

A more cost-efficient extraction method for polycyclic aromatic hydrocarbons (PAH) in sediments and soils using accelerated solvent extraction (ASE)

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Keywords

Pressurized solvent extraction,
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Goal

To verify the suitability of a one-
step extraction method to improve
laboratory efficiency and reduce
costs as well as solvent consumption

Introduction

Accelerated solvent extraction (ASE) is an extraction method that is accepted by the U.S. Environmental Protection Agency (US EPA) for extracting solid matrices.¹ During the extraction procedure, solvent is pumped into heated extraction cells under high pressure for a prescribed period of time.² After extraction, solvent containing analytes are delivered to a collection vial for further cleanup, evaporation, or analysis. While the extraction process is fully automated, additional manual procedures typically using adsorption chromatography are needed to further clean up sample extracts. These methods are often time-consuming, labor-intensive, and use large volumes of solvents.

ASE is commonly used to extract polycyclic aromatic compounds (PAC) from solid matrices. PACs are a complex class of compounds, include polycyclic aromatic hydrocarbons (PAHs), alkylated polycyclic aromatic hydrocarbons (APAHs), halogenated polycyclic aromatic compounds (HPACs), and heterocyclic aromatic compounds that contain S, O, and N atoms.^{3,4} PAHs, the most common PACs, have been identified as priority compounds by the US EPA.⁴

The development of ASE extraction methods for PAHs can be traced back to the 1990s.² Recently, a one-step ASE method that negated the need for adsorption chromatography was reported by Kim et al. to extract PAHs from marine sediments.⁵ Inspired by the previous work, the Centre for Oil and Gas Research and Development (COGRAD), which is committed to advancing the analytical measurements of oil and gas related compounds in an ISO-17025 accredited laboratory, decided to further investigate the one-step ASE method for PAHs on two standard reference materials (SRMs). The overarching goal was to verify the suitability of the one-step method and its applicability to improve laboratory efficiency.

Experimental

Equipment used

- Thermo Scientific™ Dionex™ ASE™ 350 Accelerated Solvent Extractor, with 34 mL stainless steel extraction cells
- Gas chromatograph (GC) coupled with a triple quadrupole mass spectrometer (MS/MS)
- Thermo Scientific™ Dionex™ vials for collection of extracts (60 mL P/N 048744)

Solvent

Dichloromethane

ASE 350 conditions

Oven temperature:	125 °C
Pressure:	10 MPa (1500 psi)
Oven heat-up time:	6 min
Static time:	5 min
Flush volume:	60% of extraction cell volume
Nitrogen purge:	1 MPa (150 psi) for 80 s
Solvent:	Dichloromethane
Extraction cycles:	2

Sample information

All organic solvents used were Fisher Chemical™ Optima™ grade high-purity solvents. Fisher Scientific™ silica gel (923 grade, 100-200 mesh), alumina (60-325 mesh), Ottawa sand, copper, diatomaceous earth (DE) dispersant, and anhydrous sodium sulphate were used.

The suite of labeled recovery internal standard (RIS) used for isotope dilution of PAH: d₈-naphthalene, d₈-acenaphthylene, d₁₀-acenaphthene, d₁₀-fluorene, d₁₀-phenanthrene, d₁₀-pyrene, d₁₂-benz[a]anthracene, d₁₂-chrysene, d₁₂-benzo[b]fluoranthene, d₁₂-benzo[k]fluoranthene, d₁₂-benzo[a]pyrene, d₁₂-indeno[1,2,3-c,d]pyrene, d₁₄-dibenz[a,h]anthracene, and d₁₄-benzo[g,h,i]perylene were purchased from Cambridge Isotope Laboratories Inc. (Tewsbury, Massachusetts, USA). Mass labeled (d₁₀) anthracene was used as the instrument performance internal standard (IPIS) was purchased from Accustandard Inc (New Haven, Cincinnati, USA).

Standard Reference Material (SRM) 1944 New York and New Jersey waterway sediment was purchased from the National Institute of Standards and Technology (Gaithersburg, MD, USA). A mixture of PAHs in soil was obtained from the Canadian Association for Laboratory Accreditation (CALA, Ottawa, ON, Canada).

Procedure

CALA samples (n=6) and SRM 1944 (n=6) were extracted using the one-step method. For comparison, CALA samples were also extracted using the conventional method used at COGRAD.⁶ Details for preparing the ASE cell for the one-step extraction are as follows:

1. A Thermo Scientific™ glass fiber filter was placed in the bottom of the 34 mL ASE cell.
2. The following materials were added sequentially: 5% deactivated alumina (1.5 g), silica gel (11 g), 5% deactivated alumina (1.5 g), Ottawa sand (thin layer), reduced copper (thin layer), and 5% deactivated alumina (1.5 g).
3. Samples (0.5 g) mixed with 1.5 g DE dispersant were added to the top of the cell.
4. Ottawa sand was added to fill the dead volume of the cell to approximately 0.5 cm below the top of the cell.
5. The sample was then spiked with a RIS (100 ng).

The extraction cells were placed into the autosampler tray; the 60 mL collection vials were pre-cleaned, capped with septa, and loaded on the collection tray. To pre-clean, the collection vials were soaked in Contrad® overnight, rinsed with distilled water, and baked at

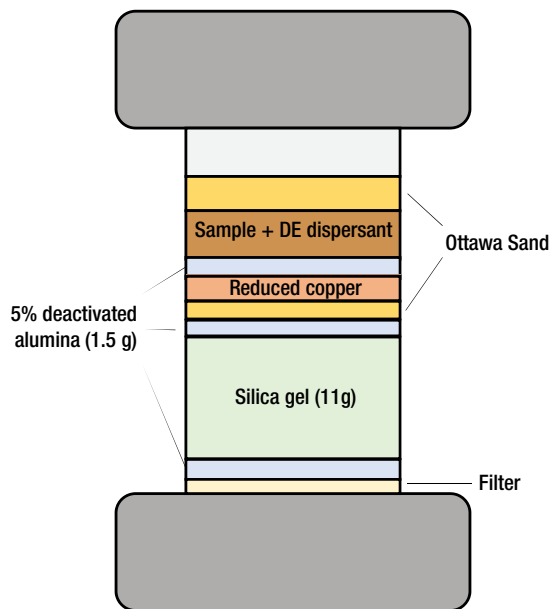


Figure 1. The assembly of the ASE cells for the one-step extraction method

350 °C for 12 h prior to use. The method conditions were set on the ASE 350 system and the run was initiated. A schematic of the ASE cell is shown in Figure 1. After extraction, the extract was treated with sodium sulphate to remove moisture, and subsequently reduced to 5 mL in a round bottom flask. IPIS was added to a concentration of 100 pg/μL in the sample. Extracts were injected directly on a GC-MS/MS using a procedure previously validated by our laboratory.⁶

Results and discussion

Results from the one-step extraction method for 16 priority PAHs in the CALA and SRM 1944 samples are shown below in Table 1. In most cases, recoveries are in the range of 70% to 120% and the precision values (expressed as % relative standard deviation) are less than 20%.

For comparison purposes, recoveries of PAHs using the one-step extraction method and the conventional method were compared in the CALA sample. As shown in Figure 2, results of recoveries for 16 PAHs are similar for the two methods; therefore, the one-step extraction is suitable and applicable for PAH extractions in sediments and soils.

Table 1. Average recovery (%) and precision (expressed as the RSD) of PAHs from SRM 1944 and CALA samples (n=6)

Compound	SRM 1944		CALA samples	
	Recovery	Precision	Recovery	Precision
Acenaphthene	n/a	12.1	71.6	15.7
Acenaphthylene	n/a	16.9	69.8	8.1
Anthracene	64.3	5.2	90.1	18.5
Benz[a]anthracene	66.8	6.0	76.1	14.2
Benzo[a]pyrene	65.9	9.0	85.5	19.1
Benzo[b]fluoranthene	76.8	6.0	78.7	13.3
Benzo[g,h,i]perylene	85.3	6.8	95.5	17.0
Benzo[k]fluoranthene	86.1	9.8	88.4	14.3
Chrysene	101.3	6.0	88.9	14.6
Dibenzo[a,h]anthracene	148.2	5.7	80.2	15.7
Fluoranthene	81.0	6.0	77.5	17.1
Fluorene	n/a	12.5	57.1	17.3
Indeno[1,2,3-c,d]pyrene	68.5	5.0	82.8	14.7
Naphthalene	53.3	12.2	123.2	7.9
Phenanthrene	87.0	7.6	80.6	15.3
Pyrene	67.9	5.9	71.2	18.4

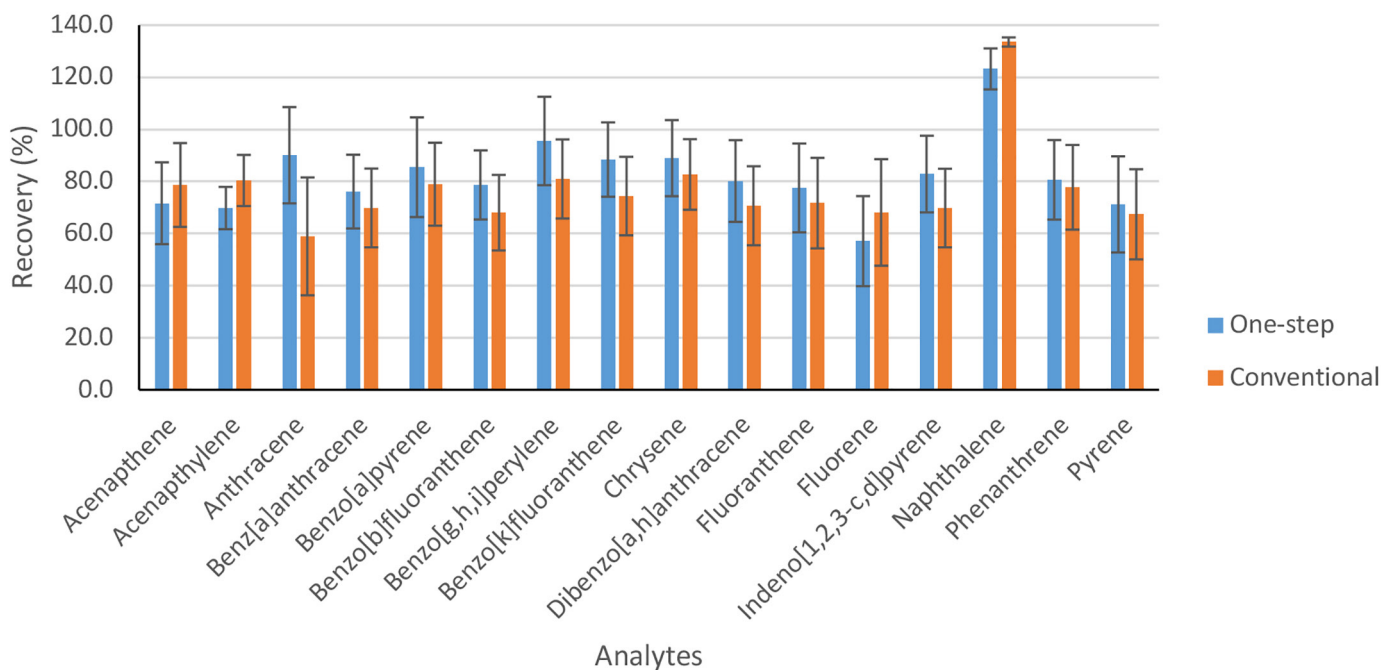


Figure 2. Comparison of recoveries of PAHs by using conventional (n=6) and one-step method (n=6) in the CALA sample. The bars shown are the mean \pm SD.

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