Determination of Benzo [*a*] pyrene in Airborne Particulates by Automated Thermal Desorption Gas Chromatography

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More than eighty kinds of polynuclear aromatic hydrocarbons (PAHs) have been identified in airborne particulates. Not a few PAHs have been recognized as carcinogens. Among these, benzo [*a*] pyrene (B [*a*] P), which is one of the strongest carcinogens, has been regarded as an important analytical target in airborne particulates.

The analytical techniques utilized to determine PAHs include gas chromatography, mass spectrometry, thin-layer chromatography, liquid chromatography, fluorescence spectrometry and combinations of these techniques. In most cases, the first analytical procedure is started by conventional solvent extraction of the organic compounds from the airborne particulate sample collected on a glass-fiber filter.

An ultrasonicator was effectively used to reduce extraction time.^{1,2} Vacuum sublimation was also proposed as an alternative rapid extraction method of PAHs in airborne particulate matter.³ These preliminary treatments still take more than 40 or 50 min. Furthermore, these off-line extraction methods are to some extent subjected to sample loss and/or contamination from the glass-ware, solvents and the laboratory atmosphere.

On the other hand, a gas-phase thermal desorption was proposed as a rapid, sensitive and contamination-free sample preparation method.⁴ By this solvent-free method, the whole analytical procedure was drastically simplified, although the off-line thermal desorption was still adopted. Recently, the authors proposed a new automated thermal desorption system for gas chromatography of volatile components in environmental and polymeric samples.⁵ By this system, the volatile components in sample matrices stripped dynamically by on-line thermal desorption were followed by gas chromatographic separation.

In the present work, the automated thermal desorption system was applied to make rapid determination of B [*a*] P in airborne particulates. The photodegradation processes of some PAHs on the glass-fiber filter, which might cause inaccurate and/or

less precise analytical results, were also studied and discussed.

Experimental

The details of the automated thermal desorption system were published elsewhere.⁵ Airborne particulate samples were collected on glass-fiber filters (25×20 cm=500 cm²) by a high-volume air sampler through which passed 2000–2700 m³ of environmental air from the Kawasaki area. A piece of each filter sample (50 mmφ=19.6 cm²) was subjected to the thermal desorption at 330°C for 8 min. The trap column packed with Chemipack-RH (80–100 mesh) was used for the trapping of thermally desorbed components at room temperature. The subsequent selective stripping of the trapped components was done by adjusting its temperature at 230°C for 4 min (purging) and then at 290°C for 5 min (sampling). The subsequent gas chromatographic separation of the selectively introduced fraction was carried out by using a glass column (6 mm o.d.×1 mm i.d.×80 cm long) packed with Gaschrome-Q (80–100 mesh) coated with 2.5wt% of a liquid crystal stationary phase; BBBT [*N,N'*-(*p*-butoxybenzylidene)- α,α' -*bi-p*-toluidine].⁶ The temperature of the column was programmed from 190 to 270°C at 10°C/min. The other detailed sequential steps for the desorption system are basically the same as those described.⁵ Standard samples for determination were prepared by depositing aliquot amounts of the benzene solution of analytical grade PAH reagents on pieces of fresh glass-fiber filter by a micropipet.

Results and Discussion

The B [*a*] P values in twelve different particulate samples were cross-checked by the proposed thermal desorption method and a conventional one in which

Fig. 1 Correlation diagram of B[a]P values estimated for twelve airborne particulate samples by thermal desorption gas chromatography and a conventional method.

Fig. 2 Decomposition rate of independently deposited B[a]P and B[e]P under daylight as a function of exposure time.

the ultrasonicator-aided solvent extraction was followed by thin-layer chromatographic separation and fluorescence detection. Figure 1 shows the correlation of the values estimated by this method against those by the conventional one. Although a slight systematic deviation is observed, there exists a fairly acceptable correlation between them. In the present method, the total analysis time for one run was about 50 min, including the baking-out time for the next run, and the relative standard deviation for five repeated runs was within 8%. Furthermore, the proposed method does not require any preliminary sample treatment and is highly sensitive since it uses only a couple of percents of one sheet glass-fiber. Therefore, this technique could be applicable to practical monitoring of the level of environmental B[a]P.

One possible source of the systematic error could be the photo-degradation of PAHs during the sample treatment for analysis under illumination in the laboratory. Three kinds of glass-fiber sheets (1.0×4.0

Fig. 3 Decomposition rate of coexisting B[a]P and B[e]P under daylight as a function of exposure time.

mm) are prepared, on which 300 ng of B[a]P, 300 ng of benzo[e]pyrene (B[e]P) and 300 ng of B[a]P plus 300 ng of B[e]P are deposited from the benzene solutions with a micropipet. These sheets are exposed to daylight for different times up to 60 min. The contents of B[a]P and B[e]P are determined by thermal desorption-gas chromatography. As shown in Fig. 2, both B[a]P and B[e]P are fairly rapidly photo-oxidized under daylight, and about 30% is decomposed after 60 min of exposure. On the other hand, as shown in Fig. 3, when B[a]P and B[e]P coexist on the same glass-fiber sheet, the decomposition rate of B[a]P is much enhanced, while that of B[e]P remains almost unchanged. This phenomenon suggests that the co-existence of B[e]P, which is the usual case in environmental samples, significantly sensitizes the photo-oxidation of B[a]P. The same tendency was observed when the samples are exposed to illumination of fluorescent lamps. Therefore, in case of determining trace amounts of PAHs in environmental samples, the effect of such photo-oxidation reactions has to be considered during their sampling, storage and treatment.

References

1. G. Chatot, R. Danay-Caye and R. Fontages, *J. Chromatogr.*, **72**, 202 (1972).
2. H. Matsushita, K. Arashidani and T. Handa, *Bunseki Kagaku*, **25**, 263 (1976).
3. H. Matsushita, Y. Esumi and K. Yamada, *Bunseki Kagaku*, **19**, 951 (1972).
4. H. P. Burchfield, E. E. Green, R. J. Wheeler and S. M. Billedeau, *J. Chromatogr.*, **99**, 697 (1978).
5. S. Tsuge, Y. Matsushima, N. Watanabe, A. Shintai, K. Nishimura and Y. Hoshika, *Anal. Sci.*, **3**, 101 (1987).
6. G. M. Janini, G. M. Muschink and W. L. Zlelinski, Jr., *Anal. Chem.*, **48**, 809 (1976).

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