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Determination of selected polycyclic aromatic compounds in particulate matter: a validation study of an agitation extraction method for samples with low mass loadings using reduced volumes

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Abstract

A simple analytical method using low volumes of solvent for determining selected PAHs and NPAHs in PM samples is presented. The proposed extraction method was compared with pressurized fluid (PFE) and microwave (MC) extraction techniques and intermediate precision associated to analytical measurements were estimated. Extraction by agitation with 8 mL of dichloromethane yielded recoveries above 80% compared to those obtained from PFE extraction. Regarding intermediate precision results, values between 10-20% were reached showing increases of dispersion for compounds with high volatility and low levels of concentration. Within the framework of the INTA/CIEMAT research agreement for the PM characterization in gas turbine exhaust, the method was applied for analysis of aluminum foil substrates and quartz filters with mass loading ranged from 0.02 to 2 mg per sample.

1. Introduction

The analysis of polycyclic aromatic compounds (PACs) usually involves High Performance Liquid Chromatography with fluorescence detector (HPLC/FD) which is well known because of its good selectivity and high sensitivity [1]. Regarding classical sample-preparation techniques, soxhlet (SX), microwave solvent (MC), pressurized fluid extraction (PFE) and ultrasonic extractions (US) are mostly used. However, important disadvantages associated includes time-consuming/large amount of solvent for SX, expensive for PFE and MC, and lower extraction efficiency for US. Current trends in analytical chemistry have focused to simplify sample preparation and minimize solvent volume, so efforts are directing towards miniaturization of extraction procedures by reducing the amount of sample mass and volume of organic solvent.

Because of this, it is very important to develop analytical protocols which assesse quality of results. Additionally, the validity of results has to be demonstrated. Regarding method validation, the best option would be to participate in inter-comparison exercises for the compounds in the selected matrix to determine the accuracy and precision of methodology. When it is not possible, the use of multiple



methods could be recommended as a validation to obtain comparable data, because of the advantages and disadvantages of different analytical methods give additional credence to the results.

This work presents the results obtained for validation of a simple sample treatment procedure to analyze selected PACs by agitation extraction using reduced volumes of solvent. The main focus was the analysis of PACs in particulate matter with low mass loading, such as impactor substrates used to determine the nano and submicron size distribution.

2. Experimental

2.1. Sample collection

The sampling site was the National Institute for Aerospace Technology (INTA), situated to 20 km Northeast of Madrid city. The site is an open urban area with direct influence from airport sources. A high volume MCV CAV-Amb sampler loaded with Whatman glass fibre filters (102 mm diameter) was used for the sampling of the particulate matter (PM₁₀). Ambient air samples were taken during 24 – 48 hours (30 m³ h⁻¹) for consecutive days of November and June (2014). The Samples then were divided into four sub-samples which were weighted and then considered as independent sub-samples for analysis.

2.2. Sample preparation and chromatographic analysis

- Microwave Solvent Extraction (MC): PM sub-samples were extracted using an Ethos Sel (Milestone) at 900 W (120°C) and dichloromethane as solvent (15 mL).
- Pressurised Fluid Extraction (PFE): PM sub-samples were extracted using an ASE350 (Dionex Corporation) and dichloromethane (100 °C, 10.34 psi and 1 static cycles). The total volume of extract corresponded to 55 mL.
- Sonication/agitation (AGITATION): PM sub-samples were extracted in closed tubes containing dichloromethane (8 mL), sonicated (15 min) and shaken for short-time. Re-extraction was done to assure recovery and the combined extracts were then treated as follows.

The extracts were then filtered (0.22 µm pore size PTFE) and slowly concentrated under nitrogen flow to change solvent (methanol, 150-200 µL) for HPLC/FLD analysis.

Once selected PAHs were determined, derivatisation reaction of extracts was performed for NPAH determination [2]. 0.5 mL aqueous solution of CuCl₂ (0.05%) and 0.05 g of NaBH₄ were added to methanol extract. 1 mL of dichloromethane was added and then shaken for extraction of amino-PAHs. Extract was concentrated under nitrogen flow to change solvent (acetonitrile, 100 µL).

3. Results

3.1. Comparison of results among microwave, pressurized extraction and agitation extraction

The detection limit was considered as twice the standard deviation on average of replicate analyses of 3 standard solutions (1 ng mL⁻¹). Experimental values varied between 0.002-0.003 and 0.15 ng injection⁻¹ for investigated PAHs and NPAHs, respectively. More volatile PAHs, such as methyl naphthalene, acenaphthene and fluorene also corresponded to 0.15 ng injection⁻¹ as detection limits. Five ambient air samples (about 40 mg of mass aerosol loading/filter) were divided as 4 parallel sub-samples. The first sub-sample was extracted by MC, the second one by PFE and the third by AGITATION, using dichloromethane as extraction solvent. The comparison was performed by grouping results corresponding to extraction technique and deducing mean and standard deviation for normalised values (figure 1). Results were similar among extraction methods, reaching recoveries above 80% for AGITATION if compared with those of PFE extraction.

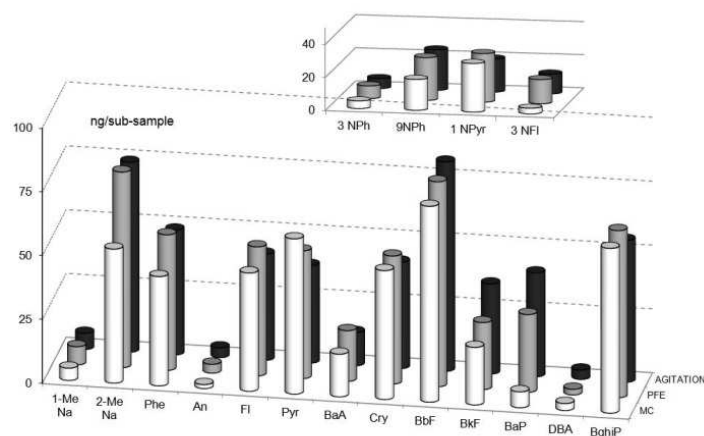


Figure 1. Mean values ($\text{ng sub-sample}^{-1}$) of selected PACs measured using microwave (MC), pressurised fluid (PFE) and sonication/agitation (AGITATION).

Methyl-naphthalene (Me-Na), phenanthrene (Ph), anthracene (An), fluoranthene (Fl), pyrene (Pyr), benz[a]anthracene (BaA), chrysene (Cry), benz[b]fluoranthene (BbF), benz[k]fluoranthene (BkF), benz[a]pyrene (BaP), dibenz(a,h)anthracene (DBA) and benzo[g,h,i]perylene BghiP

3.2. Estimation of the intermediate precision associated to results from real sample analyses

- MC: Four samples were divided into four sub-samples and analysed by pairs to compare microwave and agitation procedures. Sub-sample mass loading was 5 - 8 mg of collected particulate matter.
- PFE: Analogously, three ambient air filters were divided and analysed by pairs to compare PFE/AGITATION. Sub-sample mass loading was 0.7 - 2.8 mg of collected particulate matter.

Once all data obtained, intermediate precision estimations of measurements was performed based on pooled precision (RSD_{pool})

The term corresponds to the intermediate precision of the method and has been considered as the standard deviation values deduced from duplicate analysis of each air sample using both techniques. In particular, we have considered the relative standard deviations (RSD) of the results of each ambient air sample in duplicate (RSD_{fv_n}), grouping and deducing the value of pooled relative standard deviation (RSD_{pool}). For comparison between the two techniques of extraction, the calculation was separately carried out in both cases using the following equation [3]:

$$\text{RSD}_{\text{pool}} = \sqrt{\frac{\sum \text{RSD}_{\text{fv}_n}^2 (n_{\text{fv}_n} - 1)}{\sum (n_{\text{fv}_n} - 1)}}$$

From the results of agitation procedure, as can be seen, the RSD associated to PAH analysis was generally below 10 % for concentration levels above $10 \text{ ng sub-sample}^{-1}$ (for mass loading of sample: 5-8 mg). Higher variability was associated (10-15%) when concentration levels were between 1 and 5 $\text{ng sub-sample}^{-1}$ (for mass loading of sample: 0.7-2.8 mg).

Table 1. Values of intermediate precision deduced from results by analysing samples using MC and agitation (mass loading of sample 5-8 mg) and those for PFE and agitation procedures (mass loading of sample 0.7-2.8 mg). Estimations were based on pooled standard deviations (RSD pool).

	mass loading of sample: 5-8 mg		mass loading of sample : 0.7-2.8 mg	
	MC	AGITATION	PFE	AGITATION
1-Me Na	0.45	0.27		
2-Me Na	0.48	0.23		
Ace	0.15	0.20		
F	0.12	0.15		
Phe	0.19	0.14	0.36	0.28
An	0.20	0.15		
Fl	0.07	0.06	0.15	0.10
Pyr	0.07	0.14	0.12	0.08
BaA	0.08	0.06	0.15	0.10
Cry	0.09	0.07	0.18	0.15
BbF	0.06	0.06	0.16	0.12
BkF	0.06	0.06	0.16	0.11
BaP	0.21	0.07	0.11	0.09
BghiP	0.08	0.07	0.17	0.11
3 NPh	0.29	0.26	0.27	0.43
9 NPh	0.17	0.11	0.20	0.36
1 NPyr	0.12	0.27	0.16	
3NFl	0.29	0.22		

For microwave results, an important reduction in the recovery and increases of variability (up to 50 %) were found for methyl naphthalene, the most volatile. These observations likely correspond to losses due to the heat applied and the more volatile nature of these compounds.

For NPAHs, intermediate deviation values were higher, around 20 %, which is justified by the increase of experimental variability associated with additional derivatization step for chromatographic analysis. Calculations could be performed when concentration levels were well measured (mass loading 5-8 mg), but in the case of low concentrations (mass loading 0.7-2.8 mg) no enough data were obtained for 3NFl (PFE and agitation) and 1 NPyr (agitation). PFE shows a slightly lower variability of the results regarding the agitation extraction.

3.3. Analytical application

Several aerosol samples were taken on quartz and aluminium substrates (by means of a Low Pressure Impactor and a holder filter) during the preliminary studies on characterization from the turbofan engine exhaust [4]. Mass loadings greater than 2 mg per sample were collected on quartz filters and exceeding to 20 µg per sample on aluminium foil substrates.

In total, 16 sampling substrates were analysed and maximum/mean concentration values were below 10 ng substrate⁻¹ as it is compiled in table 5. No selected NPAHs were detected in this kind of samples.

Table 2. Concentration range (ng substrate⁻¹) measured from quartz and aluminum substrates.

ng substract ⁻¹	mass loading> 2mg	mass loading> 20µg
	quartz	aluminum
1-Me Na	<0.4-2.3	<0.4-9.6
2-Me Na	<1.0-5.2	<1.0-39
Ace	<0.4-1.7	<0.4-0.6
F	<0.2-2.3	<0.2-1.3
Phe	<0.7-16	<0.7-9.5
An	<0.03-1.2	<0.03-0.3
Fl	<0.01-11	<0.01-1
Pyr	<0.01-18	<0.01-1.8
BaA	<0.01-5.5	<0.01-0.04
Cry	<0.05-11	<0.05
BbF	<0.01-6.4	<0.01-0.2
BkF	<0.004-9.2	<0.004-0.1
BaP	<0.01-9.2	<0.01-0.3
DBA	<0.01-2	<0.01
BghiP	<0.02-5.8	<0.02-2.2

4. Conclusions

It has been developed an analytical method for the determination of certain PACs in PM samples collected on filters by sonication/agitation and subsequent analysis by HPLC/FD. The method is simple and requires the use of low volumes of solvent for extraction.

Due to the lack of availability of reference materials at these low mass loadings, we chose to analyse real PM samples divided into four aliquots which were tested by agitation, microwave and pressurized fluid extractions for comparison. An estimation of the variability of results has been also conducted for intermediate precision calculations. Finally, the effectiveness of the proposed method was evaluated by analysing aerosol samples collected on quartz and aluminum substrates in extremely low concentration range, such as impactor substrates used to determine the nano and submicron size distribution.

5. References

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