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Sequential Extraction of Polycyclic Aromatic Hydrocarbons and Metals from Airborne Particulate Matter

A.H. ABDOLLAH†, M. GHEISARI†, S.M. TALEBI* and A. ABDOLLAHI
Department of Chemistry, University Putra Malaysia, Selangor, Malaysia
E-mail: smtalebi@yahoo.com

Polycyclic aromatic hydrocarbons (PAHs) and metals are two groups of air pollutants and monitoring of their atmospheric concentrations in mega cities is of extreme importance. Normally the concentrations of PAHs and metals are determined in different samples. The individual sampling and determination of these two groups of air pollutants is time consuming and it is difficult to investigate their relationship in a site or in the same sample. The possibility of analyzing of PAHs and metals in the same sample has been investigated. The results showed that the extraction of PAHs by supercritical fluid extraction before leaching of samples for metals have no effect on the concentration of metals.

Key Words: Extraction, Polycyclic aromatic hydrocarbons, Airborne particulate matter.

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are products of incomplete combustion or pyrolysis of carbonaceous material at high temperature and enter into the atmosphere[1]. The sources of PAHs into the atmosphere can be divided into two groups: (i) natural sources such as volcanic activity and forest fires and (ii) anthropogenic sources including; waste incineration, industrial processes, power plants and combustion of fossil fuels in automobile engines[2,3]. Anthropogenic sources are known as the major sources responsible in releasing PAHs into the urban atmosphere[4,5]. However PAHs are now the ubiquitous component of the lower atmosphere in mega cities and industrial areas[6,7]. The determination of PAHs in urban air has gained importance in last decades, Considerable attention to control of PAHs in air is a result of the high carcinogenic and mutagenic activities displayed by some PAHs even at trace level[8,9].

Metals are also released into the atmosphere from both natural and anthropogenic sources. The major source of metals and especially heavy metals into the atmosphere are anthropogenic sources including iron and steel industries, garbage incineration and power plants[10,11]. Monitoring and control of toxic and hazardous metals in urban atmosphere is a must for air quality control and planning for prevention of their adverse health effect on human health.

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†Science and Technology Research Center, Islamic Azad University (IAU), Tehran, Iran.

The individual determination of PAHs and heavy metals in airborne particulate matter has been the subject of many researches[10-14], but less information is available about the sequential extraction and simultaneous determination of PAHs and metals as the most important air contaminants.

The aim of this work was to investigate the possibility of using sequential extraction for separation and determination of PAHs and metals in the same sample of airborne particulate matter.

EXPERIMENTAL

All chemicals were of analytical grade or better aristar nitric acid highly pure hydrofluoric acid were used for digestion of exposed filters and standard reference meterials. Commercial standard stock solution of 1000 (μg/mL) of metals for atomic absorption spectrometry (BDH, Ltd.) was used.

All glass wares were cleaned by soaking over night in 0.1 N nitric acid and rinsed with acetone and triple rinsed with Milli-Q water and allowed to be dried in a dust free atmosphere. Working standard solutions were diluted from the stock standard solutions with 0.1 N nitric acid solution.

Standard solution of mixed PAHs containing; acenaphthylene, fluoranthene, naphthalene, benzo(a)anthracene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)-fluoranthene, chrysene, acenaphthene, anthracene, benzo(ghi)perylene, fluorine, phenanthrene, dibenzo(a,h)anthracene, pyrene and indino(1,2,3,-cd)pyrene in methanol: methylene chloride (50:50) was used. The standards were stored in refrigerator at 5 ºC. Standard reference samples of SRM 1648 and 1649 (NIST) were used for extraction of metals and PAHs, respectivley.

Collection of samples: Airborne particulate matter from the atmosphere of the city of Isfahan was collected on quartz fiber filter (Whatman QM-A), using a hi-vol air sampler. Sampels were collected from a height of 1.5 m above the ground level with a flow rate of 1 m^3 min^{-1}. The sampling period was 12 h in order to collect sufficient material for performing the sensitive analysis.

Extraction of PAHs: The exposed filter containing local airborne particulate matter or 100 mg of standard sample (SRM-1649) was extracted by carbon dioxide supercritical fluid extraction (SFE) using 10 % methanol as modifier. The extraction with SFE was performed at 400 atm. pressure and 50 ºC. The airborne particulate matter or reference material was placed into the stainless steel extraction cell and extracted for 1 h. The extract was collected in dichloromethane. The extract was then blown down under the nitrogen steam to dryness and finally extracted in *n*-hexane.

Extraction of metals: The local airborne particulate matter and reference materials (SRM) after extraction of PAHs or without any pre-extraction were digested for the subsequent determination of metals following the method described by Talebi and Abedi[15]. In briefly, the samples were digested with a mixture of HNO_3 and HF acids. The digestion was performed in a closed PTFE beaker and the mixture of sample and acids was heated at 90 ºC for 10 h. After the digestion, the remainder of hydrofluoric acid was removed by adding nitric acid and heating at 90 ºC. The mixture was then colled to room temperature, filtered into a 50 mL volumetric flask and made to the volume by double distilled de-ionized water.

Instrumentation: The SFE extraction were performed by using an ISCO dual pump SFE system. The ISCO 250 D pump supplied pure CO_2 and the ISCO 100 D pump supplied methanol as modifier.

The determination of PAHs was carried out on a GCQ™ gas chromatograph coupled with a quadrupole ion trap mass spectrometer (Finigan MAT San Joe, CA, USA). The GC column was BPX5 capillary column (25 m × 025 mm, i.d.). 1 μL of the extract was injected into the GC column by A 200S Finigan MAT auto-sampler *via* a splitless injector at 250 ºC. The following temperature programming was applied to the column for better separation of PAHs. The column temperature was started from 80 ºC and hold at this temperature for 5 min. Temperature was then increased to 150 ºC at a rate of 10 ºC/min. Finally the temperature was increased to 310 ºC at a rate of 5 ºC/min and hold at the latter temperature for 12 min. The GC-MS transfer line was kept at 250 ºC.

The analysis of metals was performed using indictively coupled plasma atomic emission spectrometry (ICP-AES). The determinations were carried on a Maxim system (applied research, Fisons instrument) spectrometer fitted with an axial viewing of torch. A software program called Plasma Vision perfomred control of the Maxim ICP-AES spectrometer. The system was also linked to a DECP 450 D2LP computer and an IBM 24 printer. The ignition, shut down and sample uptake rate were all computer-controlled. The instrumental conditions for the determination of metals are listed in Table-1.

TABLE-1
ICP-AES SCANNING MEASUREMENT PARAMETERS

Starting mirror	-60º	Forward power	1100 (w)
Ending mirror	+60º	Carrier flow	0.4 (L/min)
Step size	4	Analyzing pump speed	2.0 (L/min)
Pre-integration time	0 (s)	Transport pump speed	20.0 (L/min)
Integration time	1 (s)	Transport time	30 (s)
Plasma flow	0.8 (L/min)	Sample type	aqueous

RESULTS AND DISCUSSION

The extraction efficiency of PAHs with SFE was investigated by spiking the standard PAHs solution on SRM-1649 and exposed filters containing the local air-borne particulate mater. Table-2 summarized the results and indicates thaat SFE is a reliable method for extraction of PAHs from airborne particulate matter.

Table-3 shows the extraction efficiency of metals from the reference material (SRM 1648) with a mixture of nitric and hydrofluoric acid and indicates that this acid mixture is able to release relatively whole of metals from the airborne particulate matrix.

TABLE-2
EXTRACTION RECOVERY OF PAHS FROM SPIKED FILTERS

Compound	Recovery (%) SRM-1649	Recovery (%) filter	Compound	Recovery (%) SRM-1649	Recovery (%) filter
Naphthalene	57 ± 8	61 ± 10	Pyrene	100 ± 7	99 ± 7
Phenanthrene	100 ± 7	99 ± 9	Chrysene	103 ± 6	100 ± 10
Anthracene	91 ± 7	94 ± 9	Benzo(a)anthracene	106 ± 10	102 ± 7
Acenaphthene	100 ± 5	99 ± 10	Benzo(b)fluoranthene	10.5 ± 7	100 ± 8
Fluorene	92 ± 6	95 ± 6	Benzo(ghi)perylene	109 ± 6	104 ± 9
Fluoranthene	112 ± 9	103 ± 6	Dibenzo(a,h)anthracene	101 ± 5	99 ± 6
Bezo(a)pyrene	136 ± 9	119 ± 6	Indino(1,2,3-cd)pyrene	100 ± 9	98 ± 7

TABLE-3
EXTRACTION EFFICIENCY OF METALS FRO SRM-1648 WITH HF-HNO_3

Element	Mean certified value	Extracted with HF + HNO_3	SD
Pb	6550	6533	71.3
Cd	75	72	2.0
Cr	403	348	4.8
Co	19	18	2.1
Cu	609	603	18.3
Ni	82	82	2.2
As	115	112	3.1
Mn	860	852	5.7
Ca	58000	58500	387.2
Fe	39100	37900	573.0
Zn	4760	4752	27.6
Sn	–	101	4.3
Ba	737	720	12.4
Al	34200	33800	178.0

The concentration of metals in standard reference materials (SRM-1648 and SRM-1649) was determined before extraction and after extraction of PAHs. The results are shown in Table-4 and indicate that the extraction of PAHs have no considerable effect on the metal content of the residue.

TABLE-4
RELATIVE CONCENTRATION OF METALS IN EXTRACTED TO
NON-EXTRACTED REFERENCE MATERIALS OF SRM-1648 AND SRM-1649

Element	Extracted/non-extracted		Element	Extracted/non-extracted	
	SRM-1648	SRM-1649		SRM-1648	SRM-1649
Pb	0.99	0.98	Mn	0.88	0.91
Cd	0.92	0.89	Ca	1.04	1.00
Cr	0.89	0.90	Fe	1.01	1.00
Co	1.00	1.03	Zn	0.97	0.93
Cu	1.08	1.02	Sn	0.98	0.89
Ni	1.00	0.98	Ba	1.02	1.00
As	0.97	0.95	Al	0.97	1.04

The investigation followed on the exposed filters containing the local airborne particulate matter. Each filter was exactly cut into two equal pieces. One piece was directly digested for analysis of metals and the other piece was subjected to sequential extraction (extracted by SFE for PAHs and the residue was digested for metals). The results obtain from this investigation are shown in Fig. 1 and represent the same result as that for the standard reference materials. It can be concluded that sequential analysis of PAHs and metals on the same sample of airborne particulate matter is possible and it facilitates the simultaneous determination of these two important air pollutants in the same sample.

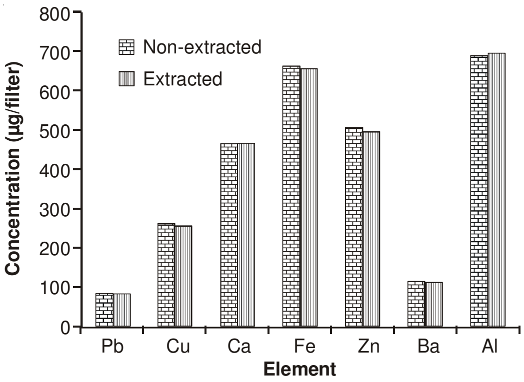

Fig. 1. Concentrations of elements in extracted and non-extracted exposed filter

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