

Evaluation of an Improved Sample Preparation Method for Quantitative Analysis of Very Low Levels of Airborne Polycyclic Aromatic Hydrocarbons for Worker Protection and Health Screening

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Introduction

Polycyclic Aromatic Hydrocarbons (PAHs) are large class of compounds comprising two or more fused aromatic rings. PAHs are naturally occurring in fossil fuels and their derived products and can be formed during incomplete combustion of carbon based fuels. As such they are a by-product of many industrial processes. PAHs vary greatly in size, nature and hazard to human health, some are not classified as toxic, where as others are known carcinogens. The IARC specified 16 as being of particular interest, others have subsequently added this list. In all, over 100 PAHs have been described.

Given the risks and potential risks to human health presented by PAHs, many high risk organisations, such as Foundries, Bitumen Works & Smoke Houses routinely monitor workers and their environment for PAH levels. Typically PAHs are trapped using filters (particulate forms) or resins such as XAD2 (gaseous forms) through which work place environmental air is drawn. Filters may be situated in a small device attached to the workers overalls, or from larger units measuring the air in a wider area. Potential problems exist when recovering the PAHs from the filters and preparing the samples for analysis, principally, losses due to PAH volatility are reported for bi- and tri-cyclic PAHs (ISO11338-2:2003). Therefore, ITGA undertook a study to improve sample recovery and therefore PAH determination when working with low and very low levels of analytes.

Sample Preparation Methodology

Methods for workplace sampling are well described in the literature (NFX43-294 and Method Metropol 011) and result in samples trapped on glass or quartz fibre filters. The filters are preserved and delivered to the analytical laboratory. The whole filter placed into a barcoded vial, 10ml dichloromethane (DCM) is added and the tube placed in an ultrasonic bath at room temperature for 15 minutes to extract the analytes. This operation is repeated once with 10ml of DCM to optimise extraction. Following extraction the sample is concentrated to 1ml using a nitrogen blowing system and then analysed via HPLC coupled to a Fluorescence detector. XAD2 resin tubes may be used as an alternative to fibre filters.

Evaluation of new Sample Preparation Methodology

A standard solution containing the US-EPA 16 PAHs (as defined by IARC, 1987) was spiked onto quartz fibre filters or XAD2 resin tubes and allowed to air dry. The filters / tubes were then extracted twice using 7ml DCM and sonication in the ultrasonic bath for 15 minutes at room temperature. The combined sample (14ml) had a 100µl aliquot removed. This was made up to 1ml with acetonitrile was taken and injected into HPLC-Fluorescence to provide a 100% reference. The remaining DCM had 100µl 2-pentanol added as a solvent keep and was evaporated via centrifugal vacuum evaporation in the Genevac EZ-2 Envi (Figure 1). Temperature and pressure during evaporation were controlled such that the DCM evaporates but the 2-pentanol does not, as previously described by Marsico (2006) and Massat *et al.* (2007).



Figure 1 – Genevac EZ-2 Envi

The samples were then made up to 1ml using acetonitrile and injected into HPLC-Fluorescence for analysis. Recoveries for all analytes, even the most volatile were in excess of 90% and the fit of the analytical curve to the reference sample was very good, and shown in figure 2 below.

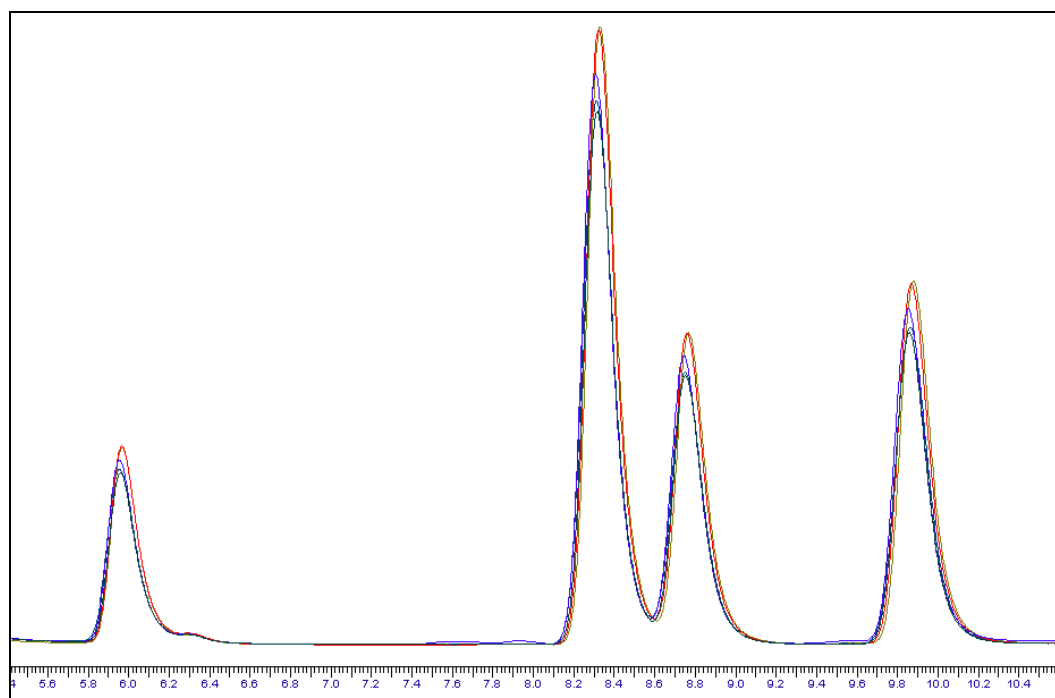


Figure 2 – HPLC-Fluorescence Chromatogram Overlay of Reference Sample to Post Concentration Sample

Red - the reference point. **Blue** - other chromatograms refer to the PAH compounds Naphthalene, Acenaphthene, Fluorene, Phenanthrene

Validation of the Process

Having delivered similar results to the existing method, and being beneficial in the sense of “automation” of the concentration process, statistical validation of the process and equipment was required. Using the above methodology, a solution containing 14 PAH samples was spiked onto quartz fibre filters and also on to XAD2 resin tubes. Filters were spiked at 100ng and 10ng. These were allowed to dry and extracted, concentrated and analysed. The process was repeated on six distinct occasions using new samples and solutions on each occasion. The results are presented in Figure 3.

Sample	100ng on Quartz Filters			100ng on XAD2 Resin Tubes		
	Mass (ng)	SD	Recovery	Mass (ng)	SD	Recovery
Naphthalene	99.8	2.5%	99.8%	99.5	1.2%	99.5%
Acenaphthene	99.6	2.1%	99.6%	98.6	0.7%	98.6%
Fluorene	100.1	1.9%	100%	100.0	0.9%	100%
Phenanthrene	99.8	2.1%	99.8%	99.1	0.9%	99.1%
Anthracene	99.0	2.0%	99.0%	98.3	1.0%	98.3%
Fluoranthene	99.8	2.1%	99.8%	98.9	0.9%	98.9%
Pyrene	99.2	2.0%	99.2%	98.3	0.8%	98.3%
Benzo [a] anthracene	99.6	2.2%	99.6%	98.6	0.6%	98.6%
Chrysene	100.6	2.2%	101%	99.5	0.5%	99.5%
Benzo [b] fluoranthene	99.9	2.1%	99.9%	98.1	1.0%	98.1%
Benzo [k] fluoranthene	99.2	0.9%	99.2%	99.2	0.4%	99.2%
Benzo [a] pyrene	100.3	1.1%	100%	97.0	1.0%	97.0%
Dibenzo [a,h] anthracene	99.4	2.7%	99.4%	97.0	1.3%	97.0%
Benzo [g,h,i] perylene	98.1	2.5%	98.1%	95.8	1.0%	95.8%

Sample	10ng on Quartz Filters			10ng on XAD2 Resin Tubes		
	Mass (ng)	SD	Recovery	Mass (ng)	SD	Recovery
Naphthalene	10.0	2.0%	100.4%	50.1	2.4%	100%
Acenaphthene	9.72	1.3%	97.2%	48.4	0.7%	96.9%
Fluorene	9.50	1.9%	95.0%	9.54	1.3%	95.4%
Phenanthrene	9.63	0.6%	96.3%	9.72	1.2%	97.2%
Anthracene	9.65	1.4%	96.5%	9.62	1.5%	96.2%
Fluoranthene	9.13	0.9%	91.3%	9.32	1.7%	93.2%
Pyrene	10.1	1.7%	101.2%	10.1	1.6%	101%
Benzo [a] anthracene	9.79	3.2%	97.9%	9.88	5.4%	98.8%
Chrysene	9.71	1.7%	97.1%	9.67	3.0%	96.7%
Benzo [b] fluoranthene	9.67	1.9%	96.7%	9.70	2.2%	97.0%
Benzo [k] fluoranthene	9.54	1.0%	95.4%	9.53	1.0%	95.3%
Benzo [a] pyrene	9.14	3.5%	91.4%	9.33	5.0%	93.3%
Dibenzo [a,h] anthracene	9.61	2.2%	96.1%	9.39	2.5%	93.9%
Benzo [g,h,i] perylene	9.87	3.3%	98.7%	9.68	2.1%	96.8%

Figure 3 – Data from Validation Studies

Mass Recovered (ng) and Recovery % are averages from each of the 6 repetitions performed. SD is the standard deviation across repetitions.

The results generally show excellent recovery and good standard deviation figures. Due to a contamination from XAD2 resin, for two compounds (naphthalene and acenaphthene) limits of quantification have been validated at 50ng instead of 10ng.

Conclusions

The new method of sample preparation was found to be superior to the existing methods. Recoveries are seemingly a little lower for the 10ng studies because this approaches the limit of detection of the analytical method. Following successful validation and external audit by COFRAC (Comité français d'accréditation) the new method and systems have been adopted into routine daily use.

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