction**

Add surrogate spiking solutions (10 ug/l, 100 ug/l) prepared in water miscible solvents, such as MeOH.

Add 5 ml MeOH to the sample bottle and mix well.

Load the sample bottle to the bottle holder, adjust vacuum for a fast flow.

- **Cartridge drying**

Dry the SPE cartridge under vacuum for about 10 min.

- **Analyte elution**

Insert glass vials (25 ml) into the SPE manifold to collect the SPE eluates.

Rinse the sample bottle with 5 ml ACN, repeat this step 2 times with 10 ml ACN.

- **Eluate drying and evaporation**

Remove the collection vials from the manifold and evaporate to the vacuum evaporator. Add 2 ml ACN to the dried extract and transfer the concentrated extract to the autosampler vial (2 ml), and analyze by high performance liquid chromatography fluorescence detector -HPLC-FLD [6,7,2].

#### Chromatographic operation

Parameter	Shimadzu Nexera X2
Solvents:	A:H <sub>2</sub> O, B: Acetonitrile
Column :	Inertsil ODS PAH, 4.6 × 250 mm, 5µm
Gradient:	0 min - 20 % B; 2min -25min - 100 % B, gradient ;25 min -30 min 20% B
Solvent flow :	1.2 mL/min
Injection volume:	5 µL
FLD:	programmed Ex/Em

### Results and discussion

The recovery of an analyte in an assay is the detector response obtained from an

amount of the analyte added to and extracted from the matrix, compared to the detector response for the true concentration of the pure authentic standard. Recovery experiments should be performed by comparing the analytical results for extracted samples at different concentrations. Recovery of the analyte need not to be 100%, but the extent of recovery (of the analyte and the internal standard) should be consistent (for all concentrations tested), precise and reproducible (better than 20%). Good percentage recoveries that ranged from 43.08 % to 62.518% were obtained for Anthracene and Pyrene. Poor recoveries were obtained for Naphthalene (2.4%), Fluorene (16.5%) and Indeno (1, 2, 3-cd) pyrene (9.44%) by SPE extraction, in concentration of 100 $\mu$ g\ L mix standard (Table 1). Naphthalene has a very poor recovery because of the structure of one ring, the molecular mass smaller than the others that can evaporate easily during the concentration by vacuum evaporator. An HPLC chromatogram and well separated compounds of the PAHs standard mixture was obtained after passing the PAHs standard mixture through the SPE adsorbent material (C18). Peaks obtained with retention times (rt) are: Naphthalene : 4.369 min; Fluorene 4.79 min; Phenanthrene: 5.069 min; Anthracene: 5.402 min; Fluoranthene: 5.782 min; Pyrene 6.328 min; Benzo(a)anthracene :7.Crysene 7.939 min; Benzo(b)fluoranthene : 9.908 min; Benzo(k)fluoranthene : 11.09 min; Benzo(a) pyrene : 12.921 min; Dibenzo(a,h)anthracene : 14.359 min; Benzo(ghi)perylene 17.855 min and Indeno(1,2,3-cd)pyrene : 19.13 min. The analytical method development was successful as shown by relatively narrow and well-separated peaks of individual PAHs compounds, but to have better recovery is necessary to develop the method by changing the elute solvent.

Table 1. Recovery% of 10  $\mu$ g/L and 100  $\mu$ g/L mix standard by SPE extraction

<b>Name</b>	<b>Recovery% of 10 <math>\mu</math>g/L</b>	<b>Recovery% of 100 <math>\mu</math>g/L</b>
Naphthalene (Naph)	0.78	2.456
Fluorene (Flu)	1.67	16.5
Phenanthrene (Phe)	15.34	19.56
Anthracene (Anth)	25.35	43.08
Fluoranthene (Fluo)	45.21	54.72
Pyrene (Pyr)	52.88	62.518
Benzo(a)anthracene (Ba anth)	49.19	59.794
Crysene (Cry)	48.72	47.484
Benzo(b)fluoranthene (BbFl)	47.44	33.985

Benzo(k)fluoranthene (BkFl)	47.72	54.827
Benzo(a)pyrene (BaPy)	42.2	49.408
Dibenzo(a,h)anthracene (DiAn)	35.82	39.174
Benzo(ghi)perylene (B Pery)	41.33	41.355
Indeno(1,2,3-cd)pyrene (InPy)	0	9.444

The recovery of PAHs results varies from 0.78%-52% to the concentration 10 µg/L of stock standard and 2.456%-62% to the concentration 100 µg/L of stock standard.



Fig. 1. Manifold apparatus of SPE extraction

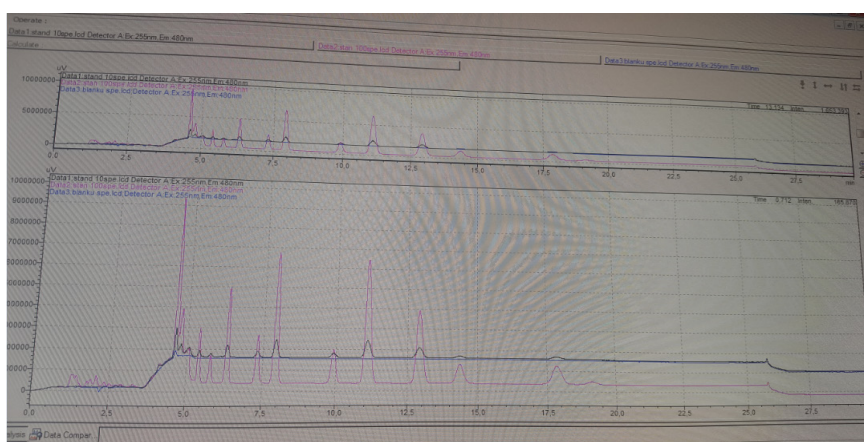


Fig. 2. The overlaped chromatogram of 10 µg/L and 100 µg/L standard obtained after SPE pre-extraction.

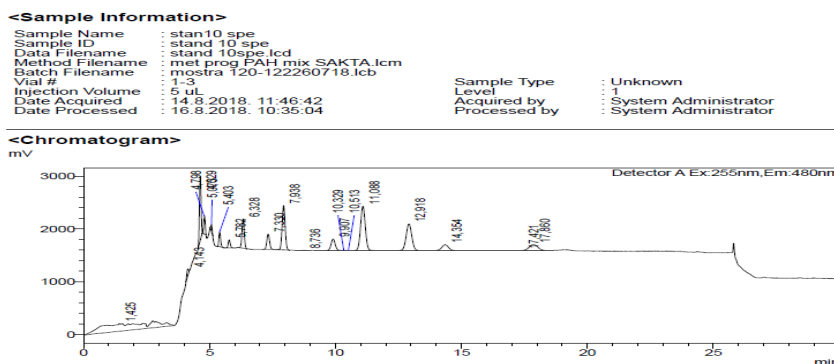


Fig. 3. The chromatogram of peaks in 10 µg/L concentration obtained after SPE pre-extraction.

In this chromatogram is very clear the detection of the PAHs compounds peaks. The column used is Inertsil ODS PAH, 4.6 × 250 mm, 5µm.

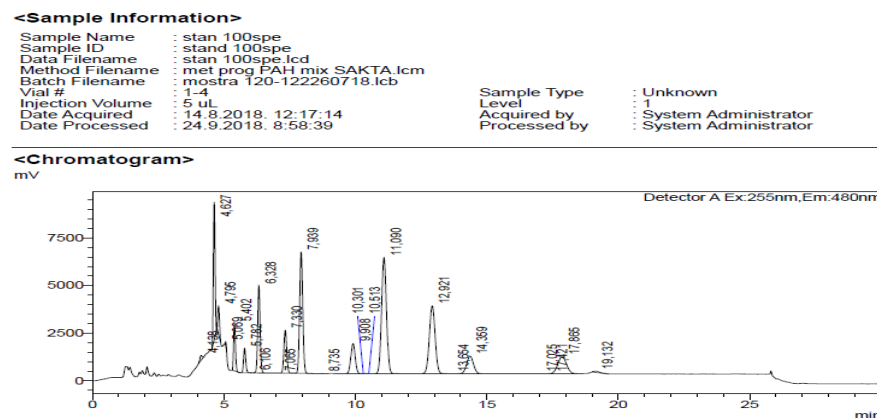
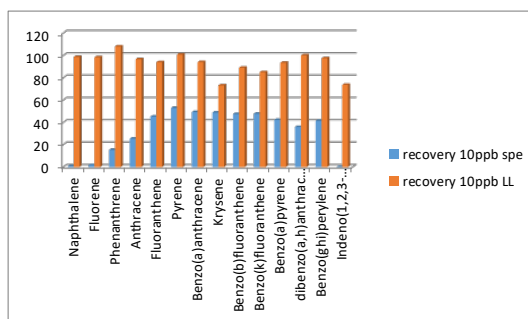


Fig. 4. The chromatogram of peaks in 100 µg/L concentration obtained after SPE pre-extraction.



Graf. 1. The recovery of 10 µg/L concentration obtained after SPE pre-extraction and LLE extraction

As it is seen from this graphic, the recovery of LLE extraction ( it is analyzed in another study) for the same concentration of mix standard (10 µg/L ) is better than SPE technique in water matrix. In this study using LLE technique is more detectable in drinking water samples.

### Conclusions

Different extraction techniques have been applied for extracting PAHs from water samples of sea, rivers, lakes, surface, ground, industrial waste and drinking water. The different extraction techniques used to release PAHs from water samples have been overviewed since proper extraction procedures were necessary to achieve optimum analytical results.

SPE method has been demonstrated for the extraction of 15 PAHs in water by EPA method 8310. Recoveries have been obtained using this SPE method, but not all parameters have significant value of recovery. Maybe these low values of recovery come from losing PAHs during the evaporation or from solvent of extraction. This method of extraction consumes less organic solvents, and yields no emulsion which is a bottleneck when using liquid-liquid extraction for real samples.

### References

- Dean JR (1998). Extraction methods for environmental analysis. John Wiley & Sons: Sussex, UK. pp.35-46.
- EPA Method 8310 Solid phase extraction of Polynuclear Aromatic Hydrocarbons in water.
- Lau EV, Gan S, Ng HK (2010). Extraction techniques for polycyclic aromatic hydrocarbons in soils. *Inter. J. Anal. Chem.* 10:1 - 9.
- Poppa P, Bauera C, Modera M, Paschkeb A (2000). Determination of polycyclic aromatic hydrocarbons in waste water by off-line coupling of solid-phase microextraction with column liquid chromatography. *J. Chromatogr. A.* 897:153-159
- Srogi K (2007). Monitoring of environmental exposure to polycyclic aromatic hydrocarbons: A review. *Environ. Chem. Lett.* 5:169-195.
- Supelco (1998). Guide to solid phase extraction. USA. pp. 2-12.
- Shadung J. Moja and Fanyana Mtunzi(2013), Application of solid phase extraction (SPE) method in determining polycyclic aromatic hydrocarbons (PAHs) in river water samples, *J. of Environmental Chemistry and Ecotoxicology*, Vol. 5(11), pp. 278-283.
- TRC (Toxicological Research Center) (2007). Solid Phase Extraction Issues. September.