

Trace Analysis of Polycyclic Aromatic Hydrocarbons Using Gas Chromatography–Mass Spectrometry Based on Nanosecond Multiphoton Ionization

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Gas chromatography/resonance-enhanced multiphoton ionization/time-of-flight mass spectrometry (GC/REMPI-TOFMS) using an ultraviolet nanosecond laser was employed in the trace analysis of polycyclic aromatic hydrocarbons (PAHs). A standard sample that contained 16 PAHs on the priority list of the Environmental Protection Agency of the United States of America (U.S. EPA) was measured. A sample of river water that had been pretreated by means of solid-phase extraction was analyzed by GC/MS based on electron impact ionization (EI) and REMPI to evaluate the performance of the analytical instrument. The results suggested that REMPI is superior to EI for soft ionization, and suppresses the background signal due to aliphatic hydrocarbons. Thus, GC/REMPI-TOFMS is a more reliable method for the determination of PAHs present in the environment.

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Introduction

Polycyclic aromatic hydrocarbons (PAHs) are chemical compounds that are emitted from natural and anthropogenic sources, such as traffic, industry, and domestic heating. Due to their high toxicity and carcinogenicity, PAHs have been monitored as persistent organic pollutants (POPs) by several research institutions.^{1,2} There are many PAH isomers, which are present in the environment at low concentrations. The combination of resonance-enhanced multiphoton ionization (REMPI) and time-of-flight mass spectrometry (TOFMS) provides a useful method for trace analysis because of their superior selectivity and sensitivity.³⁻⁶ In this approach, the PAH molecules absorb the first photon for excitation and the second photon for subsequent ionization from the intermediate levels. Therefore, this method can realize the selective determination of aromatic hydrocarbons using an ultraviolet (*e.g.*, 266 nm) laser for resonance excitation,⁷⁻⁹ and can also reduce interference arising from aliphatic hydrocarbons. A laser with a short pulse duration has been utilized for the ionization of aromatic compounds.^{10,11} For example, a femtosecond laser was successfully used for the efficient ionization of chlorinated and brominated PAHs^{12,13} before relaxation by internal conversion and intersystem crossing to triplet levels. Unfortunately, the size, monetary cost, and difficulties associated with the

maintenance and operation of such lasers prevent the practical use of this method in environmental analysis. In addition, an intense laser sometimes leads to unfavorable dissociation of both neutral and ionic species through multiphoton processes, thus making sensitive and reliable analysis more difficult.¹⁴ To date, a number of studies have investigated the laser parameters that affect the ionization yield of PAHs and related compounds.¹⁵⁻¹⁷

In the present study, REMPI-TOFMS was combined with gas chromatography (GC) for the trace analysis of 16 PAHs on the priority list of the U.S. EPA. We employed a small-frame, low-cost nanosecond laser emitting at 266 nm for the practical trace analysis of PAHs. A sample of river water that had been pretreated by means of solid phase extraction (SPE) was analyzed using both electron impact ionization (EI) and REMPI to evaluate the performance of these methods.

Experimental

Reagents and chemicals

A standard mixture of PAHs found on the priority list of the U.S. EPA, *i.e.*, acenaphthene (ACE), acenaphthylene (ACY), anthracene (ANT), benzo(*a*)anthracene (BaA), benzo(*b*)fluoranthene (BbF), benzo(*k*)fluoranthene (BkF), benzo(*ghi*)perylene (BPY), benzo(*a*)pyrene (BaP), chrysene (CHR), dibenzo(*a,h*)anthracene (DBA), fluoranthene (FLT), fluorene (FLU), indeno(1,2,3-*cd*)pyrene (IND), naphthalene (NAP), phenanthrene (PHE), and pyrene (PYR), was prepared at a concentration of 2 mg/mL in a mixture of methylene chloride

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and benzene (1:1 v/v). A mixture of deuterated internal standards (I.S.) (acenaphthene-*d*₁₀, phenanthrene-*d*₁₀, and chrysene-*d*₁₂) prepared at a concentration of 0.5 mg/mL in acetone was purchased from Supelco (Bellefonte, PA). These solutions were diluted stepwise in acetonitrile. All solutions were stored in containers made of amber glass at 4°C. Analytical-grade acetonitrile, methanol, and dichloromethane were purchased from Kanto Kagaku (Tokyo). Deionized water was obtained from a Milli-Q water purification system (Millipore, Molsheim, France).

SPE

A surface water sample was collected from a river located in the northern part of Kyushu in Japan. The water sample was spiked with 0.5 mL (200 pg/μL) of I.S. to investigate the recovery of PAHs in the SPE process. The water sample (500 mL) was passed through an SPE cartridge (Sep-Pak Plus C18) conditioned with 10 mL of dichloromethane, 10 mL of methanol, and 10 mL of Milli-Q water at a flow rate of 10 mL/min. The PAHs were eluted with 5 mL of dichloromethane from cartridge connected to a drying cartridge (Sep-Pak Dry Cartridge). The solvent in the eluted solution was evaporated under nitrogen flow, followed by the addition of 0.5 mL of acetonitrile for GC/MS.

















GC/REMPI-TOFMS

The experimental setup used in this study was described in a detail elsewhere.^{7,12,18} One microliter of the sample solution was injected into a GC system (Agilent Technologies, 6890N) using an auto-sampler (Agilent Technologies, 7683B), followed by separation using an HP-5 capillary column (length, 30 m; i.d., 0.32 mm). Helium was used as a carrier gas at a constant flow rate of 1 mL/min. The temperature of the column was increased from 40 to 120°C at a rate of 20°C/min, and was then held constant for 1 min. The temperature was then increased from 120 to 250°C at a rate of 5°C/min, and was held for 3 min, followed by an additional increase to 280°C at a rate of 5°C/min, and was held for 10 min. Both the temperatures of the injection port and the transfer line were maintained at 300°C. The analyte eluted from the GC was introduced into a linear-type TOFMS as an effusive molecular beam.¹⁹ The experimental condition of TOFMS was optimized using the signal arising from the bleeding chemical species emitting from the capillary column, and the mass resolution was determined to be *ca.* 1000. An assembly of microchannel plates (Hamamatsu, F4655-11) was utilized for detection of the ions induced by multiphoton ionization. The fourth harmonic emission of a Nd:YAG laser (Crylas, 266 nm, 1 ns, 23 μJ, 1 kHz) was employed as an ionization source. The signal for the construction of a mass spectrum was measured using a digital oscilloscope (Tektronix DPO7104, 1 GHz, 20 GS/s). Two-dimensional data were recorded by means of a digitizer (Agilent Technologies, Acqiris AP240, 1 GHz, 1 GS/s). The final results were analyzed and displayed using LabVIEW software.

GC/EI-MS

For a comparison, a gas chromatograph combined with a quadrupole-type mass spectrometer (GC/MS-QP2010 Plus, Shimadzu) was utilized to measure PAHs in the river-water sample. The temperature program was set to be almost the same as that of GC/REMPI-TOFMS, except for the final temperature (280°C → 320°C). An HP-5ms capillary column (length, 30 m; i.d., 0.25 mm) was employed in the present study. The EI voltage was adjusted to 70 eV. The temperatures of the ion source and the transfer line were maintained at 200 and

Table 1 Parameters of 16 PAHs on the EPA list and analytical results obtained using GC/REMPI-TOFMS

Elution order	Compound	Structure	<i>M_w</i>	τ_s in jet/ ns ^a	τ_s in sol/ ns ^b	PAHs in the river
1	NAP		128	nf	105	D
2	ACY		152	nf	nf	ND
3	ACE		154	nf	46	ND
4	FLU		166	nf	10	ND
5	PHE		178	76	61	D
6	ANT		178	8	6	ND
7	FLT		202	38	53	D
8	PYR		202	1400	650	D
9	BaA		228	nf	45	D
10	CHR		228	nf	45	D
11	BbF		252	nf	44	D
12	BkF		252	nf	11.3	D
13	BaP		252	270	49	D
14	IND		276	nf	nf	D
15	DBA		278	nf	37	D
16	BPY		276	nf	203	D

a. Ref. 21; nf, not found.

b. Ref. 22; nf, not found.

c. D, detected; ND, not detected.

320°C, respectively. The PAHs were measured under the selected-ion-monitoring (SIM) mode at *m/z* values that corresponded to the molecular ions of these compounds.

Results and Discussion

Standard sample

The characteristics of the PAHs are summarized in Table 1, which also includes the singlet-excited-state lifetimes (τ_s) reported in the literature. Intersystem crossing and internal conversion are the primary determinants of the photophysical properties of the compound.²⁰ There are only a few reports on the lifetime of isolated PAHs in the gas phase, although the lifetimes of PAHs in the condensed phase are well known.²¹ The lifetimes of PAHs in solution would be similar to, or slightly shorter than, those in the gas phase due to an additional relaxation pathway from collisions between the analyte and solvent molecules.²² Therefore, the lifetimes of the 16 PAHs (8 – 1400 ns in the gas phase and 6 – 650 ns in the condensed phase, except for ACY and IND) were much longer than the pulse width of the laser used in the present study (1 ns). Thus, no obvious degradation of the ionization efficiency would be expected, even with use of a nanosecond laser. Figure 1 shows a two-dimensional display of the data for the standard mixture sample that contained 16 PAHs (200 pg/μL). The signal was measured under slightly saturated conditions to enhance the signals arising from ACY, ANT and FLT. It should be noted that the background signal was negligible and fragment ions were rare. The limits of detection (LODs) were 18, 2.2 and 1.9 pg for ACY, ANT and FLT, respectively, and were well below 1 pg for the other PAHs. The higher LOD obtained in this study for ACY (18 pg) would arise from a small REMPI signal under

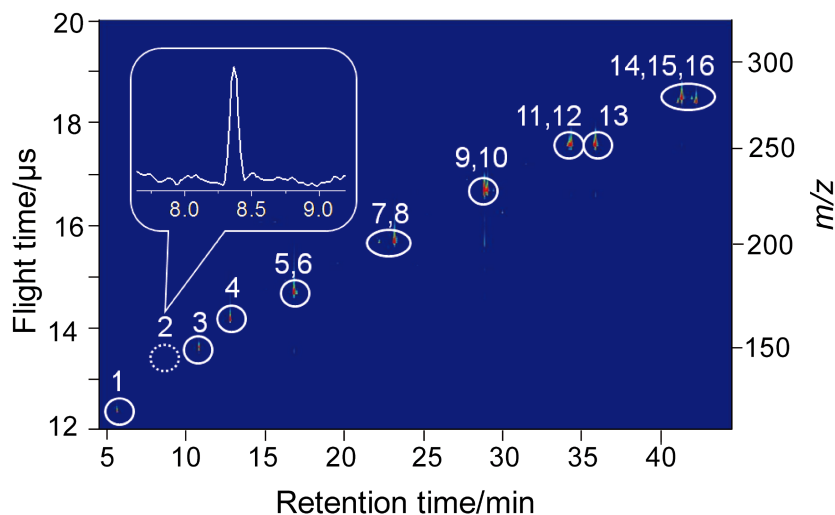


Fig. 1 Two-dimensional display for a standard mixture sample of PAHs (200 $\mu\text{g}/\mu\text{L}$ for each) measured by GC/REMPI-TOFMS. Assignment: 1, NAP; 2, ACY; 3, ACE; 4, FLU; 5, PHE; 6, ANT; 7, FLT; 8, PYR; 9, BaA; 10, CHR; 11, BbF; 12, BkF; 13, BaP; 14, IND; 15, DBA; 16, BPY.

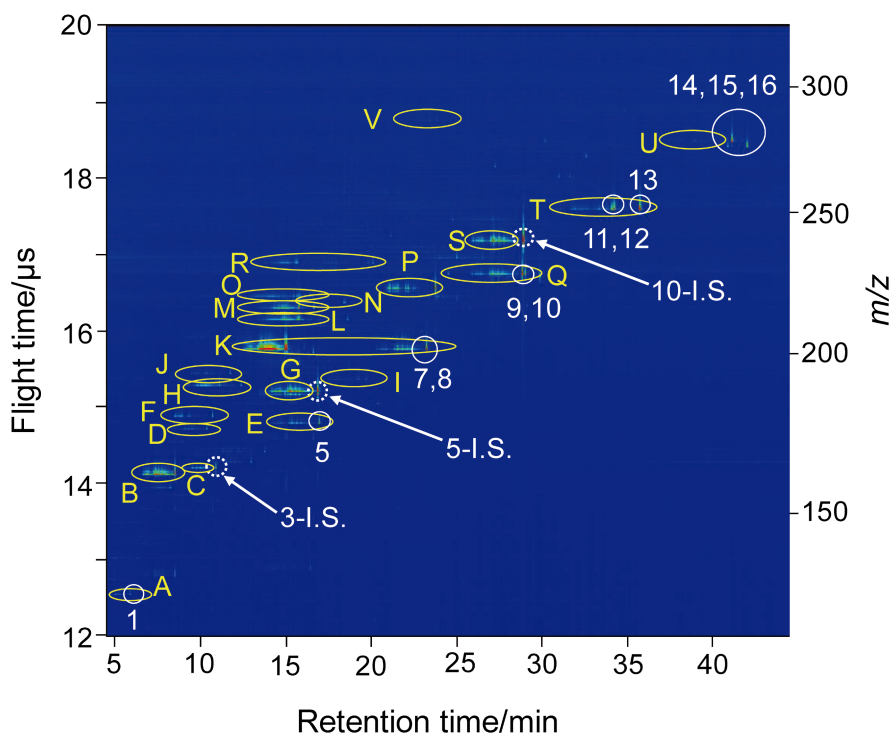


Fig. 2 Two-dimensional display for a surface water sample measured by GC/REMPI-TOFMS. Assignment: 1, NAP; 5, PHE; 7, FLT; 8, PYR; 9, BaA; 10, CHR; 11, BbF; 12, BkF; 13, BaP; 14, IND; 15, DBA; 16, BPY. Note: Suggested chemical formulae for letters A - V are given in Table 2.

nanosecond laser ionization.²¹ This unfavorable result is attributed to the short excited-state lifetime of ACY, since the molar absorptivity of this compound in the vicinity of 266 nm is nearly the same as that of NAP.²³ In ACY molecule, the major deactivation pathway from the S_1 state is an efficient $S_1 \rightarrow S_0$ internal conversion, and the lifetime of the S_1 state has been determined to be 345 ps and 0.2 ns,^{24,25} which were shorter than the pulse width of the laser in the present study. The LODs obtained in this study are similar to those reported by Rhodes

et al.: the LODs of 7 PAHs obtained using a nanosecond laser (10 ns) are in the range of 0.2 - 5.0 μg .²⁶ It is noted that Hauler *et al.* have obtained a LOD of 80 ppt for NAP with on-line measurements and LODs in the 100 μg range for PHE, CHR, and some other PAHs using a laser desorption technique.²⁷

Real sample

A sample derived from surface water was spiked with three deuterated compounds, which served as internal standards,

Table 2 Assignment of PAHs found in surface-water samples using GC/REMPI-TOFMS

	PAH No.	M_w	Formula		PAH No.	M_w	Formula
A	1	128	$C_{10}H_8$	N		218	$C_{17}H_{14}$
B		162	$C_{12}H_{18}$			218	$C_{16}H_{26}$
C		164	$C_{12}H_{20}$	O		220	$C_{17}H_{16}$
		164	$C_{13}H_8$			220	$C_{16}H_{28}$
D	3-I.S.	164	$C_{12}D_{10}$	P		223	$C_{16}H_{17}N$
		176	$C_{14}H_8$			223	$C_{15}H_{29}N$
		176	$C_{13}H_{20}$			223	$C_{14}H_{13}N_3$
E	5	178	$C_{14}H_{10}$	Q	9,10	228	$C_{18}H_{12}$
		178	$C_{13}H_{22}$	R			232
F		180	$C_{14}H_{12}$			232	$C_{17}H_{28}$
		180	$C_{13}H_{24}$	S	10-I.S.	240	$C_{18}D_{12}$
G	5-I.S.	188	$C_{14}H_{20}$				240
		188	$C_{14}D_{10}$			240	$C_{18}H_{24}$
H		190	$C_{15}H_{10}$			240	$C_{17}H_{36}$
		190	$C_{14}H_{22}$	T	11,12,13	252	$C_{20}H_{12}$
I		192	$C_{15}H_{12}$				252
		192	$C_{14}H_{24}$			252	$C_{18}H_{36}$
J		194	$C_{15}H_{14}$	U	14,16	276	$C_{22}H_{12}$
		194	$C_{14}H_{26}$				276
K	7,8	202	$C_{16}H_{10}$			276	$C_{20}H_{36}$
		202	$C_{15}H_{22}$			278	$C_{22}H_{14}$
		202	$C_{13}H_{18}N_2$			278	$C_{21}H_{26}$
L		212	$C_{16}H_{20}$			278	$C_{20}H_{38}$
		212	$C_{15}H_{32}$			278	$C_{19}H_{22}N_2$
M		216	$C_{17}H_{12}$	V		286	$C_{22}H_{22}$
		216	$C_{16}H_{24}$			286	$C_{21}H_{34}$

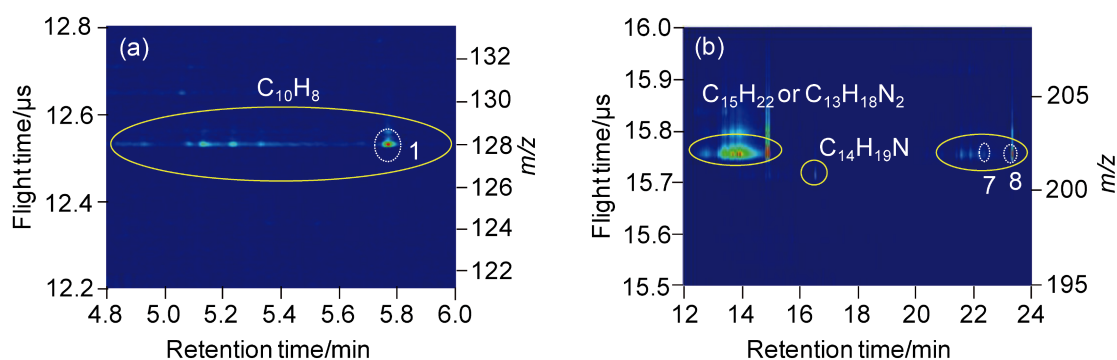


Fig. 3 Two-dimensional display for (a) NAP (1) and its isomers, (b) FLT (7), PRY (8), and other contaminants contained in the surface water sample measured by GC/REMPI-TOFMS.

and was analyzed by GC/REMPI-TOFMS. A two-dimensional display of the data is shown in Fig. 2, in which 12 PAHs (solid line) on the U.S. EPA list and the internal standards (dotted line) are evident. In addition, a large number of PAHs were also observed and were assigned from the flight times (the m/z values) and the retention times of these compounds. The observed peaks were grouped into categories specified from A to V (elliptical circle) in Fig. 2. The molecular weight, formula, and possible assignments are listed in Table 2.

We noticed that several of the chromatograph peaks had m/z values that were identical to those of the PAHs on the U.S. EPA list. These peaks might have been due to isomers of the PAHs on the priority list. Therefore, the signal peaks should be carefully identified, even though the REMPI technique had superior selectivity. For example, several NAP isomers with the chemical formula $C_{10}H_8$ are shown in Fig. 3(a). They could be assigned to either 1*H*-indene-1-methylene, azulene, or

2-methylene-2*H*-indene, which could be confirmed using the data obtained by EI (see Fig. 6). A more serious case was observed for FLT; there were several peaks with larger signal intensities than that of FLT (see Fig. 3(b)). These isomers could be either acephenanthrylene, aceanthrylene, or their analogues. These peaks could not be measured using the EI technique (see Fig. 6). These results suggest that laser ionization is more efficient for these compounds than fluoranthene, which could be due to their absorption characters. Thus, much attention should be paid to accurate identification of the peaks that appear at retention times of 12 - 15 min, because the compounds that give rise to these peaks have the chemical formula $C_{15}H_{22}$ or $C_{13}H_{18}N_2$, and have nearly identical m/z values. There is another issue that is important to consider during compound identification. The deuterated internal standard is thought to have the same retention time as that of its corresponding native compound. However, this assumption might not be correct. As shown in Fig. 4,

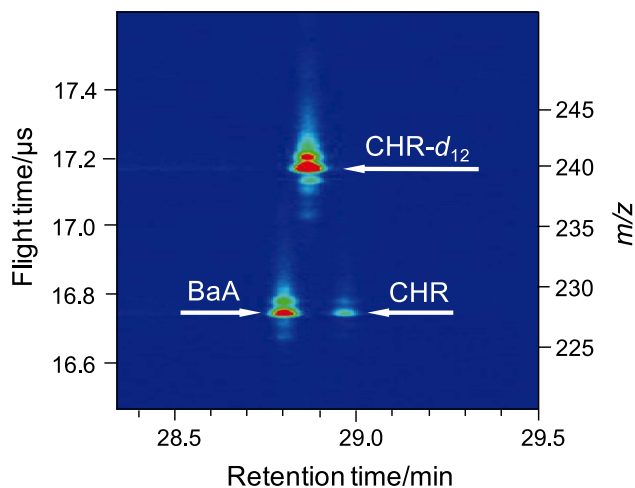


Fig. 4 Two-dimensional display for BaA and CHR contained in a surface-water sample measured by GC/REMPI-TOFMS. The internal standard (CHR- d_{12}) was added to the sample.

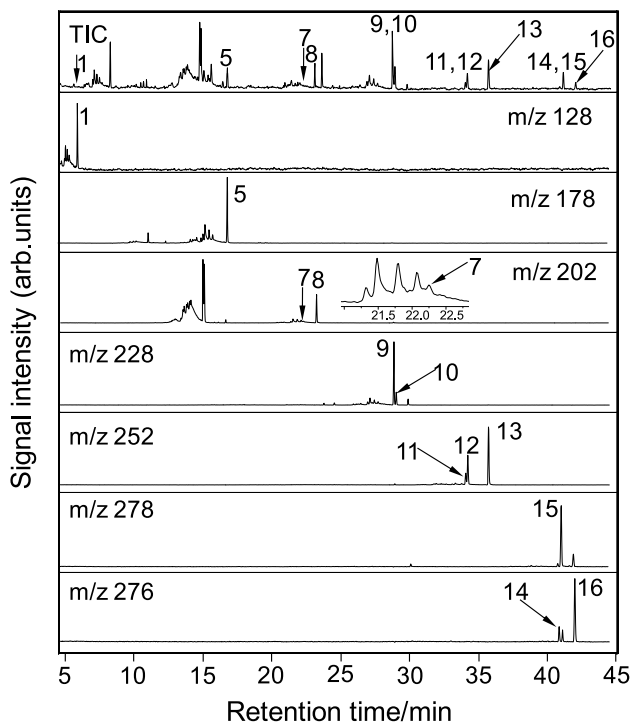


Fig. 5 TIM and SIM chromatograms of PAHs collected from river water measured by GC/REMPI-TOFMS. Assignment: 1, NAP; 5, PHE; 7, FLT; 8, PYR; 9, BaA; 10, CHR; 11, BbF; 12, BkF; 13, BaP; 14, IND; 15, DBA; 16, BPY. An internal standard was added to the sample.

the retention time of CHR- d_{12} was very different from that of CHR- h_{12} , and was similar to that of BaA. Therefore, the internal standards should be carefully used for identifying the signal peaks.

Mass chromatograms of the surface water sample are shown in Fig. 5. The total ion monitoring (TIM) chromatogram was displayed by extracting the data between $m/z = 100 - 400$. The selected ion monitoring (SIM) chromatograms at the specified

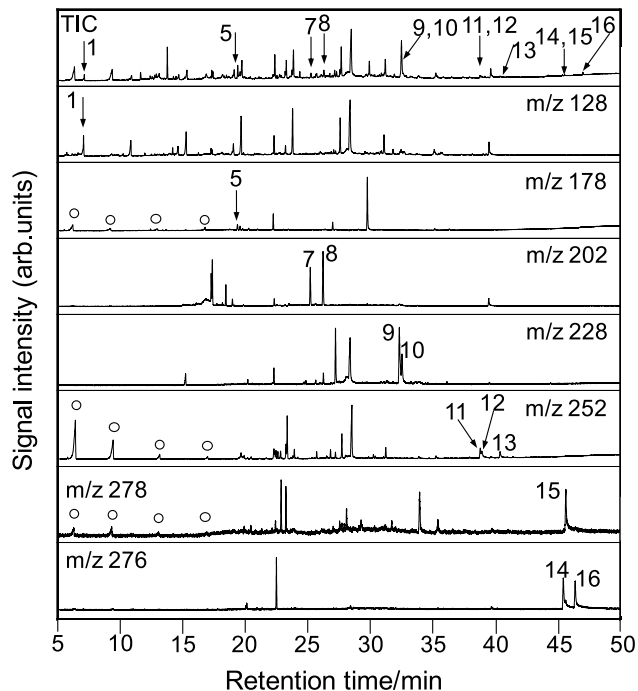


Fig. 6 TIM and SIM chromatograms of PAHs collected from the river water measured by GC/EI-QMS. Assignment: 1, NAP; 5, PHE; 7, FLT; 8, PYR; 9, BaA; 10, CHR; 11, BbF; 12, BkF; 13, BaP; 14, IND; 15, DBA; 16, BPY. An internal standard was added to the sample.

m/z values are shown below the TIM chromatogram. The chromatograph peaks were assigned from the retention times measured for the standard PAHs. A similar study was performed using GC/EI-QMS, and the results are shown in Fig. 6. Although the signals accumulated at the m/z values that corresponded to the 16 PAHs on the U.S. EPA list were used to construct the TIM chromatogram (cf., the signals between $m/z = 100 - 400$ were accumulated in the TIM chromatogram based on REMPI), numerous peaks in addition to the noise were observed in the TIM chromatogram measured by GC/EI-QMS. The more complicated chromatogram might be due to more serious fragmentation under EI (70 eV). Even in the SIM chromatogram, a large number of peaks were observed in EI, as shown in the second picture ($m/z = 128$) in Fig. 6. It should be noted that the first four peaks specified by the circles in the SIM chromatograms obtained at $m/z = 178, 252$ and 278 had exactly the same retention times. Thus, it was concluded that these peaks were due to the fragmentation of single components. The appearance of so many peaks in EI causes two problems: a difficulty with the identification and fragmentation of a molecular ion that reduces sensitivity. Thus, REMPI is a useful method for the trace analysis of PAHs in the environment because of its superior selectivity and sensitivity.

Conclusions

A feasibility study of using a nanosecond laser to analyze PAHs in the environment was conducted. The fourth harmonic emission of the Nd:YAG laser emitting at 266 nm was successfully employed to measure 16 PAHs on the U.S. EPA list. Owing to the unique properties of this method, *i.e.*, high

selectivity and soft ionization, the effect of interference in the determination of PAHs was minimal. Furthermore, the singlet-state lifetimes of PAHs are longer than the pulse width of the laser (1 ns) in most cases, thus allowing the trace analysis of PAHs at pg levels, even using a small-frame, low-cost, and easy-to-use laser. Further improvements in both the selectivity and the sensitivity could be achieved by converting the laser wavelength based on the fifth harmonic generation (213 nm) and simulated Raman scattering (frequency shift, 4155 cm⁻¹).

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