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Sorbent Thermal Desorption/Gas Chromatography/ Mass Selective Detection Method for Determination of Gaseous Polycyclic Aromatic Hydrocarbons in Indoor Air

Shugui DAI, Lin ZHANG and Tan ZHU

Department of Environmental Science, Nankai University, Tianjin, 300071, P.R. China

Abstract: Thermal desorption/gas chromatography/mass selective detection method using Tenax cartridges for the determination of gaseous polycyclic aromatic hydrocarbons(PAH) is described. Glass fiber filter can collect only PAH in particulate. Gaseous PAH may penetrate the filter. Glass cartridge packed Tenax-GC was uses for adsorption of gaseous PAH. The air of inhalation zone was collected for 2-10 hours. Cartridges were thermally desorbed in the reverse direction to sample flow. The desorption conditions were as follows: desorption temperature: 300℃; desorption time: 20min; column head pressure:30psi; inlet split vent: closed during desorption.

Keywords: Tenax adsorption, Thermal desorption, GC/MS, indoor air, gaseous polycyclic aromatic hydrocarbons

1. Introduction

PAH are probably the most wide-spread organic pollutants in the environment. Long-term observations in experimental animals, occupational medicine, and epidemiology have strongly indicated that some PAHs exhibit carcinogenic effects in humans(IARC,1983-1985). PAH are formed in natural processes during combustion of biomass(eg.forest fires)and by anthropomorphic high temperature processes. The latter are considered the major sources of PAH in the environment(1). Man-made atmospheric emissions of these compounds can originate from heat and power generation, industrial processes, refuse burning and vehicle emissions. In indoor environment, PAH exists in environmental tobacco smoke (ETS), smokes generated from coal, wool, gas, and oil burning for space heating, flaming cooking oil smoke and curing meat smoke. There are several hundreds of PAH with 2- 7 rings with molecular weight 128-300 amu, vapor pressure 10^{-2}-10^{-6}mmHg(25℃). They exist in air in particulate, vapor or both of them. The measurement of these components of the vapor-phase PAH (gaseous PAH) has implications for health effects since the retention of gaseous PAH in lungs is expected to be different from

that of particulate. PAH have a wide range of vapor pressures and of the distribution of these compounds particulate material but it has been recognized that the lower molecular weight PAH, e.g. naphthalene and anthracene, are not efficiently collected on filters. Low ring-number (2-4 rings)PAH may increase or inhibit the carcinogenic action of high ring-number PAH. The content of low rings PAH accounts for 60- 88% of total PAH in indoor environment. Impregnated filters(2-4),solid sorbents impingers(5-8), and cold traps(9) are used to collect gaseous PAH. In this paper, a new method is reported for determination of gaseous PAH in indoor environment with solid sorbent and thermal desorption.

2. Experimental section

2.1 Sample collection

Tenax-GC was chosen as the sorbent for this, study, The choice of sorbent is determined by several factors such as collection efficiency, capacity of sorbent (breakthrough volume), thermal stability for high temperature, chemical stability of sorbent during sampling, storage and desorption, low blank levels, low affinity for water vapor and high facile recovery of sorbent vapors. Tenax is a poly (p-2,6-diphenylphenylene oxide) which is porous and stable up to 400℃(10). It has a high affinity for semivolatile organic compounds and can be used repeatedly. It has been used for a number of indoor air characterization studies(11-120, and its performance characteristics are relatively well understood. Indoor air samples from residential coal burning and ETS were collected for gaseous PAH. The overall sampling design and procedure used Tanex-GC have been discussed in detail elsewhere. The Tenax-GC cartridges required no sample preparation prior to analysis by thermal desorption and gas chromatography/mass spectrometry(GC/MS)(13).

2.2 Adsorption/thermal desorption with Tenax-GC

Adsorption/thermal desorption (ATD) with Tanex-GC is used with analysis by capillary GC/MS for the determination of high-to- intermediate volatility organics. The overall sensitivity of ATD allows small, relatively between vapor and particulate phases. Sampling for PAH has traditionally relied on the collection of suspended inexpensive Tenax-GC cartridges to be used with low sample flow rates, while still demonstrating a detection limit below 1ng/m3.The method of adsorption sampling with Tenax-GC is particularly suited for the collection of organic compounds ranging in volatility from trichloroethene to coronene(14).

Tenax-GC air desorption cartridges bodies as injection insert of capillary GC were constructed of Pyrex glass with 6.52 mm od,78.5 ± 0.1 mm in length, and packed with 200 mg of 40-60 mesh Tenax-GC. All adsorbents were shielded from light during sampling, transport, and storage. Prior to sampling, the Tenax-GC cartridges were extracted with 1L mixed solvent of acetone and hexane(60:40 v/v), and then conditioned at 300℃ for 4 hr under a stream of ultrapure nitrogen. The cartridges were capped with precleaned silicone rubber caps.

For analysis, a Tenax-GC cartridge was placed in the injection inlet port of GC system. The desorption was carried at higher temperature(eg.250-320 ℃) while GC inlet split vent valve was closed and GC oven temperature was maintained at -30 ℃ with liquid nitrogen. The column head pressure was 30 psi and inlet split vent was still closed 50s during trap fire.

2.3 Analytical methods

All GC/MS analysis were performed using a Hewlett-Packard model 5890 II GC/5971A MSD/G1030A MS ChemStation(DOS series) in the electron impact (EI) mode with a scan range of 40-450 amu. GC column was a HP-5 fused-silica capillary column (25m × 0.2mm, 0.33 μ m film thickness, Hewlett-Packard Co.). The GC oven temperature was held at -30 ℃ during the thermal desorption step for 20 min and then programmed to 80℃ at 45 ℃ /min, and then at 10 ℃ /min to 300 ℃ . All species were identified on the basis of comparisons of their mass spectra and retention indexes with that of authentic standards. Quantitations were based on five point standard curves generated using standards for each individual species. Each standard-curve-experiment consisted of loading 4.0 μ L of the standard on the top of the cartridge followed by a series of 20 min desorption and

accompanying chromatographic runs.

3. Results and Discussion

3.1 Recovery of gaseous PAH from ATD/Tenax-GC

Tenax cartridges were analyzed by thermal desorption capillary GC/MS. In order to simulate the low amounts expected in the sample adsorption cartridges, the ATD/Tenax-GC recovery determinations were carried out so as to produce a final concentrated desorption level of 0.1 and 1.0 ng/ μ L per component. A 1 μ L aliquot portion of standard solution containing 0.1 and 1.0 ng/ μ L each of PAH was first injected onto Tenax cartridges respectively through the end used as the inlet during sampling. With the cartridges in a desorption apparatus the flow directed into the inlet end, and with a head pressure of 30 psi, a flow of 15 ml/min for 10 min was used to remove oxygen and solvent. The overall recoveries of 10 PAHs are shown in Table 1.

Table 1 Recoveries of 10 PAHs with ATD/Tenax-GC

PAH	Concentration(ng/ μ L)	Recovery(%)
Phenanthrene	0.11	92.1
	1.13	96.3
Anthracene	0.11	95.5
	1.10	96.8
Fluoranthene	0.11	95.4
	1.11	98.1
Pyrene	0.11	90.2
	1.14	94.4
Benzo[a]anthracene	0.11	88.7
	1.10	90.8
Chrysene	0.12	89.9
	1.17	92.7
Benzo[e]pyrene	0.10	86.6
	1.03	88.8
Benzo[a]pyrene	0.11	89.3
	1.06	90.2
Benzo[ghi]perylene	0.11	85.4
	1.12	86.5
Coronene	0.14	66.1
	1.40	70.6

3.2 Assessment of adsorption/solvent extraction and adsorption/thermal desorption for collection and analysis of gaseous PAH.

The popular sampler configuration for the determination of atmospheric PAH includes a glass fiber filter followed by an adsorbent such as polyurethane

foam(PUF)and Tenax-GC(15). PUF has the advantages of being convenient to handle and inexpensive. Solvent extraction was used to recover the analytes from some types of adsorbents in some studies(16-17).It utilizes adsorption/solvent extraction(ASE) with PUF and Tenax-GC coupled the capillary GC/MS for the determination of gaseous PAH.

The limits of detection and quantitation were determined according to published guidelines(18).These are comparable to 3 and 10 times the standard deviation above the mean value of a series of field blanks, respectively. Signal response of the blanks (in microvolt seconds) was related to a series to calibration standards run within the lower quantitation region. According to these criteria, under the sampling conditions described above, the limits of detection are shown in Table 2.

Table 2 Comparison of methods of ASE/PUF,ASE/Tenax and ATD/Tenax

PAH	Methods	Limit of detection (ng/m3)	Concentration(ng/m3)	
			Sample 1#	Sample 2#
Phenanthrene	ASE/PUF	1.8	215	13.1
	ASE/Tenax	1.8	202	12.2
	ATD/Tenax	0.1	211	13.8
Anthracene	ASE/PUF	1.4	98.0	6.6
	ASE/Tenax	1.5	101	6.8
	ATD/Tenax	0.1	112	7.4
Fluoranthene	ASE/PUF	2.2	65.5	5.6
	ASE/Tenax	2.4	60.9	5.6
	ATD/Tenax	0.2	70.1	5.8
Pyrene	ASE/PUF	2.9	29.9	1.1
	ASE/Tenax	2.8	27.6	1.0
	ATD/Tenax	0.2	27.1	1.1
Benzo[a]anthracene	ASE/PUF	1.7	4.7	2.3
	ASE/Tenax	1.9	5.1	2.6
	ATD/Tenax	0.3	4.1	2.1
Chrysene	ASE/PUF	2.1	5.9	1.1
	ASE/Tenax	2.3	6.0	1.1
	ATD/Tenax	0.2	5.5	1.0
Benzo[e]pyrene	ASE/PUF	1.8	ND	ND
	ASE/Tenax	1.6	ND	ND
	ATD/Tenax	0.2	0.6	0.2
Benzo[a]pyrene	ASE/PUF	1.5	ND	ND
	ASE/Tenax	1.7	ND	ND
	ATD/Tenax	0.2	1.1	0.2
Benzo[ghi]perylene	ASE/PUF	1.9	ND	ND
	ASE/Tenax	1.8	ND	ND
	ATD/Tenax	0.5	0.7	ND

Coronene	ASE/PUF	2.0	ND	ND
	ASE/Tenax	1.9	ND	ND
	ATD/Tenax	0.6	0.6	ND

note: Sample 1#—indoor air sample in "smoking" room ;
Sample 2#—indoor air sample in "nonsmoking" room;
ND—no detected

For the compounds which could be determined using both ASE/PUF or Tenax-GC and ATD/Tenax-GC, good agreement was obtained between the measurements. This is evidenced by ASE-PUF/ATD-Tenax and ASE-Tenax/ATD-Tenax concentration ratios in Table 2 are close to 1.00.

In indoor environment high-volume collection of air is not allowed because its capacity is finite. The method of high-volume collection and quantitation of PAH including a glass fiber filter followed by an adsorbent such as PUF is not suit for analysis of PAH in indoor air.In this care,the ATD/Tenax-GC is of better limit of detection and quantitation than that of ASE/PUF and ASE/Tenax-GC. And ATD/Tenax-GC is of simplicity of sampling and analysis for gaseous PAH in indoor environment.

3.3 effects of desorption temperature

Gaseous PAH is of higher boiling point and less volatility. The effects of desorption temperature on results of analysis for gaseous PAH were studied. The first desorption was carried out at 250℃, followed each at 270, 290, 300, 310, and 320℃. The recovery of analysis methods at each desorption temperature is shown in Table3 .

Table 3 Effects of desorption temperature on recoveries of gaseous PAHs

PAH	Desorption Temperature(℃)					
	250	270	290	300	310	320
Phenanthrene	61.4	81.6	90.6	96.3	96.5	95.8
Anthracene	58.5	80.5	90.5	96.8	95.9	96.6
Fluoranthene	52.1	85.9	90.4	98.1	96.6	97.6
Pyrene	46.5	80.5	89.5	94.4	95.7	95.7
Benzo[a]anthracene	50.9	76.7	88.2	90.8	91.2	91.0
Chrysene	52.6	70.2	89.9	92.7	92.2	92.4
Benzo[e]pyrene	43.3	77.7	84.1	88.8	89.1	89.5
Benzo[a]pyrene	45.7	78.2	85.5	90.2	90.4	90.1
Benzo[ghi]perylene	30.4	64.2	77.9	86.5	86.7	88.2
Coronene	21.0	46.5	59.9	70.6	73.6	74.3

According to the results obtained from experiment of desorption temperature,the optimal desorption temperature is 300-320℃ for the method.

4. Conclusions

This work indicates that ASE/PUF or Tenax-GC and ATD/Tenax-GC are valid methods for the analysis of gaseous PAH. But ATD/Tenax-GC is well suited for the determination of gaseous PAH at ng/m3 level in indoor air where high-volume sampling method is not used. The ATD/Tenax-GC will be applied to indoor air analysis with sensitive and simplicity.

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