Asian Journal of Chemistry; Vol. 23, No. 1 (2011), 89-91

ASIAN JOURNAL OF CHEMISTRY

www.asianjournalofchemistry.co.in

Extraction and Determination of Polycyclic Aromatic Hydrocarbons in Airborne Particulate Matter

A. ABDOLLAHI[1,*], S.M. TALEBI[2] and S. WAQIF-HOSSAIN[1]

[1]Science and Research Branch, Islamic Azad University (IAU), Tehran, Iran
[2]Department of Chemistry, Isfahan University, Isfahan, Iran

*Corresponding author: E-mail: atousaabdollahy@yahoo.com

(*Received*: 1 December 2009; *Accepted*: 21 August 2010) AJC-8994

Airborne particulate matter was collected from the urban atmosphere of the city of Isfahan. Polycyclic aromatic hydrocarbons associated with the samples were extracted by carbon dioxide supercritical fluid extraction (SFE). The capability of supercritical fluid extraction for extraction of polycyclic aromatic hydrocarbons from airborne particulate matter was evaluated in comparison with the Soxhlet as a traditional method for extraction of polycyclic aromatic hydrocarbons. An on-line HPLC-GC system was developed for the better separation and more sensitive determination of polycyclic aromatic hydrocarbons in the sample extracts. The method applied for the sensitive determination of polycyclic aromatic hydrocarbons in the atmosphere of the city of Isfahan in different periods of times.

Key Words: Polycyclic aromatic hydrocarbons, Airborne particulate matter.

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are the products of incomplete combustion or pyrolysis of carbonaceous material at high temperature[1]. Polycyclic aromatic hydrocarbons are a wide group of organic compounds have been found in urban air. The sources of polycyclic aromatic hydrocarbons into the atmosphere can be divided into two groups; (1) natural sources such as forest fires and volcanic activities and (2) anthropogenic sources including power plants, waste incineration, industrial processes and combustion of fossil fuels in automobile engines[2,3]. The anthropogenic sources are known to have the major role in releasing of polycyclic aromatic hydrocarbons into the urban atmosphere[4,5].

The occurrence of polycyclic aromatic hydrocarbons in urban air has gained importance because of the continuous nature of the exposure, the size of population at risk and that a number of these compounds are known as mutagens and carcinogens[6,7].

High performance liquid chromatography and gas chromatography are the methods have long been used for fractionation and rapid determination of polycyclic aromatic hydrocarbons[8-11]. The more sensitive methods such as GC-MS has also been developed for the sensitive determination of trace polycyclic aromatic hydrocarbons in environmental samples[12-14]. The extraction of airborne particulate matter produces a sample with complex matrix that contains a wide range of polycyclic aromatic hydrocarbons and their derivatives. As a result, it is difficult to separate the different components and perform a sensitive analysis using only HPLC, GC, or even GC-MS methods. The effective separation and sensitive determination of polycyclic aromatic hydrocarbons needs using united chromatographic techniques. In united chromatography the sample is passed through two different columns with different specifications and packing materials. As a result, a better fractionation of different classes of organic compounds and also more effective separation of the organic compounds in each class can be achieved. The united chromatographic techniques offer reliable and sensitive determination of trace polycyclic aromatic hydrocarbons in samples with complex matrices. Although different united chromatographic techniques are possible, coupling of HPLC to GC offers excellent clean up and separation of polycyclic aromatic hydrocarbons in environmental samples[14-16]. In this system, the sample is introduced into the HPLC system and passed through the HPLC column with the aid of liquid mobile phase and monitored by an UV detector. The fractions separated can be transferred into GC system one by one for more separation and sensitive determination. The HPLC-GC is easy, simple and the most useful technique for separation and determination of trace polycyclic aromatic hydrocarbons in different environmental samples[17]. Off line using HPLC-GC is not desirable due to the poor sensitivity and loss of sample during the handling. However, in on-line HPLC-GC, the sample is injected into the column of HPLC system and separated into the different fractions. The fractions can be transferred into the GC column for more separation and sensitive determination by GC detector.

In this work, the effective extraction and sensitive determination of polycyclic aromatic hydrocarbons in airborne particulate matter by supercritical fluid extraction-HPLC-GC has been investigated.

EXPERIMENTAL

Collection of samples: Airborne particulate matter from the atmosphere of the city of Isfahan was collected on quartz fiber filter (Whatman QM-A). A Greasby, Model PS2 high-volume air sampler was used for collection of particulate matter. Samples were collected from a height of 1.5 m above the ground level and at a distance of 10 m from the road shoulder at all of sampling sites. Sampling flow rate was 1 m^3 min^{-1}. The duration of sampling was 12 h in order to collect sufficient material for performing a sensitive analysis. A continuous sampling was also performed in order to investigate the variation in concentration of polycyclic aromatic hydrocarbons in days and at nights. The daytime samples were collected from 7 AM to 7 PM and night samples were collected from 7 PM to 7 AM.

Dichloromethane, methanol and other organic solvents were HPLC grade (Aldrich Chemical Co.). The individual polycyclic aromatic hydrocarbon standards and a standard solution of mixed polycyclic aromatic hydrocarbons were obtained from Supelco Inc. The mixed standard contained 16 polycyclic aromatic hydrocarbons classified by EPA as priority pollutants include; acenaphthene, 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, indino(a,2,3-cd)pyrene and pyrene in methanol and dichloromethane (50:50). The standard solutions were stored in refrigerator at 5 ºC. 9,10-Dihydroanthracene was purchased from Aldrich company and used for preparation of internal standard.

Extraction of polycyclic aromatic hydrocarbons: The exposed filter was extracted by carbon dioxide supercritical fluid extraction (SFE), using 10 % methanol as modifier. The extractions were carried out at 400 atm pressure and 90 ºC. An exposed filter was folded several times and placed into a 10 mL volume stainless still extraction cell and extracted for 1 h. Soxhlet extractions were performed for 24 h using dichloromethane.

Instrumentation: Extraction of polycyclic aromatic hydrocarbons from the samples was performed by using an ISCO dual pump supercritical fluid extraction system. The ISCO 260 D pump supplied pure CO$_2$ and the ISCO 100 D pump supplied methanol as modifier.

A Varian 9001 HPLC pump with two (250 mm × 1 mm, i.d.) stainless steel columns in series packed with aminosilane and silica were used for fractionation of polycyclic aromatic hydrocarbons. Samples were introduced into the HPLC system *via* a 20 µL injection loop. The fractions separated in column were monitored with a Hitachi UV detector at wavelength of 254 nm. A 300 µL loop was located at the end of HPLC system and samples after passing the UV detector were collected in the loop and then wasted. Concerning to the volume of the loop, flow rate of the mobile phase in HPLC and HPLC chromatogram, it was possible to transfer the HPLC fractions to the GC system section by section. A schematic diagram of the HPLC-GC system is shown in Fig. 1.

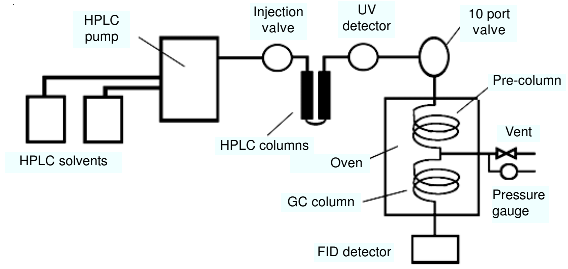

Fig. 1. A schematic diagram of HPLC-GC system

The interface between HPLC and GC systems was a 10 port Valco 4N10WT valve (Valco, Switzerland). A Varian GC model, CP-3800 equipped with a BP × 5 column (25 m × 0.32 mm, i.d.) analytical column and flame ionization detector used for more separation and sensitive determination of polycyclic aromatic hydrocarbons. A temperature programming was used for better separation of polycyclic aromatic hydrocarbons in GC column. The temperature was started from 75 ºC and stand at this position for 6 min, it was then increased to 130 ºC at a rate of 10 ºC/min, it was finally increased to 320 ºC at a rate of 5 ºC/min and was held at this position for 12 min.

RESULTS AND DISCUSSION

The ability of supercritical carbon dioxide with 10 % methanol as modifier for extraction of polycyclic aromatic hydrocarbons from airborne particulate matter was investigated by comparison of its extraction efficiency with that obtained by Soxhlet as a conventional method. Several exposed filters were exactly cut into two equal pieces. One piece was extracted by supercritical fluid extraction and the other piece was extracted with Soxhlet. Extraction with Soxhlet was performed using dichloromethane and refluxing for 24 h, while extraction by supercritical fluid extraction was carried out for 1 h. The typical results obtained from this investigation are shown in Fig. 2 and indicate that supercritical fluid extraction is not only an environmentally friendly method but also offers better extraction efficiency for many of polycyclic aromatic hydrocarbons and could be a suitable alternative to Soxhlet for extraction of polycyclic aromatic hydrocarbons from airborne particulate matter.

The sensitivity and accuracy of the developed method for analysis of polycyclic aromatic hydrocarbons in airborne particulate matter was investigated by analysis of standard reference material (SRM-1649). The results obtained from this study are shown in Table-1 and indicate that the proposed method is a quite capable and reliable technique for effective separation and sensitive determination of trace amounts of polycyclic aromatic hydrocarbons in airborne particulate matter.

The proposed method was applied for the determination of concentrations of polycyclic aromatic hydrocarbons in airborne particulate matter collected from 20 different sampling sites in the city of Isfahan. The samples were extracted by supercritical fluid extraction and analyzed for polycyclic aromatic hydrocarbons by HPLC-GC system. Table-2 summarizes the results obtained from this investigation.

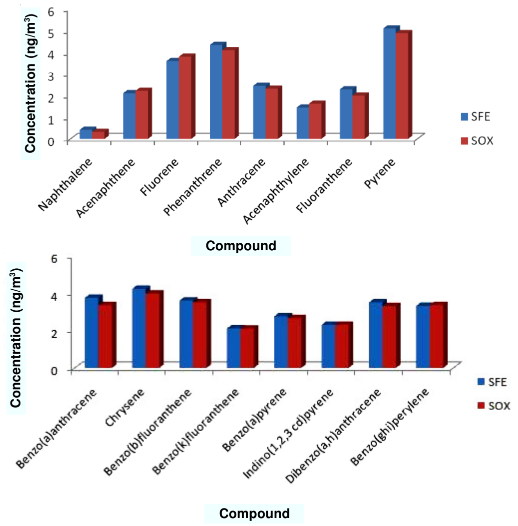

Fig. 2. Comparison of efficiencies of supercritical fluid extraction and SOX for extraction of polycyclic aromatic hydrocarbons from airborne particulate matter (μg/filter)

TABLE-1
DETERMINATION OF POLYCYCLIC AROMATIC HYDROCARBONS CONCENTRATIONS IN STANDARD REFERENCE MATERIAL (SRM-1649) (μg/g)

Compound	Certified value	Proposed method
Fluoranthene	7.1 ± 0.5	7.2 ± 0.4
Benzo(a)anthracene	2.6 ± 0.3	2.4 ± 0.3
Benzo(a)pyrene	2.9 ± 0.5	4.1 ± 0.4
Benzo (ghi)perylene	4.5 ± 1.1	4.1 ± 0.6
Indino(1,2,3c-d)pyrene	3.3 ± 0.5	2.9 ± 0.5
Pyrene	–	6.8 ± 0.4

TABLE-2
CONCENTRATIONS OF POLYCYCLIC AROMATIC HYDROCARBONS IN THE ATMOSPHERE OF THE CITY OF ISFAHAN (ng/m^3)

Compound	Mean	Range
Naphthalene	0.33	0.22-0.41
Acenaphthene	2.29	1.31-2.93
Fluorene	3.26	1.92-3.86
Phenanthrene	3.52	2.13-4.42
Anthracene	2.50	1.83-2.85
Acenaphthene	0.99	0.82-1.68
Fluoranthene	2.11	0.92-2.84
Pyrene	3.98	3.20-6.13
Benzo(a)anthracene	3.14	2.02-4.36
Chrysene	3.71	2.71-4.94
Benzo(b)fluoranthene	3.57	1.82-4.12
Benzo(k)fluoranthene	1.94	1.08-2.83
Benzo(a)pyrene	3.26	1.72-3.61
Indino(1,2,3,c-d)pyrene	2.09	1.13-2.66
Dibenzo(a,h)anthracene	3.09	2.06-3.87
Benzo(ghi)perylene	2.57	1.74-3.76

Fig. 3 shows the monthly average concentration of total polycyclic aromatic hydrocarbons associated with airborne particulate matter in the atmosphere of the city of Isfahan in year 2008.

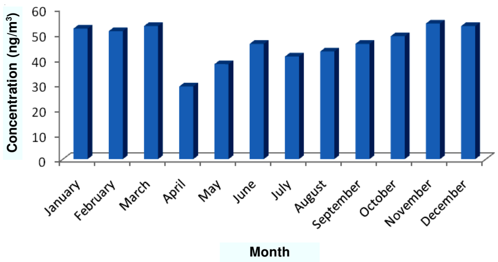

Fig. 3. Monthly average concentrations of polycyclic aromatic hydrocarbons in the city center of Isfahan (ng/m^3)

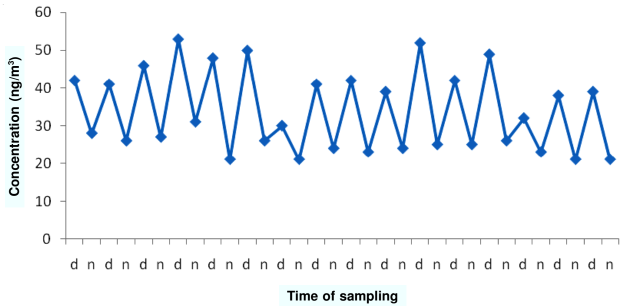

Fig. 4. Day and night variation in concentration of polycyclic aromatic hydrocarbons in the city center of Isfahan

A continuous sampling was performed in order to investigate the variation in concentrations of polycyclic aromatic hydrocarbons in days and nights. The results obtained from this investigation are shown in Fig. 4 and indicate that the polycyclic aromatic hydrocarbons levels are different in different week days and also the concentrations of polycyclic aromatic hydrocarbons in days (7 AM to 7 PM) that contain 2 ruse hours and higher traffic density is much higher than those at nights. It can be concluded that the major source for introducing of polycyclic aromatic hydrocarbons into the city atmosphere is mobile sources that consume fossil fuels.

REFERENCES

1. P. Flessel, Y.Y. Wang, K.I. Chang, J.J. Wesolowski, G.V. Guirguls and I.S. Kim, *J. Air Waste Manag.*, **41**, 276 (1991).
2. C.J. Halsal, P.J. Coleman, B.J. Davis, V. Burnett, K.S. Waterhouse, P. Harding-Jones and K.C. Jones, *Environ. Sci. Tech.*, **28**, 2380 (1994).
3. D. Sicilia, S. Rubino, D. Perez-Bendito, N. Maniasso and E.A.G. Zagatto, *Anal. Chim. Acta*, **392**, 29 (1999).
4. M.J. Nasr Yousef, H.J. Omar, M.R. Bin-Abas, K.A. Ketuly and N.M. Tahir, *Atmos. Environ.*, **36**, 247 (2002).
5. S.M. Talebi, *Iran. J. Chem. Chem. Eng.*, **17**, 54 (1998).
6. M. Pineiro-Iglesias, P. Lopez-Mahia, S. Muniategui-Lorenzo, D. Prada-Rodriguez, X. Querol and A. Allastuey, *Atmos. Environ.*, **37**, 4171 (2003).
7. S.R. Wild, K.S. Waterhouse, S.P. Mcgrath, K.C. Jones, *Environ. Sci. Tech.*, **24**, 1706 (1990).
8. P.C.M. Van-Noort and E. Wondergem, *Environ. Sci. Tech.*, **19**, 1044 (1985).
9. V. Pino, J.H. Ayala, A.M. Afonso and V. Gonzalez, *Fresenius J. Anal. Chem.*, **371**, 526 (2000).
10. J. Schulz, A. Hartung, H. Kies and K.H. Lies, *Chromatographia*, **19**, 391 (1984).
11. S.M. Talebi and A. Mohammad-Khoh, *Environ. Contam. Toxicol.*, **71**, 1042 (2003).
12. F. Yazdanparast, A. Nouri and M. Rabbani, *Int. J. Environ. Sci. Tech.*, **1**, 215 (2004).
13. X.M. Wang, C.Y. Sheng, J.M. Fu, C.Y. Chen, S.C. Lee, L.Y. Chan, Z.S. Wang, *Atmos. Environ.*, **36**, 5141 (2002).
14. K. Grobe and J.M. Stoil, *J. High Resolut. Chromatogr. Commun.*, **9**, 518 (1986).
15. T. Hyotylainen, K. Grobe, M. Biedermann and M.L. Riekkola, *J. High Resolut. Chromatogr.*, **20**, 410 (1997).
16. L. Mondello, P. Dugo, G. Dugo, A.C. Lewis and K.D. Bartle, *J. Chromatogr. A*, **842**, 373 (1999).
17. J R. Dean, M.E. Deary, B.K. Gbefa and W.C. Scott, *Chemosphere*, **57**, 21 (2004).