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In-injection port thermal desorption and subsequent gas chromatography–mass spectrometric analysis of polycyclic aromatic hydrocarbons and *n*-alkanes in atmospheric aerosol samples

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Abstract

The traditional approach for analysis of aerosol organics is to extract aerosol materials collected on filter substrates with organic solvents followed by solvent evaporation and analytical separation and detection. This approach has the weaknesses of being labor intensive and being prone to contamination from the extracting solvents. We describe here an alternative approach for the analysis of aerosol alkanes and polycyclic aromatic hydrocarbons (PAHs) that obviates the use of solvents. In our approach, small strips of aerosol-laden filter materials are packed into a GC split/splitless injector liner. Alkanes and PAHs on the filter are thermally desorbed in the injection port and focused onto the head of a GC column for subsequent separation and detection. No instrument modification is necessary to accommodate the introduction of the aerosol organics into the GC–MS system. Comparison studies were carried out on a set of 16 ambient aerosol samples using our in-injection port thermal desorption (TD) method and the traditional solvent extraction method. Reasonably good agreement of individual alkanes and PAHs by the two methods was demonstrated for the ambient samples. The in-injection port thermal desorption method requires much less filter material for detecting the same air concentrations of alkanes and PAHs.

Keywords: GC analysis of aerosol organics; Thermal desorption; Alkanes; Polycyclic aromatic hydrocarbons; Sample introduction

1. Introduction

Organic compounds make up a significant fraction of fine aerosol mass in the ambient environment. The traditional approach for analysis of individual organic compounds is to extract aerosol materials collected on filter substrates into solvents followed by solvent evaporation and separation and detection by a gas chromatography (GC) method [1–4]. The solvent extraction and evaporation steps are labor intensive and time consuming (up to 30 h). They are also prone to contamination introduced from solvent impurities. In addition, the use of large quantities of solvent makes this approach an environmentally unfriendly practice.

An alternative to the solvent extraction approach is to use elevated temperatures as a means, i.e., thermal extraction or thermal desorption (TD), to transfer organic analytes from their filter substrates to an analytical system. Organic analytes released by thermal desorption can be conveniently concentrated onto the stationary phase on a GC column head. The separation and detection can then be accomplished by progressively raising the GC column temperature, similar to the analysis of liquid samples. Thermal desorption has been commonly employed for extracting volatile and semi-volatile organic species from adsorbing matrices such as solid sorbent tubes [5,6]. In comparison, only a handful of applications have been published on using thermal desorption of various forms for the analysis of ambient aerosol organic compounds in the past two decades [7–16].

Among various forms of TD, in-injection port TD is the simplest and requires no modification to the GC injector

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port and no transfer line. Samples are placed inside the GC injector port and TD takes place in the injector port. In principle, it offers the highest transfer efficiency as a result of the elimination of transfer lines between the sample and the analytical instrument. The feasibility of in-injection port TD has been demonstrated in the analysis of ambient volatile organic compounds [17–19] and explosives [20]. Three studies [8,13,15] reported the application of in-injection port TD in the determination of aerosol organics. The first study [8] presented only qualitative results. The second study [13] reported measurements of alkane and PAH concentrations using the in-injection port TD method; however, no evaluation of the technique against an established method was presented. The third study [15] made small modifications to standard split/splitless GC injectors to accommodate a small glass vial (2.5 mm o.d., 1.9 mm i.d., 6–18 mm long) inside the GC injector where the aerosol material was loaded for thermal desorption. Validation of this TD technique was documented only for polycyclic aromatic hydrocarbons (PAHs).

We describe here the application of the in-injection port TD technique to the analysis of aerosol alkanes and PAHs. In addition, this method is compared with the traditional solvent extraction method for determination of *n*-alkanes and PAHs in a set of ambient aerosol samples.

2. Experimental

2.1. Reagents

n-Alkanes (*n*-C_8 to *n*-C_{30}) and 16 PAHs of the highest purity available were purchased from Aldrich. Benzo[k]fluoranthene was from Acros (99%, Springfield, NJ, USA) and indeno[1,2,3-cd]pyrene was purchased from Fluka (99%, Buchs SG, Switzerland). Three *n*-alkanes of higher molecular weight (*n*-C_{32}, *n*-C_{34}, and *n*-C_{36}) were obtained from Supelco (99%, Bellefonte, PA, USA). Standard mixtures of *n*-alkanes and PAHs were prepared in dichloromethane solutions (99.9%, LC grade, Mallinckrodt Laboratory Chemicals, Phillipsburg, NJ, USA). Two deuterated compounds, *n*-tetracosane-d_{50} (*n*-$C_{24}D_{50}$) (98%, Aldrich, Milwaukee, WI, USA) and phenanthrene-d_{10} (phe-d_{10}) (98%, Aldrich), were used as internal standards (IS) and prepared in dichloromethane.

2.2. Aerosol samples

A set of 16 aerosol filter samples was analyzed for *n*-alkanes and PAHs using both the solvent extraction and the thermal desorption methods. The aerosol samples were collected onto 100 mm Teflon-impregnated glass fiber filters (TIGF) at a flow rate of 0.228–0.285 $m^3\,min^{-1}$ for 12–24 h at a roadside location in Hong Kong in the winter and the summer of 2001. After collection, the filters were transported inside Uline metallic ZipTop static shielding bags (Waukegan, IL, USA) and stored below 4 °C until analysis.

2.3. The thermal desorption method

Two filter strips of 1 cm × 1.45 cm in size were cut from the 100 mm filter using a stainless steel punch over a clean surface made of a pre-baked aluminum foil sheet. Two internal standards, 8.4 ng of *n*-$C_{24}D_{50}$ and 8.2 ng of phe-d_{10} in dichloromethane, were spiked onto the filter strips. After air-drying for a few seconds to allow evaporation of the organic solvent from the application of the internal standards, each filter piece was divided into four roughly equal portions with a razor blade to facilitate the subsequent loading of the filter pieces into the TD tube. The pieces were then inserted into a Pyrex glass tube that was home-fabricated to be 78 mm long, 4 mm i.d., and 6 mm o.d. The length and the outside diameter were identical to those of an HP 5890 GC injector liner. The glass-tube was baked at 550 °C for at least 10 h before use. A small amount of pre-baked glass wool (Alltech, Dearfield, IL) was used as a plug for holding the filter parts in position. The glass wool may also help to retain heavy and polar compounds that, if desorbed from the filter, would contaminate the GC column. The loaded tubes were stored inside capped test tubes before analysis. Gloves were worn and all liner tubes and filters were handled only with cleaned forceps to avoid any contamination to the outer portion of the tubes.

Calibration standards were prepared by spiking known amounts of liquid standard mixtures and the two deuterated IS onto separate pre-baked filter strips. The standard-loaded filter strips were then cut and placed into the TD tubes in the same way as for the sample filters. The analysis of the calibration filters was carried out within several hours after their preparation. Calibration curves were constructed by plotting the peak area ratios between the analytes and the respective IS (i.e., *n*-$C_{24}D_{50}$ for alkanes and phe-d_{10} for PAHs) versus the amounts of the analytes.

The TD step was an integrated part of the analysis. It took place in the injector port of an HP 5890 GC/5791 MSD system. Fig. 1 illustrates the time events of the GC injector and the column oven in one TD/GC–MS analysis run. The sample-loaded tube was exchanged with the injector liner after the injector temperature was lowered to 100 °C. Once

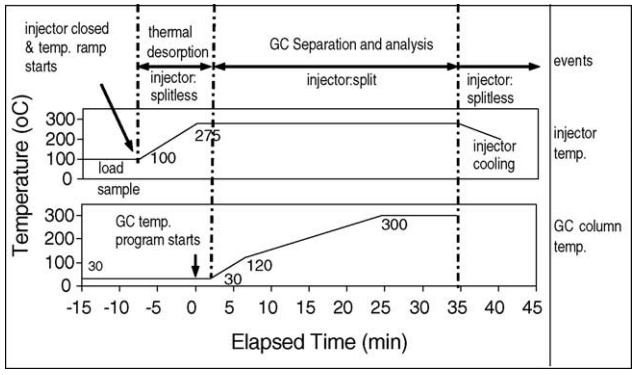

Fig. 1. Time events of the GC injector and the column oven during the thermal desorption and GC–MS analysis.

the tube was in place inside the injector port, the injector was immediately closed with a septum cap and its temperature was set to 275 °C manually. It took 7.0 min for the injector temperature to reach the new setting. During this period, the GC oven temperature was kept at 30 °C. Such a temperature condition would focus the aerosol organic analytes released from the injector port on the head of the GC column in a narrow band. The oven temperature program was then started as soon as the injector temperature achieved 275 °C. The injector was kept at 275 °C throughout the analysis. The injector was set in the splitless mode for the first 2 min in the GC temperature program, switched to the split mode at 2 min, and returned to the splitless mode at the end of the GC run. The GC oven program was initially set at 30 °C, held at this temperature for 2 min, programmed at a rate of 20 °C min^{-1} to 120 °C and 10 °C min^{-1} to 300 °C, and then held at the final temperature of 300 °C for 10 min. An HP-5MS (5% diphenyl/95% dimethylsiloxane, 30 m × 0.25 mm × 0.25 μm) was used. The carrier gas was helium held at a constant pressure of 8.0 psi. The mass spectrometer detector (MSD) was operated at 280 °C and 70 eV for electron ionization. The mass scan range was from 50 to 650 amu. A new TD tube was used for each analysis, therefore avoiding any potential contamination carry-over to the next analysis. The TD tubes were reused after cleaning of the content and baking.

2.4. The solvent extraction method

The entire remaining portion of the sample filter, after removal of the two 1 cm × 1.45 cm pieces for TD analysis, was used for the determination of *n*-alkanes and PAHs using the solvent extraction method. The IS, *n*-$C_{24}D_{50}$, was spiked on the filter before solvent extraction for monitoring losses in the whole analytical procedure. The filters were then extracted in a soxhlet extractor with 300 ml dichloromethane for at least 6 h at a rate of 5 cycles per h. The soxhlet extractor was wrapped with aluminum foil during the extraction step to minimize UV exposure. The extract was first reduced to ∼6 ml using a rotary evaporator (Model R-124, Buchi, Switzerland) before being transferred to a smaller round bottom flask for further volume reduction to less than 0.5 ml. The concentrated extract was then filtered through a syringe filter (0.2 μm, 13 mm diameter; MFS, Dublin, CA, USA) to remove particles and filter fiber residues. A second IS, phe-d_{10}, was added into the filtrate for use as an injection IS to account for variation in injection volume. The final volume of the solution was fixed at 1.0 ml using a volumetric flask. The extract solutions were kept in a refrigerator before analysis. The response ratio between *n*-$C_{24}D_{50}$ and phe-d_{10} was computed for each sample and used to track sample-to-sample variations in the sample pre-treatment procedure.

The filter extract was manually injected through the GC injector at 275 °C with an HP injector liner. The injector was kept in the splitless mode for the first 2 min and then switched to the split mode until the end of the GC oven temperature program. The GC oven program was set at an initial value of 65 °C, held at this temperature for 1 min, programmed at a rate of 25 °C min^{-1} to 140 °C and 10 °C min^{-1} to 300 °C, and then held at the final temperature of 300 °C for 5 min. This temperature program was optimized for separation of the *n*-alkanes (>C_{12}) and PAHs. With this temperature program, concentration of the analytes into a narrow band at the start of the analysis was achieved through stationary phase focusing [21]. An injection volume of 5 μl was used after the observation of enhanced peak area intensities for both alkanes and PAHs in comparison with an injection volume of 2 μl. The column and the MSD conditions were the same as those used in the TD method. Calibration curves were established by plotting the peak area ratios between the analyte and the injection IS versus the amounts of the analyte per injection.

The recoveries of the individual *n*-alkanes and PAHs in the volume reduction step and the filtration step, as well as the overall extraction procedure, were determined. For the determination of the overall procedure recoveries, standard mixtures containing 29.3–77.8 μg of individual *n*-alkanes and 5.9–10.9 μg of individual PAHs were spiked onto pre-cleaned blank filters. Extraction and GC–MS analysis of the spiked filters proceeded in the same fashion as that for the sample filters. The recovery of an analyte for the whole procedure was computed by comparing the peak area ratios between the analyte and the injection IS in the spiked filter sample with the corresponding standard sample that did not go through any sample treatment steps. The *n*-alkane and PAH concentrations reported in this work have been corrected for their individual recoveries. The recoveries of the commercially unavailable odd-number *n*-alkanes (*n*-C_{27} to *n*-C_{35}) were approximated to be the mean recovery of the two immediate adjacent even-number alkanes. For the determination of the recoveries of the volume reduction step, *n*-alkane and PAH standards were mixed with 300 ml dichloromethane. The volume was reduced to 1 ml. The recoveries of the filtration step were determined by analyzing the same standard mixtures with and without filtration.

3. Results and discussion

3.1. The thermal desorption temperature

The desirable TD temperature needs to meet two criteria, complete desorption of target analytes and absence of thermal decomposition. Four TD temperatures, 200, 250, 275, and 300 °C, were tested. Standard solutions spiked on blank filter strips were used to compare the TD efficiencies at the four temperatures. It took the injector 3.5, 5.3, 7.0, and 9.5 min to reach the set temperature of 200, 250, 275, and 300 °C, respectively. Irrespective of the time required to reach the final set temperature, the GC temperature program was started at 9.5 min after the filter was loaded into the injector line. This made the TD time a uniform value of 9.5 min.

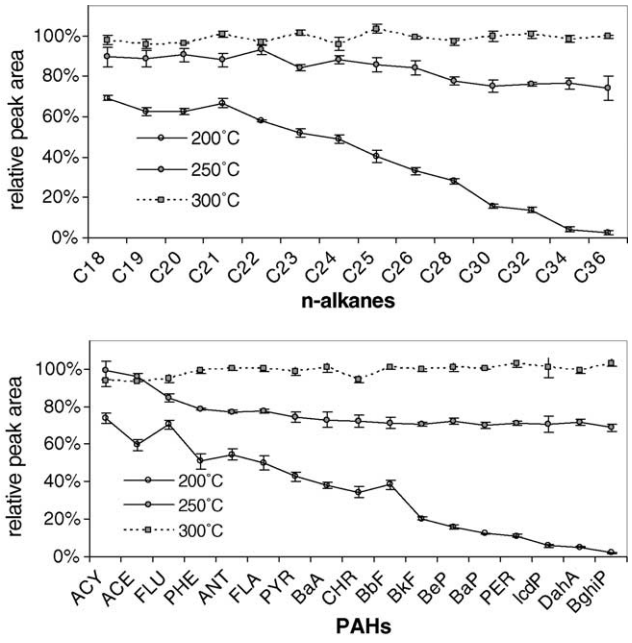

Fig. 2. Relative thermal desorption efficiencies at a thermal desorption temperature of 200, 250, and 300 °C to those at 275 °C for *n*-alkanes (top panel) and PAHs (bottom panel). Abbreviations of PAHs are given in Table 2.

Fig. 2 compares the TD efficiencies of the *n*-alkanes and the PAHs analyzed at the four different TD temperatures. No statistically significant difference was found between the results at 275 and 300 °C for all targeted species. Progressively lower desorption efficiencies were found when the injector temperature was lowered to 250 and 200 °C. The TD efficiencies of *n*-alkanes and PAHs at 250 °C were, respectively, 7–26 and 1–30% lower than those achieved at 275 °C. The TD efficiencies worsened further at 200 °C, in particular for the higher molecular weight compounds (e.g., *n*-C_{34}, *n*-C_{36}, and PAHs with five-rings or larger), which had TD efficiencies lower than 20%. The drops were small for the relatively more volatile species but prominent for those with high boiling points. The results from this experiment indicate that temperatures of 250 °C or lower are insufficient for the complete TD of *n*-alkanes up to *n*-C_{36} or PAHs up to benzo[g,h,i]perylene from the filter matrices.

3.2. Thermal desorption duration

The optimal TD duration is the minimum time that is required for complete TD of analytes from the filter substrate and subsequent transfer from the injector port to the GC column head. An unnecessarily longer TD time would lengthen the analysis time and might cause peak broadening. On the basis of the findings from the TD temperature experiment, TD at 275 °C was used to determine the optimal TD time. After the injector achieved 275 °C, three time intervals, 0, 5, and 10 min, were allowed to elapse before the GC temperature program was started. The responses of both *n*-alkanes and PAHs spiked on blank filters obtained at 5 and 10 min elapsed time deviated 5–12 and 4–14%, respectively, from those obtained at 0 min elapsed time. Similar results were obtained for aerosol samples. The difference in *n*-alkane and PAH responses ranged from 3 to 11% between 0 and 10 min

Table 1
Physical properties and the limits of detection (LODs) of *n*-alkanes using the thermal desorption and the solvent extraction methods

n-Alkane	M.W.	bp (°C)	Thermal desorption				Solvent extraction				
			Slope	Intercept	R^2	LOD (ng per sample)[a]	Slope	Intercept	R^2	LOD (ng per injection)	LOD (ng per sample)[b]
n-Tridecane (C-13)	184.4	235.4	0.0104	−0.0022	0.964	4.36	0.0134	−0.0038	0.999	0.625	125
n-Tetradecane (C-14)	198.4	253.7	0.0143	0.0363	0.992	3.00	0.0130	−0.0010	0.999	0.188	37.7
n-Pentadecane (C-15)	212.4	270.63	0.0240	−0.0165	0.993	2.73	0.0128	−0.0009	0.998	0.435	87.1
n-Hexadecane (C-16)	226.4	287	0.0346	−0.0095	0.992	3.09	0.0125	0.0002	0.998	0.483	96.7
n-Heptadecane (C-17)	240.5	301.8	0.0344	0.0066	0.990	3.36	0.0136	−0.0009	1.000	0.242	48.4
n-Octadecane (C-18)	254.5	316.1	0.0357	0.0316	0.995	1.76	0.0140	−0.0020	0.999	0.360	72.1
n-Nonadecane (C-19)	268.5	329.7	0.0372	0.0184	0.997	1.68	0.0142	−0.0023	0.999	0.349	69.7
n-Eicosane (C-20)	282.6	342.7	0.0378	0.0220	0.995	1.95	0.0140	−0.0017	0.998	0.254	50.9
n-Henicosane (C-21)	296.6	356.5	0.0353	−0.0033	0.994	1.94	0.0151	−0.0034	1.000	0.444	88.9
n-Docosane (C-22)	310.6	368.4	0.0373	0.0324	0.992	2.55	0.0150	−0.0025	0.998	0.237	47.4
n-Tricosane (C-23)	324.6	380.2	0.0361	0.0112	0.993	2.17	0.0140	−0.0017	0.998	0.304	60.8
n-Tetracosane (C-24)	338.7	391.3	0.0366	0.0194	1.000	0.41	0.0133	−0.0011	1.000	0.245	48.9
n-Pentacosane (C-25)	352.7	401.9	0.0397	−0.0047	0.995	1.77	0.0145	−0.0040	0.997	0.298	59.7
n-Hexacosane (C-26)	366.7	412.2	0.0422	0.0230	0.995	1.58	0.0145	−0.0023	0.999	0.225	45.0
n-Octacosane (C-28)	394.8	431.6	0.0443	−0.0120	0.991	2.14	0.0134	0.0002	0.998	0.332	66.3
n-Triacontane (C-30)	422.8	449.7	0.0421	0.0011	0.991	2.42	0.0110	−0.0017	0.996	0.375	74.9
n-Dotriacontane (C-32)	450.9	467	0.0398	0.0374	0.983	2.97	0.0100	0.0001	0.997	0.491	98.2
n-Tetratriacontane (C-34)	478.9	–	0.0265	−0.0453	0.987	2.51	0.0083	−0.0019	0.997	0.196	39.3
n-Hexatriacontane (C-36)	507.0	265 at 1 mm Hg	0.0217	−0.0386	0.982	2.88	0.0069	−0.0028	0.997	0.411	82.2

[a] The LOD (ng per sample) in the thermal desorption method was based on a sample size of a 2.9 cm^2 filter piece.

[b] The LOD (ng per sample) in the solvent extraction method was based on a sample size of a pre-analysis filter extract of 1.0 ml. An aliquot of 5 μl was injected for each injection.

Table 2
Physical properties and the limits of detection (LODs) of PAHs using the thermal desorption and the solvent extraction methods

PAH	Abbreviation	M.W.	bp (°C)	Thermal desorption				Solvent extraction				
				Slope	Intercept	R^2	LOD[a] (ng per sample)	Slope	Intercept	R^2	LOD	LOD[b]
Acenaphthylene	ACY	152.2	265	0.0038	−0.0080	0.995	1.60	0.0100	0.0008	0.997	0.093	18.6
Acenaphthene	ACE	154.2	279	0.0031	−0.0081	0.995	2.40	0.0046	0.0003	0.993	0.239	47.9
Fluorene	FLU	166.2	295	0.0264	−0.0044	0.992	1.35	0.0054	0.0005	0.995	0.188	37.7
Phenanthrene	PHE	178.2	340	0.0715	0.0146	0.999	0.73	0.0073	0.0007	0.995	0.189	37.7
Anthracene	ANT	178.2	340	0.0912	0.0466	0.998	1.74	0.0091	0.0004	0.992	0.249	49.8
Fluoranthene	FLA	202.3	375	0.0752	0.0578	0.994	1.68	0.0085	0.0000	0.993	0.245	49.1
Pyrene	PYR	202.3	404	0.0891	0.1523	0.998	1.21	0.0101	0.0015	1.000	0.052	10.3
Benzo[a]anthracene	BaA	228.3	437.6	0.0422	0.0351	0.999	0.76	0.0044	0.0006	0.999	0.081	16.1
Chrysene	CHR	228.3	448	0.0441	0.0516	1.000	0.38	0.0046	0.0000	0.997	0.124	24.8
Benzo[b]fluoranthene	BbF	252.3	357	0.0330	0.0148	1.000	0.24	0.0034	−0.0001	0.996	0.108	21.5
Benzo[k]fluoranthene	BkF	252.3	480	0.0576	−0.0235	0.993	0.48	0.0049	−0.0001	0.997	0.097	19.3
Benzo[e]pyrene	BeP	252.3	492	0.0463	0.0098	0.992	0.85	0.0038	0.0000	0.995	0.141	28.2
Benzo[a]pyrene	BaP	252.3	495	0.0564	0.0106	0.991	1.01	0.0047	0.0003	0.995	0.139	27.7
Perylene	PER	252.3	–[c]	0.0659	0.0086	0.993	0.81	0.0056	−0.0001	0.992	0.173	34.7
Indeno[1,2,3-cd]pyrene	IcdP	276.3	536	0.0213	0.0266	0.994	2.01	0.0017	0.0001	0.996	0.106	21.1
Dibenz[a,h]anthracene	DahA	278.4	524	0.0157	0.0057	0.992	0.71	0.0014	0.0001	0.995	0.141	28.2
benzo[g,h,i]perylene	BghiP	276.3	500	0.0325	0.0131	1.000	0.08	0.0029	0.0001	0.992	0.200	40.0

[a] The LOD (ng per sample) in the thermal desorption method was based on a sample size of a 2.9 cm^2 filter piece.
[b] The LOD (ng per sample) in the solvent extraction method was based on a sample size of a pre-analysis filter extract of 1.0 ml. An aliquot of 5 μl was injected for each injection.
[c] Not available.

TD times. Peak broadening was not observed with the longer desorption time, demonstrating that column focusing at 30 °C was effective. This experiment indicated that the TD time of 7.5 min required for the injector to reach 275 °C from 100 °C was sufficient for the complete TD.

3.3. Calibration of the thermal desorption method

The calibration mixtures included 24 *n*-alkanes from *n*-C_8 to *n*-C_{36} and 18 PAH compounds. We found that analytes with boiling points lower than 235 °C, including *n*-alkanes smaller than C_{13} and the most volatile PAH (i.e., naphthalene) of the 18 PAHs, were not detected at all calibration levels up to 120 ng for *n*-alkanes and 60 ng for naphthalene. Tables 1 and 2 list the *n*-alkanes and PAHs that were successfully quantified by the TD method. The failure to detect the more volatile compounds was attributable to losses that occurred in the warm injection port during the loading of the TD tube. These losses were verified by an experiment in which two filter strips spiked with the same amounts of alkanes and PAHs were analyzed separately with the loading step taking place at two injector temperatures, 30 and 100 °C. The lower injector temperature of 30 °C enabled the detection of *n*-C_{12} alkane and naphthalene. It increased the response of *n*-C_{13} alkane by seven-fold, *n*-C_{14} alkane by 37%, acenaphthylene by 64%, acenaphthene by 95%, and fluorene by 21%. The responses of *n*-alkanes higher than *n*-C_{13} and PAHs heavier than fluorene were not affected by the change in the injector temperature. The more volatile analytes were expected to be more sensitive to the injector temperature during the loading step. Despite the enhanced responses of more volatile

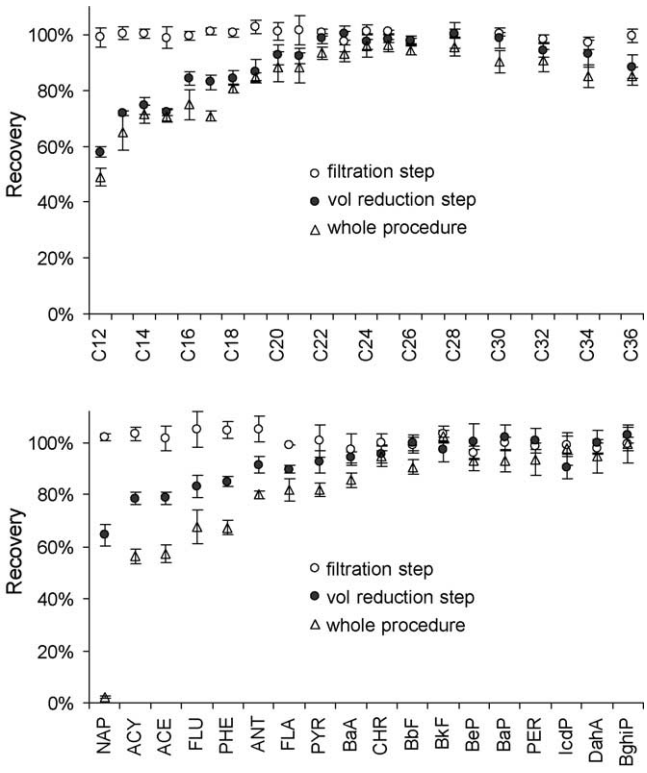

Fig. 3. Recoveries of the filtration step, the volume reduction step, and the whole procedure for *n*-alkanes (top) and PAHs (bottom). Abbreviations of PAHs are given in Table 2. (Symbols have been retained to make better distinction between different data sets.)

species at lower injector temperatures, we used 100 °C as the normal operating injector temperature for the loading step in exchange for a shorter analysis time. Without the option of cryogenic cooling, it would take a further 60 min for the injector port to cool down from 100 °C. However, if a GC is equipped with cryogenic cooling for its injector, lowering the injector to 30 °C is recommended for the TD tube loading step.

The calibration curves were plotted as the peak area ratios between the quantification ions for the analytes and the respective IS versus the amount of analytes in nanograms. The ranges of the *n*-alkanes and PAHs in the calibration samples, at levels from ten to hundreds of nanograms, encompassed the ranges encountered in the ambient samples. The largest common fragment ion at *m*/*z* 57 for *n*-alkanes was selected for quantification. The PAHs typically had an abundant presence of their molecular ions in their mass spectra. Consequently, the molecular ions were used for quantification. None of the odd number *n*-alkanes from *n*-C_{27} to *n*-C_{35} was commercially available. Their response factors were approximated to be the mean response factor of the two immediate neighboring even number alkanes. Tables 1 and 2 list the calibration slopes, intercepts, and coefficients of determination for the alkane and PAH standards. The coefficients of determination are close to 1, demonstrating that the TD technique is quantitative.

The limit of detection (LOD) of the method is defined as the minimum amount of an *n*-alkane or a PAH that generates the minimum distinguishable signal plus three times the standard deviation of the blank signals. No peaks were detected for either *n*-alkanes or PAHs in the blank calibration samples. As a result, we approximated the mean blank signal with the calibration line intercept and the blank signal standard deviation with the standard error for the *y* (peak area ratio) estimate [22]. By this approach, the LODs in nanograms per sample were calculated to be in the range of 0.41–4.36 ng for *n*-alkanes and 0.08–2.40 ng for PAHs (Tables 1 and 2). These numbers translate into air concentrations of 0.023–0.240 ng/m^3 for *n*-alkanes and 0.005–0.137 ng/m^3 for PAHs if we assume a sampled air volume of 350 m^3.

3.4. Solvent extraction recoveries

Lower recoveries were obtained for shorter chain *n*-alkanes. The extraction recoveries for *n*-C_{13} to *n*-C_{21} alkanes ranged from 69 to 87% whereas better than 91% were obtained for *n*-C_{22} to *n*-C_{32} alkanes (Fig. 3). Similar to the trend of *n*-alkanes, the lighter PAHs also showed poorer recoveries. Naphthalene had a mere 5% recovery, indicating a large evaporative loss in the solvent extraction method. The evaporative loss could occur during a few steps, including the spiking step, the soxhlet extraction step, and the volume reduction step. Similarly, low recoveries were reported by Swartz et al. [23] for naphthalene and 2-methyl naphthalene on quartz filter samples. The recoveries of heavier PAHs, i.e., benzo[b]fluoranthene and benzo[k]fluoranthene, were close to 100%. The standard deviations of the recoveries were small, ranging from 1 to 9%.

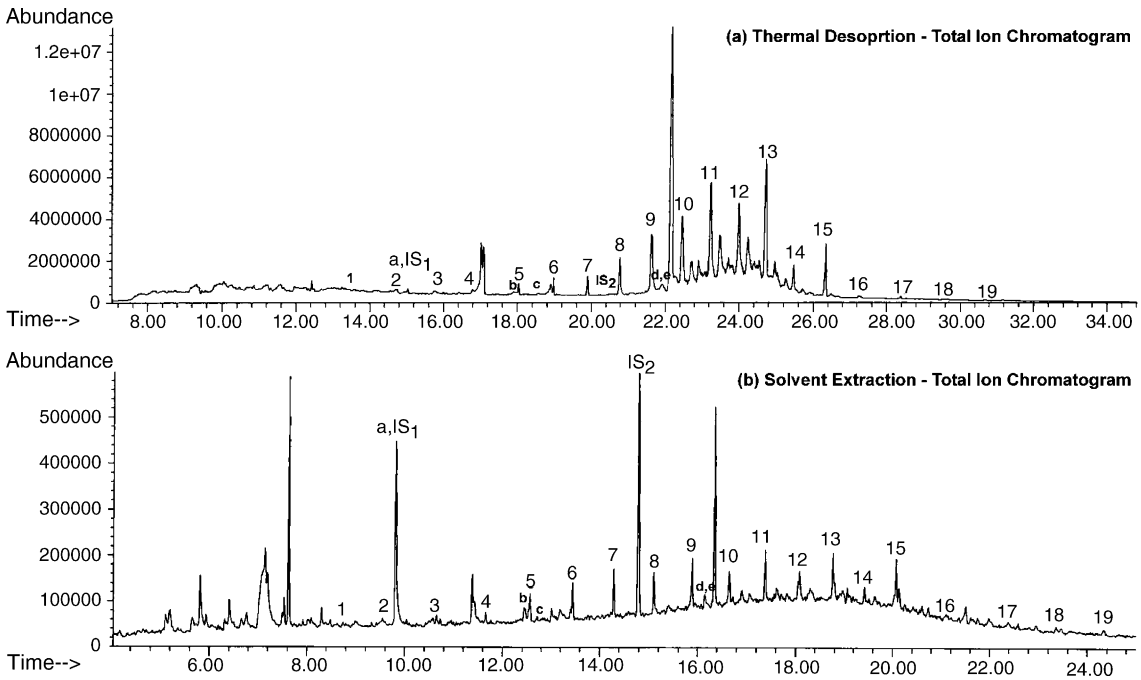

Fig. 4. Total ion chromatograms of the same aerosol filter sample: (a) thermal desorption method and (b) solvent extraction method. (Peak identification: (IS_1) phenanthrene-d10, (IS_2) *n*-$C_{24}D_{50}$; *n*-alkanes, (1) *n*-C_{17}; (2) *n*-C_{18}; (3) *n*-C_{19}; (4) *n*-C_{20}; (5) *n*-C_{21}; (6) *n*-C_{22}; (7) *n*-C_{23}; (8) *n*-C_{24}; (9) *n*-C_{25}; (10) *n*-C_{26}; (11) *n*-C_{27}; (12) *n*-C_{28}; (13) *n*-C_{29}; (14) *n*-C_{30}; (15) *n*-C_{31}; (16) *n*-C_{32}; (17) *n*-C_{33}; (18) *n*-C_{34}; (19) *n*-C_{35}; PAHs, (a) phenanthrene; (b) fluoranthene; (c) pyrene; (d) benzo[a]anthracene; (e) chrysene.)

The recoveries of two single steps in the solvent extraction method, volume reduction and sample filtration, were also separately determined in an effort to better characterize the method performance. The near unity recoveries of the filtration step indicated that filtration through a Teflon membrane syringe filter caused little loss of the target analytes. The recoveries of the volume reduction step indicated loss of analytes at a similar magnitude to those resulting from the entire extraction procedure. The differences in the recoveries of the whole procedure and the solvent reduction step were less than 10% with the exception of the three lightest PAHs (NAP, ACY, and ACE). This result indicates that the solvent evaporation step was primarily responsible for analyte loss in the solvent extraction method. The three lightest PAHs had recoveries of the volume reduction step 59, 17, and 12% higher than the recovery of the whole extraction process, respectively. These percentages suggest that other steps in the extraction method (e.g., soxhlet extraction) and likely evaporation from the filter with the spiking solvent before solvent extraction [23] also contribute to a significant portion of their losses.

3.5. Method comparison

Solvent extraction with subsequent liquid injection in GC–MS analysis is a standard method that has been widely utilized in the determination of organic compounds in aerosol filter samples. The extraction procedure has been well tested and defined [1]. The LODs of the solvent extraction method were also obtained by the same methodology used in the determination of the LODs of the TD method (Tables 1 and 2). The LOD values, when expressed as nanograms per injection (or analysis), are on average seven to eight times lower in the solvent extraction method than those in the TD method. However, the TD method utilized the whole sample while only a small fraction (0.5%) of the final solvent extract was utilized in the solvent extraction method. The higher sample utilization rate in the TD method more than compensated for its higher LODs on the basis of nanograms per analysis. Tables 1 and 2 compare the LODs in terms of ng per sample, which are better indicators for the minimal amount of analytes necessary for quantification in each method. Under the conditions specified in the experimental procedure, the TD method provides LODs (ng per sample) that were 12–120 times better for *n*-alkanes and 9–500 times better for PAHs than did the solvent extraction method. The final pre-analysis volume of the aerosol solvent extract was fixed at 1.0 ml in our work. In practice, this volume could be reduced to as low as 0.1 ml, which would reduce the LODs (ng per sample) by 10-fold in comparison with the use of 1.0 ml. If the final extract volume was pushed to the lowest limit of 0.1 ml in the solvent extraction method, the TD method would still provide LODs ranging from being comparable to 50 times lower in comparison with the solvent extraction method.

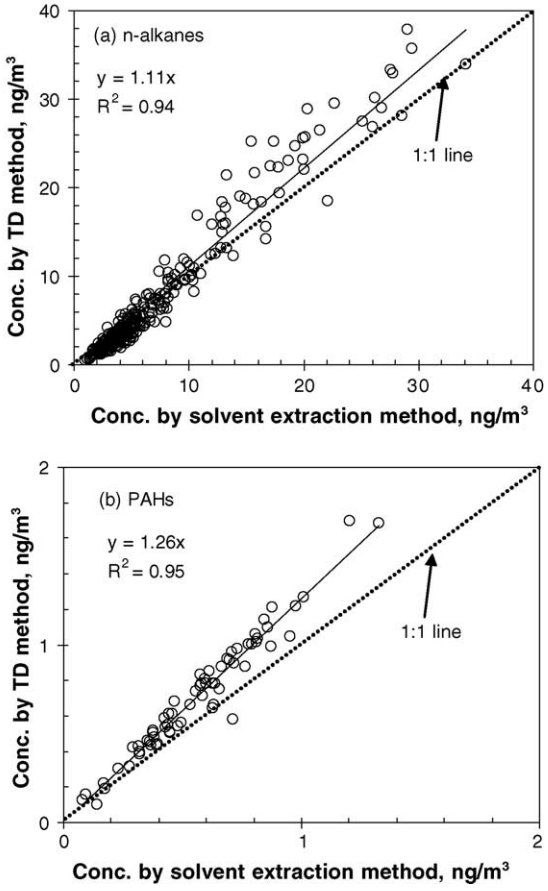

Fig. 5. Comparison of air concentrations of *n*-alkanes (a) and PAHs (b) measured by the solvent extract method and the TD/GC–MS method.

Two total ion chromatograms (TIC) for the same filter sample using the two methods are shown in Fig. 4. A comparison of the two chromatograms clearly shows that fewer contamination peaks were present in the chromatogram obtained using the TD method. This confirms that solvent impurities are major sources of interferences in the solvent-based analytical method.

The extent of agreement in the air concentrations determined using the two methods could be assessed as simple linear fits. A good correlation was found between the two methods for both *n*-alkanes ($R^2 = 0.94$) and PAHs ($R^2 = 0.95$) (Fig. 5). Table 3 summarizes the comparison results for individual alkanes and PAHs. The concentrations of a few *n*-alkanes, i.e., *n*-C_{14}, *n*-C_{15}, and *n*-C_{36}, were below their respective LODs in the solvent extraction method, although the TD method could quantify their amounts. As a result, a comparison is not possible. This again demonstrates the improved sensitivity using the TD method. Among the alkanes and the PAHs for which a comparison was possible, the ratio of the concentration measured by the TD method to that by the solvent extraction method was calculated to range from 0.60 to 1.36. The deviation from the ideal value of 1, therefore, did not exceed 40%. Such a level of agreement between

Table 3
Comparison of the measurement results for a set of 16 ambient samples using the thermal desorption method and the solvent extraction method

Compound	No. of pairs of measurement above LOD	Concentration range (ng/m^3)	Ratio of measurement by the two methods[a]	
			Average	S.D.
n-C17 alkane	15	0.5–3.2	0.63	0.08
n-C18 alkane	15	0.9–5.5	0.60	0.08
n-C19 alkane	15	1.0–5.7	0.66	0.11
n-C20 alkane	16	1.4–7.0	0.68	0.12
n-C21 alkane	16	1.9–6.7	0.73	0.10
n-C22 alkane	16	1.7–7.9	0.84	0.14
n-C23 alkane	16	2.2–11.1	0.91	0.14
n-C24 alkane	16	2.6–22.1	0.90	0.13
n-C25 alkane	16	3.5–26.8	0.96	0.21
n-C26 alkane	16	3.3–33.3	1.08	0.24
n-C27 alkane	16	3.5–37.9	1.20	0.20
n-C28 alkane	16	2.9–25.2	1.26	0.18
n-C29 alkane	16	3.3–35.7	1.17	0.15
n-C30 alkane	16	1.8–12.4	0.95	0.15
n-C31 alkane	15	1.9–28.6	1.01	0.15
n-C32 alkane	11	0.6–7.5	0.93	0.12
n-C33 alkane	14	1.3–8.7	0.89	0.11
n-C34 alkane	11	1.1–5.4	0.76	0.17
n-C35 alkane	6	1.0–4.5	0.76	0.09
Phenanthrene	15	0.3–1.7	1.33	0.09
Fluoranthene	16	0.4–1.7	1.19	0.14
Pyrene	15	0.3–1.0	1.28	0.11
Benzo[a]anthracene	9	0.1–1.0	1.36	0.14
Chrysene	10	0.1–1.3	1.15	0.17

[a] The ratio was the concentration measured by the TD method to that by the solvent extraction method. A ratio of 1 signifies perfect agreement between measurements by the two methods.

the two methods was reasonably good when one considers the following two aspects with the solvent extraction method. First, the recoveries for the solvent extraction method were established by spiking standards onto blank filters, but the matrix of blank filters could be considerably different from the matrix of atmospheric aerosol particles. Second, the recoveries were determined at a single concentration level for each analyte and as a result, any concentration-dependence was not accounted for. The complicated nature of the sample pre-treatment with the solvent extraction method also serves to demonstrate the advantages of the TD method.

The ratios appeared to be analyte-dependent among the *n*-alkanes. The ratio reached a maximum value of 1.26 for the *n*-C_{28} alkane and showed a decreasing trend for *n*-alkanes of either increasing or decreasing volatility relative to the *n*-C_{28} alkane. The *n*-C_{25} alkane had the best agreement between the two methods. However, the ratios for the five PAHs detected did not show a clear analyte-dependence. The TD method reported high concentrations of the five PAHs than the solvent extraction method by 15–36%. These five PAHs have a volatility range similar to that from *n*-C_{20} to *n*-C_{32}. Therefore, volatility alone could not explain the various measurement discrepancies among different analytes between the two methods. One possible additional cause was the concentration-dependence of the recoveries; however, this remains a speculation that needs experimental evidence.

4. Conclusions

We demonstrate the feasibility of using in-injection port thermal desorption for analysis of *n*-alkanes (*n*-C_{13} to *n*-C_{36}) and PAHs collected on aerosol filters. This approach does not require any modification of existing GC–MS. In comparison with the traditional solvent extraction method, it has the unique advantages of reduced labor and time by avoiding sample pre-treatment and requiring less filter material for analysis. The suitable analysis conditions such as thermal desorption time and duration were identified for analysis of *n*-alkanes from *n*-C_{13} to *n*-C_{36} and PAHs heavier than naphthalene. Although not included in the test standards in this study, other non-polar aerosol organics such as hopanes, steranes, phthalates, iso-, and anteiso-alkanes could be quantified along with *n*-alkanes and PAHs using the injection port TD/GC–MS method.

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