DEVELOPMENT OF AN *IN-SITU* PRESSURISED FLUID EXTRACTION METHOD FOR THE EXTRACTION OF PAHs PRIOR TO GC-MS ANALYSIS

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1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are derived from a number of sources including anthropogenic (i.e. industrial processes and combustion of fossil fuels) or natural (i.e. forest fires, volcanic activity and geological sources). The 16 PAH priority pollutants are known for their carcinogenic effect and mutagenic characteristics. Previous studies describe pressurised fluid extraction (PFE) as an effective way to extract components from soils, compared to other extraction methods, such as microwave, ultrasonic and Soxhlet extraction.[1] In this study column chromatography has been evaluated for soil clean-up following PFE. The influence of two different absorbents (florisil and alumina) on extract clean-up have been investigated with respect to PAH recovery. This approach has been compared with an *in-situ* PFE procedure.[2] The aim of this work is to establish a robust and effective procedure for the recovery of PAHs from contaminated soil prior to analysis by gas chromatography - mass spectrometry (GC-MS).

2. Materials and Methods

Chemicals

A PAH standard solution was obtained from Thames Restek U.K Ltd., Buckinghamshire, UK (2000 µg/ml in dichloromethane). A five point calibration curve was used for quantitation on the GC-MS using 4,4 difluorobiphenyl (2 µg/ml) as an internal standard.

Instrumentation

Extraction was performed with pressurized fluid extraction (PFE) on an ASE200 (Dionex UK Ltd., Camberley, Surrey). The operating conditions were organic solvent: dichloromethane : acetone (50:50, v/v); pressure: 2000 psi; temperature: 100 °C; and, extraction time: 10 minutes. The GC-MS instrument included a Trace GC Ultra coupled with a Polaris Q Ion trap MS (Thermo Scientific, UK) and a Triplus auto sampler injector. The system was controlled from a PC with Xcalibur software. Separation was performed using a capillary column Rtx®-5MS (5% diphenyl-95% dimethylpolysiloxane, 30 m x 0.25 mm ID x 0.25 µm) supplied from Thames Restek UK Ltd. The temperature programme was: start at 70 º C for 2 min and then 7 º C/min until 180 º C, then 3º C/min until 280 ºC, then hold for 3 min. The transfer line temperature was fixed at 300 ºC.

Methods

Column clean-up: A column (200 mm x 18 mm) was prepared with either 10 g of Alumina (Sigma Aldrich, 150 mesh) or Florisil (Fluka, 60-100 mesh) as absorbent with an additional 11 g of anhydrous Na_2SO_4 placed on top. Then the column was eluted with 50 ml of hexane. The eluate was discarded and just prior to exposure of the Na_2SO_4 to the air 2 ml hexane containing the PAH standard was added (50 µl of a 2000 µg/ml standard). Again just prior to exposure to the air 2 x 15 ml of hexane was added and again the eluate was discarded. Finally, the column was eluted with approximately 30 ml of dichloromethane in to a flask and then the solvent was retained. Then 60 µl of the internal standard (2 µg/ml) was added to give a final volume of 30 ml.

PFE and off-line clean-up: The soil sample (1.3 g) was mixed with a similar quantity of high purity diatomaceous earth (Hydromatix, Varian, Inc., Harbor City, CA, USA) and added in to the cell on top of a filter paper. Additional hydromatrix was added to fill the cell and a final filter paper was placed on top prior to cell closure. After PFE, the solvent (DCM : acetone) was evaporated under a gentle stream of nitrogen gas to dryness and reconstituted with 2 ml of hexane. Then, the extract was treated as per column clean-up (described above), prior to GC-MS.

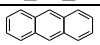
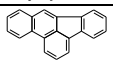
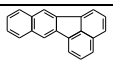
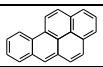
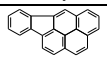
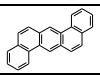
PFE and in-situ clean-up: Florisil or Alumina (0.5 g, 1 g, 2 g and 4 g) were added in to the extraction cell. Then, the soil and hydromatrix were added according to the procedure described above (PFE and off-line clean-up). After in-situ PFE, the solvent (DCM : acetone) was evaporated under a gentle stream of nitrogen gas to dryness and reconstituted with 2 ml of DCM containing the internal standard, prior to GC-MS.

Soil slurry spiking: A known quantity of soil (1.3 g) was placed inside a beaker. Then, 10 ml of dichloromethane containing 50 µl of the PAH standard solution was added to the soil. The sample was then left exposed, in a fume cupboard, for 5 days prior to PFE.

3. Results and Discussion

Calibration of GC-MS: Information for the calibration of the GC-MS for the analysis of the 16 PAHs is shown in Table 1.

Table 1: Information for GC-MS calibration of PAHs based on a 5 point calibration graph (0.5 - 10 µg/ml)

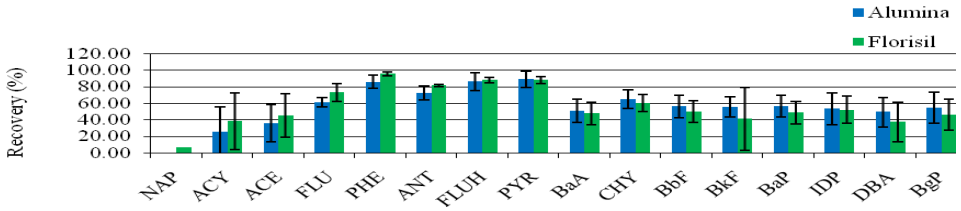
PAH structure	PAHs	PAH abbreviation	MS ion for quantitation	y = mx + c	Correlation coefficient, R^2
	*Naphthalene*	NAP	128	4.1399 X + 0.7205	0.9986
	*Acenaphthylene*	ACY	152	4.1139 X + 0.0279	0.9999
	*Acenaphthene*	ACE	154	2.3134 X + 0.1547	0.9993
	*Fluorene*	FLU	166	2.9124 X + 0.037	0.9998
	*Phenanthrene*	PHE	178	4.5264 X + 0.0952	0.9995
	*Anthracene*	ANT	178	4.2730 X - 0.2848	0.9999
	*Fluoranthene*	FLUH	202	4.5104 X - 0.8234	0.9996
	*Pyrene*	PYR	202	4.8043 X - 0.7057	0.9998
	*Benzo(a)anthracene*	BaA	228	2.9000 X - 0.9132	0.9974
	*Chrysene*	CHY	228	4.4652 X - 1.6144	0.9969
	*Benzo(b)fluoranthene*	BbF	252	2.7100 X - 0.8907	0.9972
	*Benzo(k)fluoranthene*	BkF	252	3.6894 X - 1.4761	0.9954
	*Benzo(a)pyrene*	BaP	252	2.6269 X -0.9960	0.9955
	*Indeno(1,2,3-cd)pyrene*	IDP	276	4.0229 X - 1.7347	0.9977
	*Dibenzo(a,h)anthracene*	DBA	278	4.7652 X - 2.3214	0.9970
	*Benzo(g,h,i)perylene*	BgP	276	5.6479 X - 2.7142	0.9973

PFE with off-line clean-up:

PFE followed by off-line clean-up with both absorbents gave average recoveries for mid-molecular weight PAHs (fluorene to pyrene) of approximately 80 % whereas for the heavier molecular weight PAHs i.e. benzo(a) anthracene to benzo(ghi)perylene the average recoveries were typically 50%. For the lightest i.e. small molecular weight PAHs, recoveries of <5% for naphthalene, <30% for acenaphthylene and <40% for acenaphthene were

obtained (Figure 1). Typical RSDs for the recovery of PAHs, using alumina and florisil, ranged from 11.1 to 61.4 % and 3.3 to 68.9 %, respectively.

Figure 1: Recovery of PAHs after PFE with off-line clean-up (mean +/- sd, n = 3)



PFE with in-situ clean-up:

Soil samples were spiked directly in to the PFE cell to assess the impact on PAH recovery using *in-situ* cleanup with either alumina or florisil. It can be seen in Figure 2 that good recoveries (~90%) were obtained for all PAHs when no further sample concentration takes place (no solvent evaporation post-extraction). Typical RSDs for the recovery of PAHs, using alumina and florisil, ranged from 4.0 to 10.5 % and 1.1 to 22.4 %, respectively. No specific influence is noted in terms of the use of florisil and alumina on recovery of PAHs. This is not the case in Figure 3 in which post-extraction evaporation under a stream of N_2 results in significant losses of naphthalene (>80%), and to a smaller extent for acenaphthylene and acenaphthene. Appropriate recoveries are noted for alumina for the other PAHs whereas elevated recoveries are noted for the mid-range PAHs when using florisil as the *in-situ* adsorbent. Typical RSDs for the recovery of PAHs, using alumina and florisil, ranged from 2.7 to 25.7 % and 3.8 to 22.2 %, respectively. The influence of the quantity (0.5 g, 1 g, 2 g and 4 g) of adsorbent on PAH recovery was evaluated using *in-situ* PFE. It was noted that the recovery of PAH was independent of adsorbent quantity. However the best recoveries were obtained using alumina.

Figure 2: Recovery of PAHs after PFE with *in-situ* clean-up without evaporation (mean +/- sd, n = 3)

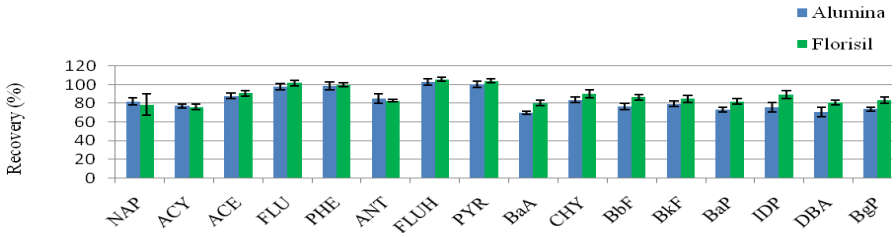
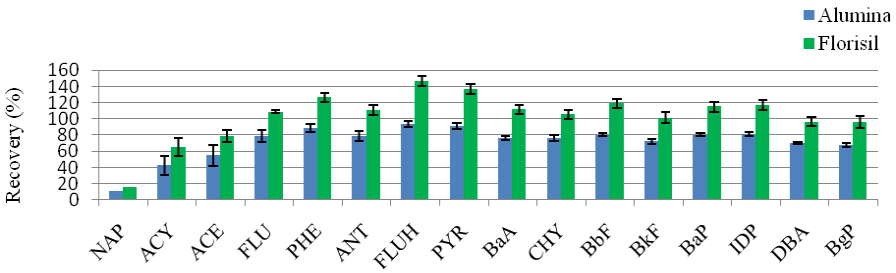
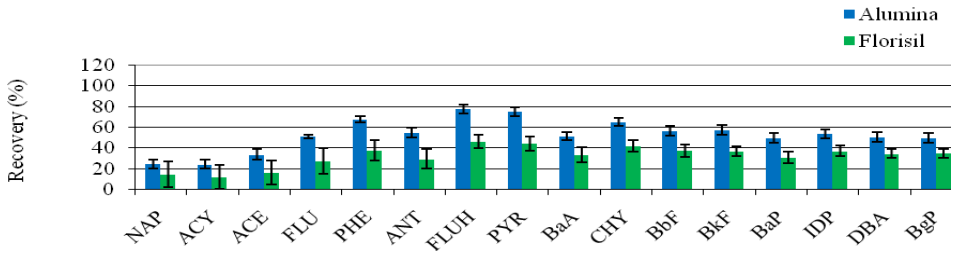


Figure 3: Recovery of PAHs after PFE with *in-situ* clean-up with evaporation (mean +/- sd, n = 3)



The process was repeated using PAH slurry spiked soil. It is shown in Figure 4 that the overall recovery of PAHs was significantly reduced (~50%) using this soil spiking approach. While higher recoveries are noted for alumina the major losses are most likely due to evaporation of the PAHs during the 5 day equilibration period. Typical RSDs for the recovery of PAHs, using alumina and florisil, ranged from 3.7 to 10.3 % and 8.7 to 24.8 %, respectively.

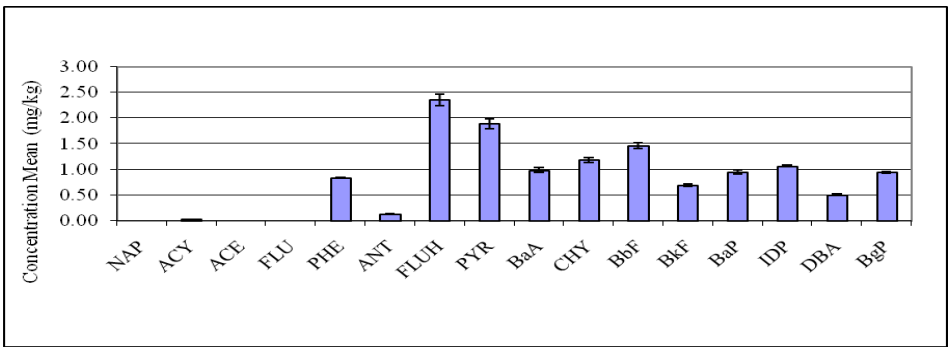
Figure 4: Recovery of PAHs from a slurry spiked soil after PFE with *in-situ* cleanup (mean +/- sd, n = 3)



Application to a contaminated soil:

The use of PFE with *in-situ* clean-up was applied to a contaminated soil sample obtained from a local site. The results are shown in Figure 5. The major PAH concentration was 2.4 ± 0.11 mg/kg for fluoranthene, with smaller quantities of pyrene (1.9 ± 0.10 mg/kg), benzo(b)fluoranthene (1.5 ± 0.05 mg/kg) and chrysene (1.2 ± 0.05 mg/kg). The absence of low molecular weight PAHs is not surprising from a contaminated land site. Future work will utilise the *in-situ* PFE approach for the extraction of PAHs from a range of soil samples collected from both anthropogenic and natural sources.

Figure 5: Determination of PAHs from a contaminated land soil after PFE with *in-situ* cleanup using Alumina (mean +/- sd, n = 3)



Acknowledgements

Northumbria University in collaboration with British Geological Survey, Keyworth is acknowledged for the award of a studentship to one of us (DL).

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2. Canosa P., Perez-Palacios D., Garrido-Lopez A., Tena M.T., Rodriguez I., Rubi E., Cela R., *Journal of Chromatography A*, 2007; 105-112: 1161.