Simplified and Sensitive Detection of Polycyclic Aromatic Hydrocarbons by Flash Desorption Mass Spectrometry

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Flash desorption and negative ion chemical ionization (NCI) mass spectrometry have been combined to study the detection of polycyclic aromatic hydrocarbons, such as benzo[*a*]pyrene, at high sensitivity. Such detection below pg orders can be readily accomplished by modifying the ionization chamber to increase the seal, and also by employing rapid heating of the sample loaded filament at a rate of 1000°C/s. This method enabled a several-fold sensitivity increase over both flash desorption with electron ionization and GC/MS with NCI. Furthermore, by setting the sampling points to 20 per second to cope with rapid ionization, a repeatability of within 10% was achieved, thereby allowing quantification utilizing an internal standard. Despite isomeric influences, simultaneous detection of homologs was also possible.

Keywords Flash desorption mass spectrometry, negative ion chemical ionization, polycyclic aromatic hydrocarbons, benzo[*a*]pyrene

Flash desorption has been initially developed to increase the volatility of thermally labile and/or involatile compounds. The method makes use of vaporization proceeding preferentially to thermal degradation in the high temperature region, when heat is applied rapidly (e.g. ambient to above 1000°C within a second) to the sample on a filament. Accordingly, the method has been applied almost exclusively to thermally labile molecules such as hormones, peptides and sucharides.¹⁻⁵ In applying this method to thermally stable compounds of high boiling points, vaporization occurs within an extremely short period of time which in turn allows the detection of exceptionally sharp peaks. Hence, a highly sensitive detection is expected when combined with selected ion monitoring (SIM), although no reports have appeared as yet. HPLC with fluorescence detection and GC/MS are available as means for analyzing polycyclic aromatic hydrocarbons (PAHs). The authors have reported that negative ion chemical ionization (NCI) enables the detection of specific PAHs such as benzo[*a*]pyrene (B[*a*]P) at extremely high sensitivity.^{6,7} In this study, flash desorption has been combined with NCI to investigate the detection of PAHs at high sensitivity. Consequently, a method with characteristics such as enhanced sensitivity over GC/MS and exceedingly short analysis time was established.

Experimental

Instrument

A Finnigan-MAT 4500 GC/MS was equipped with a

Finnigan-MAT direct exposure probe (DFP) for flash desorption. DFP consists of a powder supply, control unit and a probe body as shown in Fig. 1. The probe with a filament (approximately 0.1 mm ϕ , made of rhenium) attached to the tip, which is inserted into the ionization chamber within the ion source, is similar in appearance to the solid sample direct insertion probe. The ionization chamber depicted in Fig. 2(a) consists of a cap-shaped ion volume and an adaptor to fix and hold it in place. The adaptor possesses an aperture to enable the insertion of the filament. The ion source illustrated in Fig. 2(b) with the probe inserted, accommodates the adaptor and the ion volume. The aperture for the DEP is 4.6 mm ϕ , exceeding that of the solid sample direct insertion probe, which is 2.5 mm ϕ . Along with standard equipment, an ion volume with the collector aperture sealed, and an adaptor with a 3.3 mm ϕ aperture

Fig. 1 Direct exposure probe for flash desorption.

Fig. 2(a) Ionization chamber. a-d: aperture for various uses; a, 0.7 ϕ (filament); b, 0.85 ϕ (outlet of ions); c, 2.3 ϕ (inlet for GC eluents/reagent gas); d, 1.5 ϕ (collector).

Fig. 2(b) Ion source with probe inserted for flash desorption. a, filament for flash desorption; b, filament for ionization; c, ceramic insulators; d, ion source block; e, adaptor; f, ion volume; g, collector electrodes; h, lens electrodes.

were employed to ensure the tightness of the ionization chamber.

A Finnigan-MAT TSQ-70 was also utilized for comparing sensitivity.

Materials

All standard reagents of special grade purchased from Tokyo Kasei Kogyo, Wako Pure Chemicals or Aldrich Chemical were used without further purification. The reagents were dissolved in benzene (Wako Pure Chemicals, special grade) at a concentration of 1–10 ng/ μ l and thereafter mixed and/or diluted before usage. Methane (Takachiho Kogyo, 99.95%) was used as the reagent gas. Deuterium labeled d_{12} -B[a]P (MSD Isotope) was employed as an internal standard for preparing the calibration graph.

Measurement

After loading 1–2 μ l of the sample solution onto

the tip of the filament attached to the probe, 5 mA (equivalent of heating up to approximately 50°C) of current was applied for 30 s to evaporate the solvent. The probe was inserted into the ionization chamber at once where it was heated at 10–1000 mA/s for sample volatilization. The filament current for flash desorption was maintained at 1000 mA for 10–20 s. One thousand mA corresponds to 1000°C. The filament for ionization was switched on immediately before initiating the heating. It was possible to use the one flash desorption filament repeatedly over one hundred times. Although the ionization was mainly carried out in the NCI mode, under which PAHs possessing high electron affinities are expected to be sensitively detected, electron ionization (EI) and positive ion chemical ionization (PCI) were also performed for comparison. The ion source temperature was 100°C regardless of the ionization mode, and the ionization chamber pressure in performing CI was maintained between 0.1–0.8 Torr (usually at 0.4 Torr) (1 Torr=133.3 Pa). TSQ-70 was operated in EI and NCI with an ion source temperature of 130°C and an ionization chamber pressure of 0.5 Torr in the NCI mode.

Benzo[a]pyrene has been analyzed by means of GC/MS [DB-5 (0.25 mm i.d. $\times$ 7 m), 150°C upwards at a rate of 10°C/min] and also conventional solid sample direct introduction (standard solution was loaded onto the capillary for solid sample direct introduction after which the solvent was removed by evaporation and thereafter heated up to 300°C at a rate of 30°C/s) in the NCI mode for comparison with the current method.

Results and Discussion

Comparison of sensitivity among ionization modes

Sensitivity in detecting B[a]P was compared among the employed ionization modes using the standard adaptor. Ten picograms of B[a]P loaded onto the filament was heated at a rate of 1000 mA/s and detected by SIM in the EI, PCI and NCI modes at M^+ (m/z 252), MH^+ (m/z 253) and M^- (m/z 252), respectively. The signal to noise (S/N) ratios of the detected peaks were 40, 130 and 40, the peak profiles are shown in Fig. 3. An oxide ion of rhenium (ReO_4^-) appearing at m/z 251 was found to affect the NCI detection. These results were somehow unexpected, since it is known that the NCI mode exceeds the PCI mode considerably in terms of sensitivity under optimum GC/MS (with an exclusive adaptor, measured at an ionization chamber pressure of 1 Torr) conditions.⁷ That the ionization chamber lacked tightness was considered responsible for this phenomenon, i.e. the 4.6 mm ϕ aperture of the ionization chamber adaptor used in the flash desorption mode, contributes in losing the thermal electrons required for NCI. Some loss of sample was also anticipated. Hence the aperture diameter was adjusted to 3.3 mm ϕ , the minimum size in order not to hinder filament insertion, thereby reducing the area of the aperture to approximately a half. The

Fig. 3 Detection of B[a]P by flash desorption using various ionization method with normal adaptor. (a), EI (M^+ , m/z 252); (b), PCI (MH^+ , m/z 253); (c), NCI (M^- , m/z 252); sample, B[a]P (10 pg); heating rate of filament, 1000 mA/s (1000°C/s).

Fig. 4 Detection of B[a]P by flash desorption NCI with modified adaptor. (a), B[a]P (10 pg); (b), B[a]P (100 fg); heating rate of filament, 1000 mA/s (1000°C/s).

aperture for the collector of the ion volume was also clogged. Under identical measuring conditions, the S/N ratio in the NCI mode was improved by over an order of magnitude to 420. The profile is shown together with that measured on 100 fg (S/N ratio is about 5) of sample, in Fig. 4. The peak due to an oxide ion of rhenium could be reduced by aging the filament to a level which would not affect practical measurements.

The experiments carried out in the EI and NCI modes using 10 pg of B[a]P on TSQ-70 exhibited S/N ratios of approximately 1000 in both cases, implying that detection of several tens of fg is readily achievable using a new instrument. NCI by the usual GC/MS and solid sample direct introduction showed S/N ratios of 80 and 2 respectively on 10 pg of B[a]P, demonstrating the

aptitude of flash desorption for the trace analysis of high boiling points compounds such as B[a]P.

Various parameters

Temperature programming. The rate heating (the rate of increasing the filament current) was investigated using 10 pg of B[a]P. As a consequence, both the sharpness of the peak and the S/N ratio were enhanced at higher programming rates as shown in Fig. 5(a) where the detection sensitivity (peak area) has improved. For example, the sensitivity at 1000 mA/s was more than twice that when measured at 100 mA/s.

Ionization chamber pressure. The dependence of ionization chamber pressure on detection sensitivity was investigated using 10 pg of B[a]P and benzo[k]fluoranthene isomer. The results for B[a]P are shown in Fig. 5(b). In either case, the sensitivity increases swiftly from around 0.1 Torr, reaching a maximum at 0.3 Torr and 0.4 Torr for B[a]P and benzo[k]fluoranthene, respectively, then declining moderately thereafter. Therefore, an ionization chamber pressure of 0.4 Torr was employed

Fig. 5(a) Relationship of heating rate of filament versus detected relative peak profile area. The maximum value of relative peak profile area was normalized as 1.0. Sample, B[a]P (10 pg); ionization chamber pressure, 0.4 Torr.

Fig. 5(b) Relationship of ionization chamber pressure versus detected relative peak profile area. The maximum value of relative peak profile area was normalized as 1.0. Sample, B[a]P (10 pg); heating rate of filament, 1000 mA/s (1000°C/s).

Table 1 Influence of data acquiring conditions on flash desorption

Total sampling time/s	Net acquisition time/s	Detected peak area/ 10^4	Repeatability {RSD(%), $n=3$ }
0.25	0.21	4.3	58
(4 scan/s)	0.105	0.86	19
	0.052	0.55	13
	0.026	0.28	20
0.125	0.105	3.6	8.2
(8 scan/s)			
0.1	0.052	1.9	7.9
(10 scan/s)	0.026	0.84	14
	0.013	0.69	31
0.05	0.026	2.5	5.8
(20 scan/s)	0.013	1.8	5.2

Sample, B[a]P (10 pg); rate of flash heating, 1000 mA/s; ionization mode, NCI.

for further studies.

Sampling time. Under the standard heating rate of 1000 mA/s, PAHs of less than pg order are vaporized and ionized within a second. Hence plenty of sampling points are required in order to accomplish precise measurements by means of SIM. The influence of sampling time (net acquisition time+dead time) on data acquisition has been investigated. In this study, the acquisition method of SIM employed sweep mode, that is SIM at mass number x corresponded to scanning of mass number from $(x-0.5)$ to $(x+0.5)$. The results on measuring 10 pg of B[a]P in the NCI mode using the M-ion at m/z 252 as the only mass number to be monitored by SIM, are shown in Table 1. As can be interpreted from Table 1, although there was a complex relationship between peak area (sensitivity), repeatability and sampling and net acquisition time, it is desirable to increase sampling points (20/s) and the ratio of net acquisition time within the sampling time. A sampling time of 0.05 s and net acquisition time of 0.026 s were employed for further studies. When multiple mass number were to be monitored, the net acquisition time was segmented within the available time frame. The repeatability (relative standard deviation) was found to come within 10% under such conditions. The above findings apply for mass chromatographic measurements as well, *i.e.* after establishing as appropriate measuring mass range, it is necessary to set the shortest possible total scan time (*e.g.* 0.1 s) depending on the performance of the instrument.⁸

Quantification. A calibration graph for 100 fg–100 pg of B[a]P was prepared at an ion source temperature of 100°C, filament current of 1000 mA (programmed at 1000 mA/s), and total sampling time of 0.05 s using 10 pg of d_{12} -B[a]P as internal standard. The mass numbers employed were m/z 252 and 264 corresponding to M^- of B[a]P and d_{12} -B[a]P. The net acquisition time for both mass numbers was 0.013 s. An adequate linearity was

Table 2 Relative sensitivities of PAHs by flash desorption NCI

Compound	Selected m/z for SIM (M^-)	Relative sens. ^a
Benz[a]anthracene	228	0.05
Benzo[a]pyrene ^b	252	1.0
Benzo[e]pyrene ^b	252	0.01
Benzo[b]fluoranthene ^b	252	0.35
Benzo[j]fluoranthene ^b	252	0.18
Benzo[k]fluoranthene ^b	252	0.27
Perylene ^b	252	0.04
Indeno[1,2,3- <i>c,d</i>]pyrene	276	0.91
Dibenzo[a,e]pyrene	302	0.40

a. The value of B[a]P was normalized to 1.0.

b. These compounds are isomers of $C_{20}H_{12}$.

obtained in the pg range, but it was not quite as satisfactory in the fg range. This is probably due to sample loss associated with heating and evacuation for solvent removal. Therefore the amount of internal standard was kept as equivalent as possible to B[a]P, which in turn enhanced the linearity even below the pg order. As a result, the linear range of the calibration graph became 0.1–100 pg.

The influence of co-existing isomers and homologs

The influence of isomers. The relative detection sensitivity (B[a]P=1.0) of B[a]P isomers and homologs using 10 pg of sample is summarized in Table 2. Benzo[a]pyrene was influenced by only a factor of 1 and 4% by co-existing benzo[e]pyrene and perylene, respectively, whereas the benzo[fluoranthenes were found to affect it by as much as 18–35%. When the amount of these co-existing isomers can be anticipated beforehand (*e.g.* airborne particulates in certain regions), B[a]P could be determined by utilizing correction factors.

The influence of homologs. The PAHs, being potentially sensitive analytes for NCI, exhibit almost exclusively the molecular anions M^- , enabling them to be monitored simultaneously with B[a]P.

The current method is a rapid and simple means of detecting PAHs at high sensitivity. Sample size can be kept to a minimum, and should prove powerful in such cases as analyzing trace amount of sample deposited on the biological respiratory organs and airborne particulates sampled within a short period of time. For example, it was possible to determine the amount of B[a]P within airborne particulates collected from 10 liters of indoor air, which was in good agreement with GC/MS results. The results for actual samples will be presented elsewhere.

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