

## Determination of PAHs in atmospheric particles by direct thermal desorption and comprehensive two dimensional gas chromatography coupled to quadrupole mass spectrometer

Ieda T<sup>1</sup>, Ochiai N<sup>1</sup>, Sasamoto K<sup>1</sup>, Fushimi A<sup>2</sup>, Hasegawa S<sup>2</sup>, Tanabe K<sup>2</sup>, Kobayashi S<sup>2</sup>, Hoshi J<sup>3</sup>, Amano S<sup>3</sup>, Sasaki Y<sup>3</sup>.

<sup>1</sup>GERSTEL K.K., Tokyo, 152-0031, Japan; <sup>2</sup>National Institute for Environmental Studies, Tsukuba, 305-8506 Japan; <sup>3</sup>Tokyo Metropolitan Research Institute for Environmental Protection, Tokyo, 136-0075 Japan.

### Abstract

A method is described for determination of selected PAHs in atmospheric particles including size-resolved particles (Diameter of particles:  $D_p$ : 0.029-10.12 $\mu\text{m}$ , >10.12 $\mu\text{m}$  (13 fractions, S1-13)). The method is based on thermal desorption (TD) of a sample followed by comprehensive two-dimensional gas chromatography (GC x GC) coupled to quadrupole mass spectrometer (qMS): TD - GC x GC - qMS. A limited scan range ( $m/z$  177-280) was used for acquiring a sufficient number of data points per peak (> 6 points), which allowed a 27 Hz scanning rate. The method showed good linearity ( $r^2 > 0.988$ ) and high sensitivity (limit of quantification (LOQ) : < 10 pg) for most of the target PAHs. Quantitative analysis of selected 7 PAHs in several total suspended particle samples were performed by use of the TD - GC x GC - qMS. The results were compared with those of a conventional method. Also, the method was applied to the analysis of size-resolved particle samples (including nano-particle fraction).

### Introduction

Polycyclic aromatic hydrocarbons (PAHs) in atmospheric particles have received increased attention because some of these compounds have some potential to cause health problems. Especially, particle matters smaller than 100 nanometers in diameter are thought to pose the greater health risk because such small particles can reach deeply into the lungs. Therefore, quantification of size-resolved particles is important to estimate their toxicity.

Recently, thermal desorption (TD) has been used for extracting organic compounds from atmospheric particles. It has many advantages, e.g. no off-line sample preparation, small sample amount, high sensitivity, in comparison with the traditional solvent extraction procedure. Hays et al reported the analysis of PAHs in size-resolved particles from wood combustion with the TD - 1DGC - MS<sup>1</sup>, however, the method could not provide a sufficient resolution for a separation of large numbers of organic compounds in unresolved complex mixtures (UCM).

In these several years, comprehensive two dimensional gas chromatography (GC x GC) was applied to the analysis of atmospheric particles<sup>2</sup> expecting to its high separation power and high sensitivity. In GC x GC, typical peak widths at the end of the second column can be 100–600ms. Consequently, the detector for GC x GC is required very fast data acquisition capabilities and an ideal data acquisition rate for GC x GC is more than 100 Hz. Thus, time-of-flight mass spectrometry (TOFMS) has been selected as a detector for GC x GC when structural information is needed. Recently, quadrupole mass spectrometer (qMS) operating with a limited scan range, has been successfully applied to a detector for GC x GC. Several authors reported the applicability of a qMS with a rapid-scanning (10,000 Da/s) for GC x GC. A sufficient number of data points per peak (> 6 points) for quantification could be obtained with a limited scan range which allowed approximately 20-33 Hz acquisition rate<sup>2</sup>.

In this study, TD - GC x GC - qMS with a limited scan range was applied to determination of PAHs in atmospheric particles. Seven PAHs in several total suspended particle samples were analyzed with the method and the results were compared with those of a conventional method<sup>3</sup>: Ultra sonic extraction - high performance liquid chromatography (USE - HPLC). Also, quantitative analysis of 12 PAHs in several size-resolved particle samples (includes nano-particle fraction) was performed by the proposed method.

### Sampling

Total suspended particles

Sampling was carried out at the Yawatayama air-pollution monitoring station at the roadside in Tokyo, Japan. Total suspended particles were collected for 24 hours (May, August, November, 2004 and February 2005) by high volume air sampler using heat-treated (550°C, 8 hours) grass fiber filter at a flow rate of 1000 L/min<sup>4</sup>.

Size-resolved particles

Sampling was performed at the Ikegami-Shincho crossing in Kawasaki, Japan. A roadside air-pollution monitoring station is located near the crossing, where one of the worst atmospheric pollution levels in Japan was observed. Size-resolved particles (13 size fractions; S1-S13) were collected for 24 hours (January 27-28, 2004) with low pressure impactor (LPI) using ungreased aluminum foils as the collection substance<sup>5</sup>.

### Materials

U.S. EPA 610 PAHs mixture containing 16 analytes was purchased from Supelco (Bellefonte, PA, USA). NAGINATA internal standard mixture containing a 5 deuterated PAH mixture was purchased from Kanto Kagaku (Tokyo, Japan). All solvents used were high-purity pesticides grade (Kanto Kagaku).

### Methods

A sample filter was cut into pieces (total suspended particles: 0.25 cm<sup>2</sup>, size-resolved particles: 5.6-36 µg-PM), and placed in a thermal desorption grass liner with glass frit. One micro-liter of the internal standard solution (100 ng mL<sup>-1</sup>) was added for quantification. Thermal desorption of a sample was performed by programming a TDS2 (Gerstel, Mulheim an der Ruhr, Germany) from 50 °C (held for 1 min) to 350 °C (held for 3 min) at 60 °C min<sup>-1</sup> with 50 mL min<sup>-1</sup> desorption flow. Desorbed compounds were cryo-focused at -100 °C on a quartz wool packed liner in the CIS4 (Gerstel) for subsequent analysis by 6890 GC-5973 inert MSD with high performance electronics (Agilent Technologies, Palo Alto, CA, US) equipped with a Zoex KT2004 loop type modulator (Zoex corporation, Houston, TX, USA). Scan ranges were set from *m/z* 177 to 280 (acquisition rate: 27 Hz) for quantification and *m/z* 54 to 280 (acquisition rate: 18 Hz) for qualification. After desorption, the inlet temperature was programmed from -100 °C to 330 °C (held for 10 min) at 720 °C min<sup>-1</sup> to inject trapped compounds onto the analytical column. Injection was performed in the splitless mode with a 3 minute splitless time. During the injection, the GC was held at the initial temperature of 50 °C. The GC was programmed from 50 °C (held for 3 min) to 350 °C at 5 °C min<sup>-1</sup>. The separation was performed on the column set of a BPX-5 fused silica capillary column (30 m x 0.25 mm i.d., 0.25 µm film thickness, SGE International, Australia) as the first column and a BPX-50 fused silica capillary column (1 m x 0.10 mm i.d., 0.10 µm film thickness, SGE International) as the second column. Helium was used as a carrier gas supplied at 2.5 mL min<sup>-1</sup>. The modulation period was 6 s. The hot gas temperature was programmed from 250 °C to 350 °C at 10 °C min<sup>-1</sup>. The hot gas duration time was 300 ms.

### Results and Discussion

For quantification of 12 PAHs by the TD - GC x GC - qMS, linearity of calibration curve, limit of quantification (LOQ) and repeatability were examined. Results are shown in Table 1 together with selected ion for the quantification. Correlation coefficients (*r*<sup>2</sup>) of calibration curves at five levels between 10 and 500 pg were in the range of 0.980 to 0.998. LOQ (S/N=10) was calculated based on the signal-to-noise ratio obtained for the largest sliced peak in the raw chromatogram of lowest standard of calibration curve. Very low LOQ in the range of 0.79-11 pg was obtained. Repeatability was also assessed by replicate analyses (n = 5) of the middle level standard of the calibration curve (100 pg). The repeatability of retention times for both first column and second column was very good and in the range of 0.0-0.86 % as relative standard deviation (RSD). The repeatability of quantification was also good and in the range of 2.8-8.2 % as RSD.

Table 1. Linearity, repeatability and LOQ for selected PAHs by TD - GC x GC - qMS.

	Abbreviation	$m/z$ <sup>a</sup>	Linearity ( $r^2$ )	Repeatability <sup>b</sup> (RSD %, n = 5)			LOQ <sup>c</sup> (pg)
				Response	$t_R$ (min)	$t_R$ (sec)	
Phenanthrene	PHE	178	0.995	6.7	0.12	0.86	0.79
Anthracene	ANT	178	0.994	6.9	0.00	0.00	1.2
Fluoranthene	FLU	202	0.998	2.8	0.13	0.00	0.58
Pyrene	PYR	202	0.995	4.6	0.00	0.00	0.85
Benzo [a] anthracene	BAA	228	0.995	3.7	0.00	0.75	4.4
Chrysene	CRY	228	0.997	3.5	0.11	0.00	3.7
Benzo [b] fluoranthene	BBKF	252	$\Sigma = 0.981$	$\Sigma = 4.2$	$\Sigma = 0.00$	$\Sigma = 0.73$	$\Sigma = 9.2$
Benzo [k] fluoranthene							
Benzo [a] pyrene	BAP	252	0.980	4.9	0.00	0.00	5.2
Indeno [1,2,3-cd] pyrene	IND	276	0.988	8.2	0.00	0.00	4.6
Dibenzo [a,h] anthracene	DAH	278	0.988	6.6	0.00	0.53	11
Benzo [g,h,i] perylene	BHG	276	0.994	4.5	0.00	0.00	7.1

<sup>a</sup> Selected ions used for method validation

<sup>b</sup> Repeatability was assessed by replicate analyses (n = 5) of the middle level of calibration curve (100 pg).

<sup>c</sup> The signal-to-noise ratio obtained for the smallest sliced peak in the raw chromatogram at the lowest level was used to calculate the LOQ at a signal-to-noise ratio of ten.

Figure 1 shows the two-dimensional total ion chromatogram and the two-dimensional reconstructed ion chromatograms (RIC; sum of six selected ions for PAHs;  $m/z$  178, 202, 228, 252, 276 and 278) of total suspended particles (November, 2004). The targeted PAHs were clearly detected, although the sample amount needed for the TD - GC x GC - qMS was a quarter of that for the USE - HPLC.

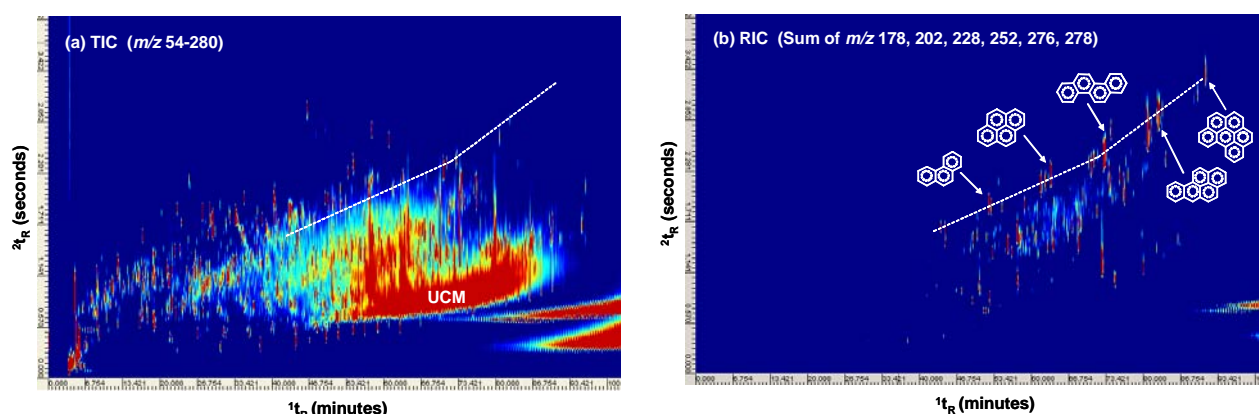


Figure 1. 2D map of GC x GC chromatograms obtained by TD - GC x GC - qMS  
(a) TIC, (b) RIC (sum of selected ions;  $m/z$  178, 202, 228, 252, 276, 278)

The method was applied to determination of 7 selected PAHs in 4 total suspended particle samples (seasonal representatives). Figure 2 shows the results obtained by the TD - GC x GC - qMS and the USE - HPLC. Concentrations determined by the TD - GC x GC - qMS were slightly higher than those measured by the USE - HPLC. Almost identical seasonal variation was observed in the results obtained by the two methods.

Relative concentrations of PYR (PYR / total PAHs) measured by the TD - GC x GC - qMS and the USE - HPLC were in the ranges of 0.06-0.11 and 0.05-0.13, respectively, for the 4 samples. Except for BAP, the relative concentrations showed good agreement between the two methods. Relative concentration of BAP by the TD - GC x GC - qMS ranged from 0.18 to 0.22, which was apparently higher than 0.10 - 0.14 by the USE - HPLC.

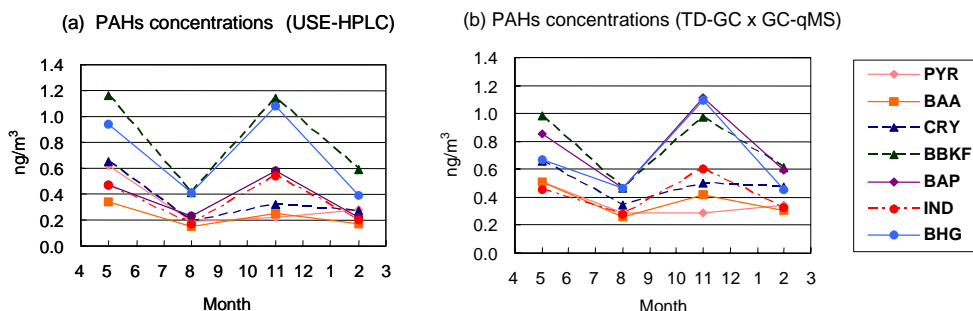


Figure 2. Concentrations of 7 selected PAHs in 4 total suspended particle samples (seasonal representatives) determined by the USE-HPLC and the TD-GC x GC-qMS

Finally, the TD-GC x GC-qMS was applied to several size-resolved particle samples such as S1 ( $D_p$  29-58 nm; 5.6  $\mu\text{g-PM}$ , nano-particle fraction), S3 ( $D_p$  102-163 nm; 36  $\mu\text{g-PM}$ ) and S9 ( $D_p$  1.60-2.44  $\mu\text{m}$ ; 36  $\mu\text{g-PM}$ ). Though the sample amount was so small (5.6  $\mu\text{g-PM}$ ), all 12 PAHs were detected in nano-particles. Figure 4 shows 2D mass chromatograms (sum of  $m/z$  178, 202, 228, 252, 276, and 278 of S1) obtained by the TD-GC x GC-qMS in 3D landscape-plot. Figure 5 shows the comparison of the PAHs concentrations per PM mass among the size resolved samples. For all PAHs, the concentrations per PM mass in S1 (4.2-39  $\text{pg } \mu\text{g-PM}^{-1}$ ) were remarkably higher than those in larger size particles such as S3 (0.44-20  $\text{pg } \mu\text{g-PM}^{-1}$ ) and S9 (1.6-17  $\text{pg } \mu\text{g-PM}^{-1}$ ). For BHG, which has the lowest vapor pressure among the measured PAHs, the concentration per PM mass was remarkable in S1<sup>5</sup>.

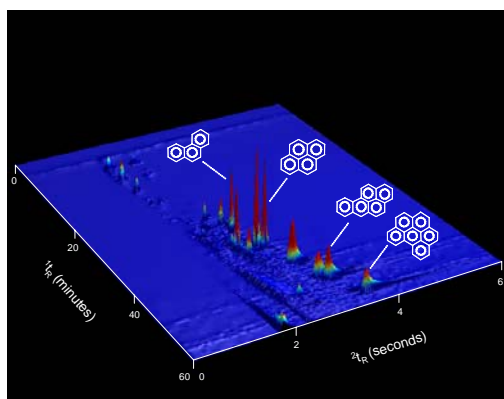


Figure 4. 3D map of a GC x GC mass chromatograms obtained by TD-GC x GC-qMS (sum of selected ions;  $m/z$  178, 202, 228, 252, 276, 278)

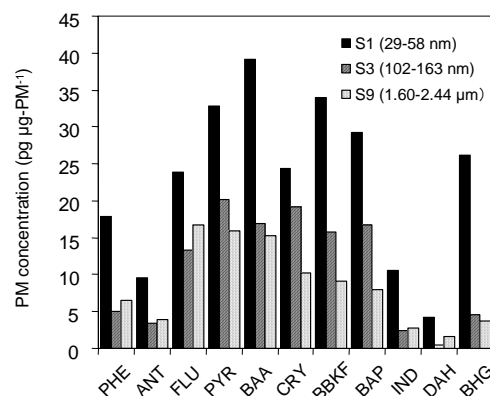


Figure 5. Comparison of the PAHs concentrations per PM mass among size-resolved particles

### Acknowledgements

The authors thank our colleagues Mr. Hirooki Kanda of GERSTEL K.K for his support and technical comment.

### References

1. Hays M. D, Richard J. L, *Trends Anal. Chem.* 2006; 26:88.
2. Adahchour M, Beens J, Vreuls J.J, Brinkman U. A, *Trends Anal. Chem.* 2006; 25:438
3. Manual of analytical methods for hazardous air pollutants, Ministry of the Environment, Japan, 1999
4. S. Amano, J. Hoshi, Y. Sasaki, Tokyo Metropolitan Research Institute for Environmental Protection, Report 2003, p161-
5. N. Ochiai, T. Ieda, K. Sasamoto, A. Fushimi, S. Hasegawa, K. Tanabe and S. Kobayashi, *J. Chromatogr. A*, 1150 (2007) 13