

Determination of benzo(a)pyrene in Soil, Sediment and Water by Gas Chromatography–Mass Spectrometry

Hee Kyung Jeon, Hae Yeon Choi and Jae–Chun Ryu*

Toxicology Lab., Bioanalysis and Biotransformation Research Center,
Korea Institute of Science and Technology, Seoul 136–791, Korea

기체크로마토그래피/질량분석기에 의한 토양, 저질 및 수질시료 중 benzo(a)pyrene의 분석

전 희 경, 최 해 연, 류 재 천*

한국과학기술연구원 생체대사연구센터, 독성연구실

요 약

본 연구는 GC/MS를 이용하여 수질, 토양 및 저질 시료 중의 benzo(a)pyrene (BaP)을 분석하는 방법을 확립하고자 하였다. BaP은 수질 시료(100 mL)에서 n-hexane으로 추출하였으며, 토양 및 저질 시료(10 g)에서는 먼저 메탄올로 추출한 후 hexane으로 다시 추출하여 농축시켜 분석하였다. 수질 시료 중의 BaP 회수율은 94.8% 이상 이었으며 토양에서의 회수율은 약 93%를 보였고 재현성은 10.49% 이하였다. 검정 곡선은 상관계수(R^2) 값이 수질과 토양 모두에서 0.996 이상의 좋은 직선성을 보여주었다. 토양 시료의 경우 35지역 중 6지역의 토양에서 0.5~223.5 $\mu\text{g}/\text{kg}$ 의 농도 범위로 BaP가 검출되었으며 수질과 저질 시료에서는 모든 지역에서 검출한계 이하로 나타났다. 이 분석방법은 환경 중에 미량으로 존재하는 BaP의 분석과 모니터링에 유용하게 사용할 수 있는 적합한 방법이라 사료된다.

Key words : benzo(a)pyrene, gas chromatography–mass spectrometry, soil, sediment, water

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) made of two or more fused benzene rings are a wide spread class of environmental chemical pollutants (Neff, 1979; McElroy *et al.*, 1989). There are several possible sources for PAHs in the environment. Two classes of PAHs inputs must be considered as natural processes and anthropogenic activities, but the later

is generally considered to be the major source of PAHs input into the environment. They are formed as by-products of incomplete combustion of organic materials. The most significant anthropogenic sources of PAHs include burning of fossil fuels, coke and aluminum production, cracking of crude petroleum, incineration of industrial and domestic waste, vehicle exhaust, domestic heating, cigarettes, fireplaces and chemical manufacturing (Suess, 1976; Bence *et al.*, 1996; Lim *et al.*, 1999; Bakker *et al.*, 2000). Some PAHs can also be derived from biogenic precursors such as pigments and steroids (Wakeham *et al.*,

* To whom correspondence should be addressed.

Tel: +82–2–958–5070, E-mail: ryujc@kist.re.kr

1980).

PAHs in environmental system (soil, sediment and water) can arise from a number of pathways. Point sources include hydrocarbon spillage (Benner Jr. *et al.*, 1990), incomplete products of combustion of fossil fuels eg. wood burning, use of organic waste as compost and fertilizer, and power plants and blast furnaces (Freeman and Catteil, 1990; Van Brummelen *et al.*, 1996; Smith *et al.*, 2001). However, the major pollution is likely to be from diffuse sources such as deposition from the atmosphere and there is evidence to indicate that PAH are transported over long distances by atmosphere movement (Lunde and Bjorseth, 1977; Aamot *et al.*, 1996; Bakker *et al.*, 2001; Halsall *et al.*, 2001).

Many PAHs are potential or proven toxicant and they are among the most carcinogenic, mutagenic and toxic contaminates found in aquatic systems (Kennish, 1992). The US EPA currently regulates sixteen of these compounds as priority pollutants (Hatjian *et al.*, 1995; Simpson *et al.*, 1995). Furthermore, benzo (a)pyrene (BaP) is listed in the table of endocrine disrupting chemicals by National Institute of Health Sciences in Japan (Jobling *et al.*, 1995) and World Wildlife Fund. Hence, monitoring of this compound in the environment including ground water, soil and sediment is necessary for evaluating the extent of environmental contamination and applying to the risk characterization and assessment. Recently, PAHs including BaP were analyzed in the agricultural soils (Nam *et al.*, 2003) and in the surficial sediments (Yang, 2000) for environmental monitoring by gas chromatography and gas chromatography-mass spectrometry. Our laboratory involved in the determination of some chemical contaminants from environmental matrices such as ground water, soils and sediments (Kwon *et al.*, 2000; Lee *et al.*, 2000; Eo *et al.*, 2000; Kwon *et al.*, 2001; Kwon *et al.*, 2003; Park *et al.*, 2003).

In the present study, BaP was selected among the PAHs because a good correlation between BaP and the total concentration of PAHs ($r = 0.953$) has been pointed out (Magi *et al.*, 2002). The clean-up proce-

dures for the GC/MS analysis of BaP developed by Japan National Institute of Environmental Studies is tedious and labor-intensive because a large amount of samples (such as 1 L of water) are used and distillation and purification steps with a silica gel column from water and soil samples are required even if the detection limit in water reached to 10 ng/L (NIES, 1998). Therefore, the purpose of this study was to develop the rapid method of analysis and to determine the concentration of BaP in real environmental samples (soil, sediment and water) using gas chromatography-mass spectrometry.

EXPERIMENTAL METHODS

Chemicals

Benzo(a)pyrene was obtained from Sigma (St. Louis, MO, USA). Benzo(a)pyrene-d₁₂ was purchased from Supelco (Bellefonte, PA, USA). Acetone, n-hexane (95%, for organic residue analysis), isopropanol, methanol, methylene chloride, and anhydrous sodium sulfate were of analytical grade and purchased from J. T. Baker (Phillipsburg, NJ, USA). Sodium chloride was obtained from Mallinckrodt (Mexico). Sodium chloride and anhydrous sodium sulfate were baked in a furnace at 500°C for 8 hr before use. High purity of helium as a carrier gas was used for the gas chromatographic separation. Distilled water prepared by Milli-Q water system apparatus (Milford, MA, USA) was used. The other agents were of analytical grade.

Sample collection

Non-contaminated blank soils were obtained in the vicinity of Korea Institute of Science and Technology. Real water (43 sites), soil (35 sites) and sediment (11 sites) samples were collected at nation-wide sites by Korea National Institute of Environmental Research. The soil was dried under room temperature and mixed in a porcelain dish before use for recovery test. Double distilled water was used for blank and recovery tests.

Gas chromatography–mass spectrometry

A gas chromatograph/mass spectrometer (GC/MS; HP 6890 plus/HP 5973, Hewlett Packard, USA) was used and the instrument was controlled by Chem-Station (G1701AA, Version A.03.00, Hewlett Packard, USA). Samples were injected into the GC/MS by an auto liquid sampler (HP7673).

For analyzing benzo(a)pyrene 50% phenylmethylsiloxane capillary column (HP-50+; 20 m, length \times 0.25 mm, internal diameter \times 0.25 μ m, film thickness) was used. The flow rate of helium as carrier gas was 0.7 mL/min. Sample injection (1 μ L) was in splitless mode. The flow rate of septum purge was 5 mL/min. The GC column temperature was programmed from 50°C, ramped at 20°C/min to 260°C, ramped at 25°C/min to 290°C, held for 10 min. For the mass selective detector, electron impact mode was selected at 70 eV. The temperature of transfer line was set at 280°C. BaP was detected by using a selected ion monitoring mode. The selected ions was m/z 252 (molecular ion; $[M]^+$), m/z 126 and m/z 113 for BaP. The ions values for quantification was m/z 252 for BaP. Benzo(a)pyrene- d_{12} (m/z 132 and m/z 264 $[M]^+$) was used as an internal standard.

Calibration curves of benzo(a)pyrene

To 100 mL of distilled water or 10 g of soil and sediment, benzo(a)pyrene (1–250 ng) was fortified and benzo(a)pyrene- d_{12} (100 ng; 10 ppm \times 10 μ L) was added as an internal standard. The other steps were the same as described below (Extraction).

Table 1. Recoveries of benzo(a)pyrene in water and soil (n = 5)

Matric	Added (ng)	Found (ng)	Recovery (%)	SD (%) ^a	RSD (%) ^b
Water (in 100 mL)	5	4.79	95.9	14.79	15.43
	10	9.48	94.8	7.22	7.62
	50	50.85	101.7	2.24	2.29
Soil (in 10 g)	10	9.36	93.6	3.32	4.39
	50	46.55	93.1	9.76	10.49

^a SD : Standard deviation, ^b RSD : Relative standard deviation

Extraction of benzo(a)pyrene in water

One hundred mL of water samples was added to 250 mL of a separatory funnel and 10 g of sodium chloride was added and dissolved by gentle shaking. Benzo(a)pyrene- d_{12} (100 ng; 10 ppm \times 10 μ L) was added as internal standard. To the funnel 50 mL of *n*-hexane was added. The separatory funnel was agitated rigorously in a vertical shaker (D0647, Dongyang Inc., Seoul, Korea) for 20 min. After the separation of *n*-hexane layer by discarding an aqueous layer, 50 mL of 5% sodium chloride solution was used for cleansing the organic layer. The organic layer was transferred to a 100 mL round flask and evaporated to about 3 mL with rotary evaporator (Buchi 461, Switzerland). This solution was transferred to a 15 mL centrifuge tube with tapering end and the round flask was washed twice with small amount of *n*-hexane for combining washed solution to the centrifuge tube. The combined solution was evaporated to 100–200 μ L of final volume. One μ L of the solution was injected to the GC/MSD by an auto liquid sampler.

Extraction of benzo(a)pyrene in soil and sediment

To 40 mL of centrifuge tubes 10 g of soil and sediment was added and mingled homogeneously with the same amount of anhydrous sodium sulfate. Benzo(a)pyrene- d_{12} (100 ng; 10 ppm \times 10 μ L) was added as internal standard. The soil and sediment was extracted with 20 mL of methanol by a shaker (Edmund Buchler 7400, Tubingen, Germany) for 20 min and centrifuged (RT 6000B, Sorvall Inc., New town, CT, USA) for 15 min at 1,660 \times g. The methanol layer was transferred to a 100 mL round flask and evaporated to the final volume of about 3 mL which was transferred to a 15 mL centrifuge tube. To the centrifuge tube 1 mL of 5% sodium chloride solution was added and mixed in a vortex-mixer. After 5 mL of *n*-hexane was added, the tube was extracted by a shaker, centrifuged and put into a freezer (–30°C) for the separation of the organic layer. The organic layer was transferred to a centrifuge tube with tapering end

and evaporated for concentration until the final volume reached to about 100~200 μL . One μL of this solution was injected to the GC/MSD by the auto liquid sampler.

RESULTS

Recoveries and accuracy

To further validate the precision and accuracy of the method recovery testing was carried out by spik-

ing a known amount of the standard to distilled water and soil, which do not contain the test chemicals. Recovery of BaP was determined at 5, 10 and 50 ng spiked in 100 mL water and 10 and 50 ng spiked in 10 g soil. The results obtained are shown in Table 1. In water matrix, the recovery of BaP was ranged from 94.8 to 101.7% and the relative standard deviation (RSD) values were below 15.43% in all cases. Recoveries in soil of BaP was about 93% and the RSD of all recovery experiments was less than 10.49%. The precision of the method is therefore very good.

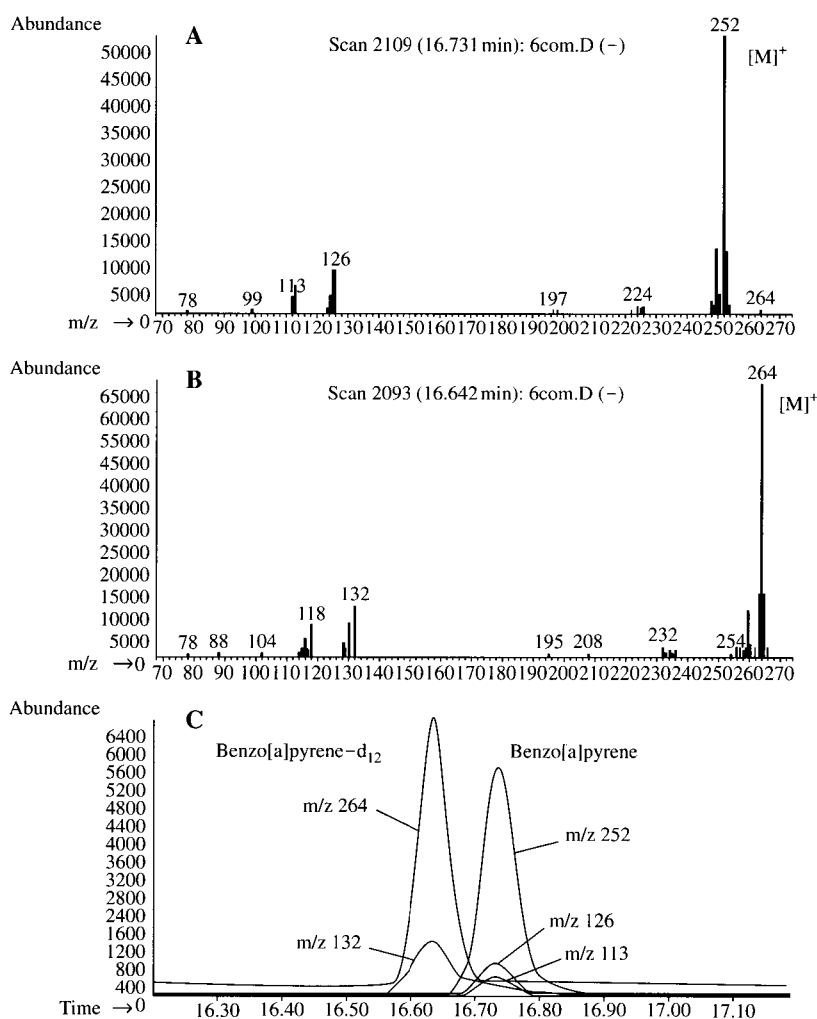


Fig. 1. Gas chromatograph/mass spectrometry (GC/MS) spectra of benzo(a)pyrene (A) and benzo(a)pyrene-d₁₂ (B); and ion chromatograms (C) obtained by GC/MS/selected ion monitoring of benzo(a)pyrene (m/z 113, 126 and 252). benzo(a)pyrene-d₁₂ (m/z 132 and 264) were used as an internal standard for the analysis of benzo(a)pyrene.

Selection of quantification ions

Selected ion values for analysis of BaP in water and soil was m/z 113, m/z 126 and m/z 252 ($[M]^+$) for BaP and m/z 132 and m/z 264 ($[M]^+$) for BaP- d_{12} as shown in Fig. 1. Ion values used for quantification was m/z 252 for BaP. Retention times were 16.64 min for BaP- d_{12} and 16.73 min for BaP.

Ion chromatograms for the selected ions of BaP in water (Fig. 2) and soil (Fig. 3) were shown to compare with those for BaP-free blanks. For the selected

ions for BaP (m/z 252), no major interfering peaks were found.

Linearity of standard calibration curves

The linear range of GC-MS method for the determination of BaP was tested by increasing amounts of standards at 1, 5, 10, 25, 50, 100, 250 ng/100 mL water and fixed amount (100 ng/100 mL) of internal standards in distilled water, and the analytes were extracted and concentrated as described above. Linear equations of

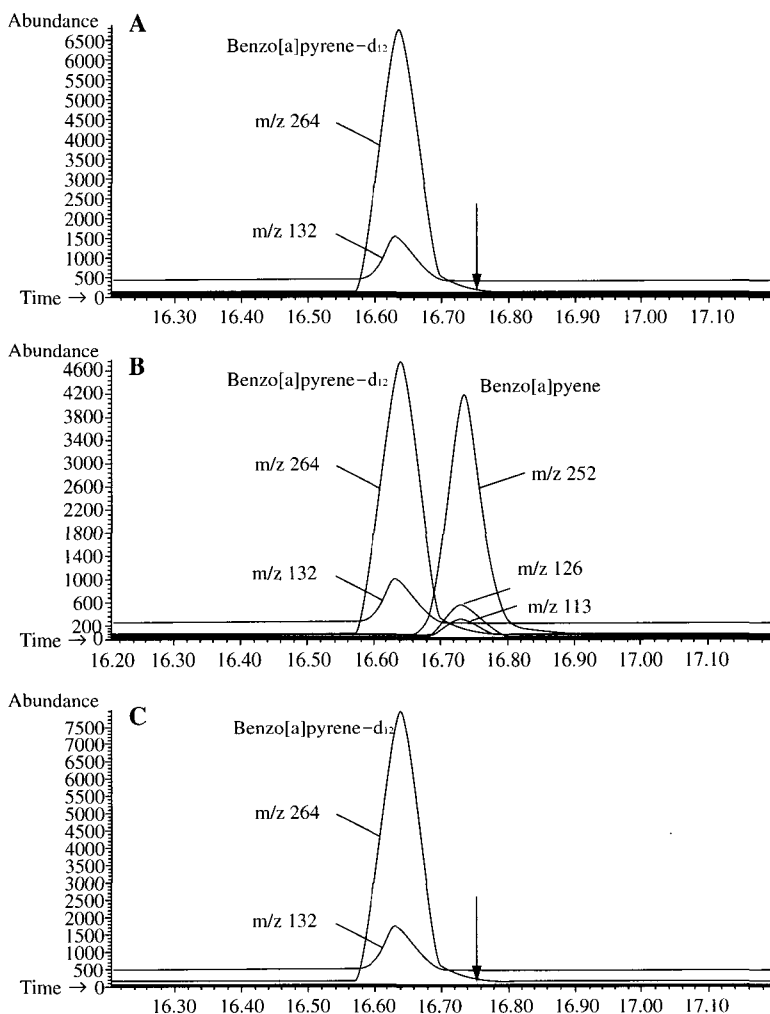


Fig. 2. Ion chromatograms obtained from water blank (A), water fortified standards (B, 250 ng for benzo(a)pyrene spiked), and a river water sample (C). The values of characteristic ions selected for the quantification of benzo(a)pyrene was m/z 252. Internal standard of 100 ng was added.

BaP calibration curves were obtained by linear regression. The curve was plotted concentrations at x-axis with the area ratio of BaP to internal standards BaP-d₁₂ at y-axis. The experiments were repeated in soil (10 g) matrices. The curves showed a good linearity ($r^2 > 0.996$, 7 points, $n = 3$ per point) at concentration ranges spiked (Table 2). Linear equation in water was determined to $y = 0.0086x - 0.0100$ ($r^2 = 0.9995$) for BaP. In soil, linear equation was $y = 0.0084x + 0.2194$ ($r^2 = 0.9962$) for BaP.

Limit of detection and limit of quantification

The limits of detection (LOD), defined as the peak having a signal-to-noise ratio of 3, was measured by integrating peak area for analyte in 10 independent performances with distilled water and soil. The limit of quantification (LOQ) is the lowest BaP concentration the can be quantified in a sample with acceptable precision under the stated operational conditions of the method. LOQ was determined as

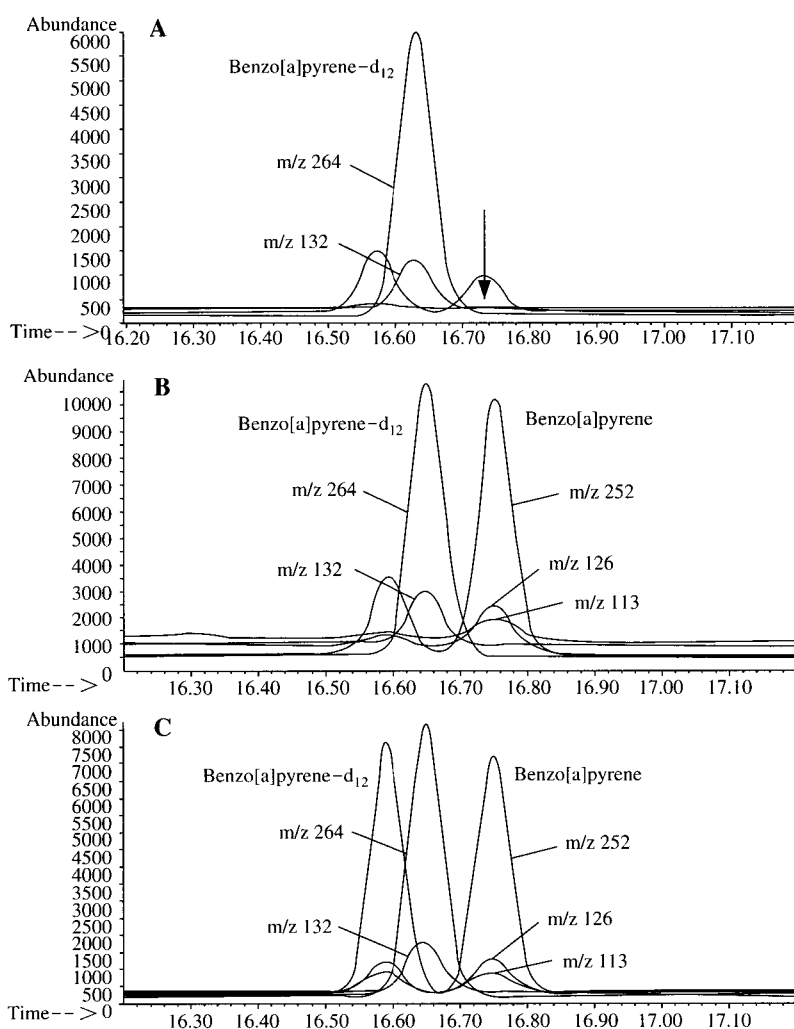


Fig. 3. Ion chromatograms obtained from soil blank (A), soil fortified standards (B, 250 ng for benzo(a)pyrene spiked), and a soil sample (C). The values of characteristic ions selected for the quantification of benzo(a)pyrene was m/z 252. Internal standard of 100 ng was added.

Table 2. Calibration and detection limit of benzo(a)pyrene in water and soil

Matrix	Conc. range	y = ax + b			LOD ^a	LOQ ^b
		a	b	r ²		
Water (µg/L)	0.01 ~ 2.50	0.0086	-0.0100	0.9995	0.01	0.04
Soil (µg/kg)	0.1 ~ 25	0.0084	0.2194	0.9962	0.1	0.4

^a LOD : Limit of detection, ^b LOQ : Limit of quantification

the analyte concentration corresponding to a signal-to-noise ratio of 10. The method described showed very good sensitivity with detection limit in the low 1 ng/100 mL in water and 1 ng/10 g in soil for BaP. Based on this detection limits, LOQ for BaP was estimated to 4 ng/100 mL water and 10 g soil (Table 2).

The analysis of benzo(a)pyrene in water, soil and sediment

Water, sediment and soil samples collected in 2000 at nation-wide sites were analyzed. Among 35 soil sites, BaP was detected in 6 sites (17.1%). The BaP concentration ranged from 0.5 to 223.5 µg/kg with a mean of 49.43 µg/kg. In water, BaP was not detected because it has the value below quantification limit in all samples. Also, BaP was not found in all sediment samples. Advantages of this method are using small amounts of sample (100 mL of water and 10 g of soil and sediment), are time-saving and simple with a similar sensitivity, compared to the previous method (Jobling *et al.*, 1995) which employed 1,000 mL of water and 20 g of soil, as well as required distillation and purification steps.

DISCUSSION

The characteristic ions of BaP were selected based on their spectra of which the ions of base peak and molecular weight or ions with high intensity such as base peaks were used for quantification and confirmation (Fig. 1). It is useful to select more than 3 ions for a compound in the process of its confirmation.

Characteristic ions of m/z 252 for BaP was used for the quantification of target compounds. Although other ions also can be used for the quantification, the ion of m/z 252 gives better sensitivity than other ions for determination of BaP and was selected for using the advantage of molecular weight. The use of internal standards of radio-labelled compound (deuterated form) of BaP was essential for better reproducibility of data.

In soil, a light solvent like hexane may be not mixed with soil and absorbed well to soil. The penetration of a solvent into soil and solubility of chemicals to the solvent may become important factors for the extraction of soil. For soil analysis, using methanol at first step without hexane extraction as the second step did not get good results if small amount of water could not be removed completely. This problem was solved by addition of hexane extraction step.

PAHs are highly hydrophobic and lipophilic compounds ($\log K_{ow} = 3-8$) with very low water solubility (Karcher, 1988). For these reasons, PAHs are often strongly bound to particles in surface and ground water systems causing soil or sediment contamination, and their concentrations in water are very low (Nesterova *et al.*, 1982). Hence, soil and sediments in lake, river and marine systems are the primary repositories for PAHs (and other hydrophobic contaminants) gaining widespread attention in the past decades (Yunker and Mc Donald, 1995; Bence *et al.*, 1996).

High molecular weight PAHs, those with four or more rings are found adsorbed onto particulate matter released during combustion (Oanh *et al.*, 1999), unlike the most volatile PAHs, those with two or three rings, which are emitted in the gaseous phase and

therefore carried farther from their source than large PAHs (Van Metre *et al.*, 2000). PAH concentration in soil correlates significantly with the corresponding levels in air (Vogt *et al.*, 1987), therefore, PAH determination in soil may provide important information on the environmental pollution state. Our method is relatively simple and rapid to determine BaP in water, soil and sediment samples.

CONCLUSION

Analytical method for determining BaP in soil, sediment and water samples was developed by gas chromatography/mass spectrometry. This method is simple, time-saving and reliable enough to analyze BaP in small amounts of environmental samples such as soil and ground water. This method may be applied for monitoring the exposure of BaP to the environment.

REFERENCE

- Aamot E, Steinnes E and Schmid R. Polycyclic aromatic hydrocarbons in Norwegian forest soils: Impact of long range atmospheric transport, *Environ Pollution* 1996; 92: 275–280.
- Bakker MI, Casado B, Koerselman JW, Tolls J and Kolloffel C. Polycyclic aromatic hydrocarbons in soil and plant samples from the vicinity of an oil refinery, *Science of the Total Environment* 2000; 263: 91–100.
- Bence AE, Kvenvolden KA and Kennicutt MC. Organic geochemistry applied to environmental assessment of Prince William Sound, Alaska after the Exxon Valdez oil spill—a review, *Organic Geochemistry* 1996; 24: 7–42.
- Benner BA, Bryner Jr NP, Wise SA, Mulholland GW, Lao RC and Fingas MF. Polycyclic aromatic hydrocarbon emission from the combustion of crude oil on water, *Environ Sci Technol* 1990; 24: 1418–1427.
- Eo YW, Park HM, Ryu JC, Hong JK, Kim YM and Lee KB. Analysis for polybrominated biphenyls (PBBs) existing in water, soil and sediment samples of Korea, *Environmental Analysis* 2000; 3(2): 109–115.
- Freeman DJ and Catteil FCR. Wood burning as source of atmospheric polycyclic aromatic hydrocarbons, *Environ Sci Technol* 1990; 24: 1581–1585.
- Halsall CJ, Sweetman AJ, Barrie LA and Jones KC. Modeling the behavior of PAHs during atmospheric transport from the UK to the Arctic, *Atm Environ* 2001; 35: 255–267.
- Hatjian BJ, Edwards JW, Harrison J, Williams FM and Blain PG. Ambient, biological, and biological effect monitoring of exposure to polycyclic aromatic hydrocarbons (PAHs), *Toxicology Letters* 1995; 77: 271–279.
- Jobling S, Reynolds T, White R, Parker MG and Sumpter JP. A variety of environmentally persistent chemicals including some phthalate plasticizers are weakly estrogenic, *Environmental Health Perspective* 1995; 103(6): 582–587.
- Karcher W. *Spectral Atlas of Polycyclic Aromatic Compounds* vol. 2, Kluwer, Dordrecht, The Netherlands, 1988.
- Kennish MJ. Poly-nuclear aromatic hydrocarbons. In: *Ecology of Estuaries: Anthropogenic Effects*, CRC Press, Boca Raton 1992; 133–181.
- Kwon OS, Kim EY and Ryu JC. Simultaneous determination of 4-nitrotoluene and benzophenone in ground water and soil by gas chromatography–mass spectrometry, *Analytical Science and Technology* 2003; 16(1): 59–69.
- Kwon OS, Kim EY and Ryu JC. Analysis of Benzophenone in Sediment and Soil by Gas Chromatography/Mass Spectrometry, *Kor J Environ Toxicol* 2001; 16(3): 121–126.
- Kwon OS, Rhee HK and Ryu JC. Analysis of Benzophenone in Water by Gas Chromatography/Mass Spectrometry, *Environmental Analysis* 2000; 3(1): 1–5.
- Lee HK, Kwon OS and Ryu JC. Analysis of 4-Nitrotoluene in Water by Gas Chromatography/Mass Spectrometry, *Kor J Environ Toxicol* 2000; 15(1, 2): 45–51.
- Lim LH, Harrison RM and Harrad S. The contribution of traffic to atmospheric concentrations of polycyclic aromatic hydrocarbons, *Environmental Science and Technology* 1999; 33: 3538–3542.
- Lunde G and Bjorseth A. Polycyclic aromatic hydrocarbons in long-range transported aerosol, *Nature* 1977; 268: 518–519.
- Magi E, Bianco R, Ianni C and Di Carro M. Distribution of polycyclic aromatic hydrocarbons in the sediments of the Adriatic Sea, *Environ Pollut* 2002; 119(1): 91–98.
- McElroy AE, Farrington JW and Teal JM. Bioavailability of polycyclic aromatic hydrocarbons in the aquatic environment. In: U. Varanasi, Editor, *Metabolism of poly-*

- cyclic aromatic hydrocarbons in the aquatic environment. CRC Press, Boca Raton 1989; 1-40.
- Nam JJ, Song BH, Eom KC, Lee SH and Smith A. Distribution of polycyclic aromatic hydrocarbons in agricultural soils in South Korea, *Chemosphere* 2003; 50(10): 1281-1289.
- National Institute for Environmental Studies (NIES). Analytical methods for endocrine disruptors, Japan. 1998.
- Neff JM. Polycyclic aromatic hydrocarbons in the aquatic environment, sources: fates and biological effects. Applied Science, London, UK 1979.
- Nesterova NP, Den'Gia YM and Vorob' Yev VA. Aromatic hydrocarbons in surface waters of the north Atlantic Ocean and Mediterranean Sea, *Oceanology* 1982; 22: 709-711.
- Oanh NTK, Reutergardh LB and Dung NT. Emission of polycyclic aromatic hydrocarbons and particulate matter from domestic combustion of selected fuels, *Environmental Science and Technology* 1999; 33: 2703-2709.
- Park H, Agustin MR, Park HM, Ryu JC, Lim BJ and Lee KB. Monitoring on Residual Volatile Organic Compounds Remaining in Industrial Waste Water, *J Korean Soc Environ Analysis* 2003; 6(3): 169-177.
- Simpson CD, Cullen WR, Quinlan KB and Reimer KJ. Methodology for the determination of priority pollutant polycyclic hydrocarbons in marine sediments, *Chemosphere* 1995; 31: 4143-4155.
- Smith KEC, Green M, Thomas GO and Jones KC. Behavior of sewage sludge-derived PAHs on Pasteur, *Environ Sci Technol* 2001; 35: 2141-2150.
- Suess MJ. The environmental load and cycle of polycyclic aromatic hydrocarbons, *Sci Total Environ* 1976; 6: 239-250.
- Van Brummelen TC, Verweij SA, Wedzinga SA and Van Gestel CAM. Enrichment of polycyclic aromatic hydrocarbons in forest soils near a blast furnace plant, *Chemosphere* 1996; 32: 293-314.
- Van Metre PC, Maher BJ and Furlong ET. Urban sprawl leaves its PAH signature, *Environmental Science and Technology* 2000; 34: 4064-4070.
- Vogt NB, Brakstad F, Thrane K, Nordenson S, Krane J, Aamot E, Kolset K, Esbensen K and Steinnes E. Polycyclic aromatic hydrocarbons in soil and air: Statistical analysis and classification by SIMCA method, *Environ Sci Technol* 1987; 21: 35-44.
- Wakeham SG, Schaffner C and Giger W. Polycyclic aromatic hydrocarbons in recent lake sediment--II. Compounds derived from biogenic precursors during early diagenesis, *Geochim Cosmochim Acta* 1980; 43: 27-33.
- Yang GP. Polycyclic aromatic hydrocarbons in the sediments of the South China Sea, *Environ Pollut* 2000; 108 (2): 163-171.
- Yunker MB and Mc Donald RW. Composition and origins of polycyclic aromatic hydrocarbons in the McKenzie River and the Beaufort Sea shelf, Arctic 1995; 48: 118-129.