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Development and optimization of a plunger assisted solvent extraction method for polycyclic aromatic hydrocarbons sampled onto multi-channel silicone rubber traps

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ABSTRACT

A plunger assisted solvent extraction (PASE) method for multi-channel silicone rubber trap samplers was developed and evaluated as an alternative to direct thermal desorption for the monitoring of polycyclic aromatic hydrocarbons (PAHs). The proposed extraction method was simple, fast (a total of 2 min for extraction), and used a small volume of solvent (a total of 2 mL from two sequential 1 mL extractions). The PASE method presented an advantage over thermal desorption in that samples could be re-analyzed, as only a portion of the extract was injected. Additionally, this approach is cost effective and can be applied in laboratories which do not have thermal desorption systems, hence allowing for the more widespread use of the polydimethylsiloxane samplers which can be employed as denuders in the monitoring of gas and particle partitioning of air pollutants. The method was validated over a wide concentration range (0.005–10 ng μL^{-1}) and the limits of detection ranged from 13.6 ng m^{-3} for naphthalene to 227.1 ng m^{-3} for indeno[1,2,3-cd]pyrene. Overall extraction efficiencies of the target PAHs were good (from 76% for naphthalene to 99% for phenanthrene) with relative standard deviations below 6%. The PASE method was successfully applied to the analysis of domestic fire air emission samples taken at 10 and 20 min after ignition, using a sampling flow rate of 500 mL min^{-1} for 10 min in each case. The samples were found to contain primarily naphthalene (maximum concentration of 9.5 $\mu g\, m^{-3}$, 10 min after ignition), as well as fluorene, anthracene, phenanthrene, fluoranthene and pyrene.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are abundant environmental pollutants, which are released in gaseous and particulate-associated phases from the incomplete combustion or pyrolysis of organic materials [1]. PAHs may persist in the environment and are well known for their potential carcinogenic and mutagenic properties. They are mostly released as a result of human activities, especially in urban and industrial areas. Sources of PAHs include vehicular emissions, coal-powered plants, petroleum refineries, domestic fires and burning of biomass [2]. Principal stages in the measurement of PAHs in ambient air generally consist of sampling, extraction, sample clean-up and analysis. Most conventional atmospheric analyte sampling methods for gas and particulate phases are based on high volume samplers which may introduce analytical artefacts and unreliable estimations of human exposure to PAHs [3,4]. Typical sampling media for particulate phase PAHs include quartz-fibre, glass fibre, Teflon coated glass fibre and Teflon membrane filters, whilst sampling media for gas-phase PAHs include polydimethylsiloxane (PDMS), polyurethane foam (PUF), XAD and mixed sorbents [5–7]. Over the past years, PAHs have been monitored globally in different environmental matrices such as water, air, soil, food and beverages [8–11]. Significant technological improvements in sampling methods and extraction techniques have had an impact on the extent of environmental monitoring of PAHs but further monitoring is still needed to improve the understanding of the status of PAH concentrations in developing countries [12].

Recent research activities in sample collection and preparation are mainly focused on the development of miniaturized, simple, efficient and solvent minimized techniques. The sampling of gaseous semi-volatile organic compounds (SVOCs) has developed very rapidly in terms of the technology employed and the applications thereof [13–15]. Our research group has been focusing on the monitoring and risk assessment of PAHs in air and water samples and has reported several trends and applications for portable sampling devices [16,17]. Multi-channel silicone rubber traps, which consist of 22 parallel PDMS tubes of 0.3 mm i.d. housed in a 178 mm

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Table 1
List of PAHs included in the study in order of elution and increasing molar mass. Internal standards (IS) used for each group of PAHs are shown. Linear regression analysis results of both liquid splitless injection (PASE) and TDS experiments are included (n = 3).

Analyte	Abbreviation	Quantification ion m/z	R^2	
			PASE	TDS
Naphthalene d$_8$	**IS**	**136**		
Naphthalene	Nap	128	0.983	0.988
Acenaphthylene	Acy	152	0.999	0.995
Acenaphthene	Ace	154	0.999	0.999
Phenanthrene d$_{10}$	**IS**	**188**		
Fluorene	Flu	166	0.998	0.995
Phenanthrene	Phe	178	0.998	0.994
Anthracene	Ant	178	0.994	0.996
Pyrene d$_{10}$	**IS**	**212**		
Fluoranthene	FluAn	202	0.997	0.995
Pyrene	Pyr	202	0.996	0.993
Benz[a]anthracene	BaA	228	0.997	0.995
Chrysene d$_8$	**IS**	**240**		
Chrysene	Chr	228	0.998	0.998
Benzo[b]fluoranthene	BbF	252	0.994	0.996
Benzo[a]pyrene	BaP	252	0.991	0.996
Indeno[1,2,3-cd]pyrene	IcdP	276	0.994	0.990
Benzo[g,h,i]perylene	BghiP	276	0.993	0.994
Dibenz[a,h]anthracene	DahA	278	0.992	0.993

long glass tube, have been prepared in our laboratory for gaseous semi-volatile organic analyte sampling [18]. The efficiency of these multi-channel silicone rubber traps as novel denuder devices has also been investigated from both theoretical and experimental perspectives and they have been utilized in a number of applications including household fire emissions, sugar cane burning emissions, tunnel air pollution studies and in underground mining environments in South Africa [16,19,20]. However, more research is still needed in this area, as there is an increasing demand to develop guidelines for the measurement and analysis of PAHs in both ambient air and working environments in developing countries, as well as globally.

Extraction methods for PAHs from PDMS-based air samplers typically involve techniques such as shaking silicone rubber samplers in about 360–500 mL of organic solvent for 48 h [21] or Soxhlet extraction using approximately 60 mL of organic solvents for 8 h [22]. In addition, post extraction clean-up steps such as solid phase extraction or gel permeation chromatography are also performed in these protocols which are time-consuming. In addition, the shaking methods, in particular, use relatively large volumes of organic solvents, which is unfavorable from cost and environmental perspectives. However, in some cases where resin cartridges are used for sample collection, only certain extraction methods, such as microwave or accelerated solvent extraction, are effective [5,23]. In recent years, there has been a growing effort to reduce solvent use when extracting analytes of interest from various matrices and hence limit the impact of solvent waste on the environment. Solvent-less or low-volume solvent-extraction pretreatment for environmental analysis has emerged, for example thermal desorption and single-drop microextraction. Thermal desorption has the advantages of being time efficient and solvent free, therefore the silicone rubber traps were designed to be thermally desorbed for analysis [16,17,19]. In addition, detection limits are improved with some TD systems as the entire sample (analytes) can be transferred to the gas chromatograph-mass spectrometer (GC–MS) for analysis. Incomplete desorption of heavier analytes may, however, be a limitation of this technique.

Despite the introduction of many solvent-free procedures over the past decades, solvent extraction techniques remain the most common option for PAHs in gas or particle phases. In light of this, our aim was to develop and optimize a new method in which a plunger system is used to extract PAHs from silicone rubber traps. Our method uses a plunger made of steel wire and a carefully sized Teflon tip which is inexpensive and easy to assemble. This proposed novel and miniaturized plunger assisted solvent extraction (PASE) setup provides an alternative procedure to thermal desorption that is time-efficient and uses low volumes of organic solvents, in addition to not requiring specialized desorption equipment and associated liquid nitrogen. PASE reduces costs and at the same time allows for the widespread use of the silicone rubber traps. The PASE method was applied to the monitoring of domestic fire emission samples from a traditional *imbawula* stove. Furthermore, the liquid splitless injection method was compared to direct thermal desorption in terms of extraction versus desorption efficiencies. General parameters of the methods such as analysis time, equipment requirements and cost, limits of detection (LODs) and limits of quantitation (LOQs) are also compared.

2. Materials and methods

2.1. Chemicals and reagents

The overall analytical procedure, including calibration, was performed using a certified standard PAH mix solution obtained from Supelco (St Louis, MO), containing 15 priority PAHs. The nominal concentration of each compound in the mixture dissolved in methylene chloride was 2000 ng μL^{-1} and the names and abbreviations of the PAHs included are given in Table 1. Stock solutions at a concentration of 100 ng μL^{-1} were prepared in toluene and working solutions were prepared by appropriate dilutions of the stock solutions before use. Pure individual PAH standards were obtained from Sigma Aldrich. All solvents were of analytical grade (99% purity) including toluene, dichloromethane (DCM) and n-hexane which were purchased from Sigma Aldrich. Acetone was obtained from Associated Chemical Enterprises (ACE, South Africa). Deuterated internal standards (IS), d8-naphthalene, d10-phenathrene, d10-pyrene and d12-chrysene were obtained from Isotec Inc (Sigma Aldrich, Bellefonte, USA).

2.2. Multi-channel silicone rubber traps

The PDMS traps were prepared according to the method described by Ortner and Rohwer [18]. Each trap consisted of 22 parallel PDMS tubes (55 mm long, 0.3 i.d., 0.6 mm o.d. Sil-Tec, Technical Products, Georgia, USA) in a 178 mm long glass tube (6 mm o.d., 4 mm i.d.). The plungers consisted of carefully sized Teflon tips which were designed and machined in- house. 10 μL Hamilton syringes (Supelco, Nevada, USA) were used to spike standards onto traps and the traps were then end-capped with Teflon sleeved glass stoppers to prevent analyte loss. In order to avoid unnecessary sample dilution and extraction solvent use, the open volume in the traps was calculated as illustrated in Fig. 1a, where V_A represents the volume of the empty tube portion and V_B the open volume in the silicone portion of the trap, respectively.

The total volume (V_{total}) of the multi-channel silicone rubber trap that the extraction volume would occupy was *ca.* 0.7 mL, therefore 1 mL of organic solvent was used for extractions (full calculation is given in Equation S1). All the multi-channel silicone rubber traps used in this study were pre-conditioned before use at 280 °C for approximately 24 h with a hydrogen gas flow of *ca.* 10 cm^3 min^{-1}.