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Proposal of a procedure for the analysis of atmospheric polycyclic aromatic hydrocarbons in mosses

Estefanía Concha-Graña, María Piñeiro-Iglesias, Soledad Muniategui-Lorenzo*, Purificación López-Mahía, Darío Prada-Rodríguez

Grupo Química Analítica Aplicada (QANAP), Instituto Universitario de Medio Ambiente (IUMA), Departamento de Química Analítica, Facultade de Ciencias, Universidade da Coruña, Campus de A Coruña, 15071 A Coruña, Spain

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ABSTRACT

A useful analytical procedure for the analysis of 19 polycyclic aromatic hydrocarbons (PAHs) in moss samples using microwave assisted extraction and programmed temperature vaporization-gas chromatography-tandem mass spectrometry (PTV-GC–MS/MS) determination is proposed. The state of art in PAHs analysis in mosses was reviewed. All the steps of the analysis were optimized regarding not only to the analytical parameters, but also the cost, the total time of analysis and the labour. The method was validated for one moss species used as moss monitor in ambient air, obtaining high recoveries (between 83–108%), low quantitation limits (lower than 2 ng g^{-1}), good intermediate precision (relative standard deviation lower than 10%), uncertainties lower than 20%. Finally, the method was checked for other species, demonstrating its suitability for the analysis of different moss species. For this reason the proposed method can be helpful in air biomonitoring studies.

1. Introduction

Monitoring of polycyclic aromatic hydrocarbons (PAHs) in ambient air is of great interest due to the implications on human health of the presence of those compounds in the atmosphere. The specialized cancer agency of the World Health Organization, the International Agency for Research on Cancer (IARC), classified outdoor air pollution as carcinogenic to humans (Group 1) [1]. PAHs levels can vary considerably in space, and thus it is of great interest the use of sampling tools that are able to assess spatial deposition of PAHs at a local scale. The use of moss as passive accumulators for organic compounds has gained popularity in the last decades because of their usefulness for the large scale monitoring [2]. Directive 2004/107/EC allows the use of alternative sampling methods which it can demonstrate give results equivalent to the reference method to assess spatial deposition of PAHs [3]. The morphological and physiological characteristics of mosses make them excellent tools for biomonitoring [4,5]. The growing interest by using moss as monitors for PAHs sampling makes necessary the development of efficient analytical procedures for the analysis of this kind of samples.

A review of the state of the art in the analysis of PAH in moss can be seen in Table 1. The most common technique for the determination of the PAHs is gas chromatography coupled to mass spectrometry. The most common technique used in the extraction of PAHs from mosses is the Soxhlet extraction. However, it demands large volumes of highly purified organic solvents and long extraction times are need. For these reasons it is interesting the use of alternative techniques that allow a more efficient extraction of the analytes from the matrix by improving the contact of the target compounds with the extraction solvent. By this way a reduction of both the extraction time and the organic solvent consumption is achieved, and also an increase in sample throughput.

In the last years other authors have introduced accelerated solvent extraction (ASE) [4,6–9] or dynamic sonication-assisted solvent extraction (DSASE) [10] as alternative extraction procedures for the analysis of PAHs in moss. Microwave assisted extraction (MAE) has been widely used for the analysis of inorganic elements in moss, but, as far as we know, not for organic compounds.

MAE is more efficient and faster than the traditional liquid-solid procedures, allows the simultaneous extraction of several samples (between 6–12) and is less expensive than ASE. Moreover, the volume of solvent used is about 10 times lower than the required in Soxhlet extraction and also below the required in sonication [11]. The use of MAE for PAHs analysis is very frequent in matrices such as air particulate [12–18], soils [19–21] and sediments [22–26]. Few papers

* Corresponding author. Tel.: +34 981 167000; fax: +34 981167065.
E-mail address: smuniat@udc.es (S. Muniategui-Lorenzo).

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Table 1
Review of the state of art in PAH analysis in moss. ACN:acetonitrile, ASE: accelerated solvent extraction, NM: not mentioned.

Compounds	Sample	Extraction	Cean-up	Determ.	Recovery	Sensitivity	Uncertainty/RSD	Ref.
16 PAHs EPA	*Fontinalis antipyretica*	Soxhlet 200 ml ACN24h.	Florisil . Elution 30 ml CAN	HPLC-FLD	60–107%	NM	RSD:20–24%	[35]
13 PAHs	*Dicranum scoparium* *Hypnum cupressiforme* *Thamnobryum alopecurum* *Thuidium tamariscinum*	Soxtec (moss+sodium sulphate+Florisil)	Florisil cartridges 1 g	HPLC-FLD	25–79%	LOQ 3–52 pg instrumental	RSD < 20%	[34]
16 PAHs	*Hylocomium splendens* *Pleurozium scheberi*	ASE, DCM	–	GC–MS	74–96%	LOQ 1-5 ng g^{-1}	U: 10–25%	[6]
17 PAHs	*Hylocomium splendens* *Pleurozium scheberi*	Soxhlet, DCM.	–	GC–MS	74–96%	NM	U: 10–25%	[48]
16 PAHs	*Hypnum cupressiforme*	Sonication 5 g +100 ml H:A (1:1), twice	Silica column	HPLC	65–85%	NM	RSD: 10–15 %	[40]
13 PAHs	*Hypnum cupressiforme* *Isothecium myosuroides*	ASE, H 80 °C, 5 min, 2 cycles	Florisil cartridge 1 g, 8 ml H/DCM (60:40)	HPLC	68–70%	3–52 pg instrumental	RSD: 1–22%	[4,7,49]
11 PAHs	*Fontinalis antipyretica*	Soxhlet 200 ml DCM 16 h	Florisil cartridges	HPLC-FLD	65–78%	NM	NM	[36]
15 PAHs	*Pleurozium scheberi*	Soxhlet 200 ml DCM 16 h	Alumina column, 10 ml DCM	GC–MS	NM	NM	NM	[38]
18 PAHs	*Tortula muralis*	Sonication 5 g 30 min, 100 mL H	No clean up	GC–MS	Average 70%	NM	NM	[50]
16 PAH	*Hypnum plumaeformae*	ASE 5 g, 1500 psi, 100 °C, 2cycles, 5 min DCM:A (1:1)	5 g alumina+5 g florisil+10 g silica, 60 ml DCM GPC: 10 g Biobeads S-X3, 80 ml H:DCM (1:1)	GC–MS	49–99%	MDL:3.3–7.8 ng g^{-1}	RSD:5–8%	[8]
9 PAH	*Hypnum cupressiforme*	Microsoxhlet 3 h immersed in H, and 2 h reflux	–	HPLC-FLD	81–98%	NM	RSD:5.5–24%	[46]
PAHs and OCPs	*Pleurozium scheberi*	ASE 40 °C+120 °C, 3*10 min, H	15 g florisil 160 ml H:DCM (1:1), first 60 ml passed through 3.5 g active florisil 60 ml H:DCM (1:1)	GC–MS	25–78%	NM	NM	[9]
16 PAHs EPA	*Hylocomium splendens* *Scleropodium purum* *Hypnum cupressiforme* *Abietinella abietina*	Soxhlet 5 g, H	PAH soil cartridges 1.5 g. DCM:petroleum ether(1:4)	GC–MS	47–114%	NM	RSD:10–19%	[51,52]
16 PAHs	*Hypnum cupressiforme*	Soxhlet , 8 h DCM. Sulphuric clean up	Florisil column	GC–MS	80–98%	0.3–1 ng g^{-1}	RSD: 3–8%	[37]
16 PAHs	*Leptodon smithii*	Sonication, 3 g, 3*100 ml DCM:A (1:1)	–	GC–MS	NM	LOD 1–3 ng ml^{-1}	NM	[53]
15PAHs 8nPAHs	*Hypnum cupressiforme*	DSASE, 0,2 g, H, 2 ml	0.05 g Florisil+0.5 g NH2-SPE 2 ml H:DCM (65:35)	APGC-Q-TOF-MS	79–98%	instrumental LOD: 7–350 ng g^{-1}	RSD 1.8–17%	[10]
PAHs	*Hypnum cupressiforme*	Soxhlet 5 g, 200 ml DCM.	Silica column	HPLC-UV	NM	NM	NM	[39]
19 PAHs	*Pseudoscleropodium purum*	MAE, 20 ml H: A (90:10)	Dual layer Florisil-Silica (2 g+2 g).	GC–MS/MS	83–108%	MQL: 0.1–1.7 ng g^{-1}	U 8–22%	This work
	Sphagnum sp		5 ml H+15 ml DCM:H (20:80)		56–108%			
	Hypnum cupresiforme				62–112%			