Technical note

Precautions for in-injection port thermal desorption-gas chromatography/mass spectrometry (TD-GC/MS) as applied to aerosol filter samples

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ABSTRACT

In-injection port thermal desorption-gas chromatography/mass spectrometry (TD-GC/MS) allows for analysis for >130 non-polar organic compounds on small quartz-fiber filter samples without extraction chemicals. TD-GC/MS has been applied to samples from long-term U.S. networks since it is cost effective and less labor intensive. However, analysis of large numbers of samples results in sensitivity reductions over time. Instrument sensitivity and reproducibility were examined after 100, 200, and 500 sample analyses. Analyses of standards between batches of heavily loaded samples from China and Japan showed signal decreases of 28–78% for major organic classes. In the GC injection port, residues can accumulate on the gold-plated seal resulting in analyte adsorption as well as elevating signal background. Decreases in signal response were 28–43% for n-alkanes, 33–45% for hopanes and steranes, 28–56% for PAHs, and 38–78% for phthalates when the gold-plated seal was not replaced after 500 TD-GC/MS sample analyses. Limits of detection (LODs) also increased by 14–76% for the targeted non-polar organic compounds. Residues trapped in the capillary column head can cause peak broadening and overlap. The GC/MS system, including the injection port and gold seal, the column head (where the eluted sample is pre-concentrated), and the ion source should be cleaned after every batch of 50–100 samples.

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1. Introduction

Thermal desorption (TD) extraction of organic compounds followed by gas chromatographic (GC) separation and mass spectrometric (MS) detection (Chow et al., 2007a; Hays and Lavrich, 2007) can be applied to portions of quartz-fiber filters that are commonly acquired for organic and elemental carbon (OC and EC) analysis (Chow et al., 1993, 2007b, 2010). More than 130 organic compounds, including straight-chain and branched alkanes, hopanes, steranes, cycloalkanes, alkenes, polycyclic aromatic hydrocarbons (PAHs), and phthalates can be quantified from a ~1-h analysis, making possible speciated emission inventories (Zhang and Tao, 2009) and more precise source attribution (Chow et al., 2007c; Fujita et al., 2007; Watson et al., 2008).

The TD function can be undertaken with an external heating unit and transfer line (Ballesteros et al., 2009; Bates et al., 2008; Ding et al., 2009; Greaves et al., 1985; Hallama et al., 1998; Jeon et al., 2001; Labban et al., 2006; Ma and Hays, 2008; Sheesley et al., 2007; Tsytsik et al., 2008; Van Drooge et al., 2009; Waterman et al., 2001) or by desorption within the heated GC injection port (De Konig et al., 2002; Falkovich and Rudich, 2001; Helmig et al., 1990; Ho and Yu, 2004; Lin et al., 2007; Ono-Ogasawara et al., 2008; Schnelle-Kreis et al., 2005; Sklorz et al., 2007; Yang et al., 2005) and allows for solvent venting (Van Drooge et al., 2009) that may mitigate some of the issues described here. In-injection port TD removes some of the complexity and minimizes the length of transfer lines in which some of the desorbed material might be lost. In-injection port TD-GC/MS measurements are comparable to those obtained from solvent extraction (SE) (Ho et al., 2008) while using smaller samples at a fraction of the cost and environmental consequences.

Undesirable non-volatile organics, debris physically ejected from the quartz-fiber filter, and compounds with active functional groups can contaminate the GC injection port, the capillary column, and the MS ion source. This contamination can cause analyte loss,

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background signal elevation, and peak broadening and overlap. This study examines the effects of injection port cleaning, GC column head conditions, and MS ion source maintenance on signal sensitivity. Recommendations are provided to enhance the quality of concentrations achieved from injection port TD-GC/MS.

2. Methodology

TD-GC/MS was evaluated for $PM_{2.5}$ (particles with <2.5 μm aerodynamic diameter) samples from six cities in China and Japan during 2007–2009. $PM_{2.5}$ was collected on pre-fired (800 °C, 3 h) quartz-microfibre filters (QMA,Whatman, Clifton, NJ, USA) by a medium-volume sampler at a flow rate of 113 L min⁻¹ for 12 or 24 h. After sampling, filters were sealed and archived at <4 °C to minimize evaporation of semi-volatile components. Six filter portions of 1×0.5 cm dimensions were spiked with 50 ng of an internal standard (IS), cut into smaller strips, and inserted into a Pyrex TD tube (78 mm long, 4 mm I.D., and 6.35 mm O.D.) for placement into the split/splitless injector liner of an Agilent 6890 GC/5975 MS detector (Santa Clara, CA, USA). Pre-baked glass wool plugged both ends of the TD tube. Temperature in the injector port was set at 50 °C before analysis; the septum cap was closed and the injector port temperature was manually raised to 275 °C over 11 min to desorb the organic materials in splitless mode. The oven was maintained at 30 °C during sample heating to concentrate the released organic analytes on the head of the GC column. After the sample temperature achieved 275 °C, the GC oven temperature was retained at 30 °C for 2 min, increased at a rate of 10 °C min⁻¹ to 120 °C, followed by an increase of 8 °C min⁻¹ to 310 °C, and then held at 310 °C for 20 min. An HP-5ms capillary column (5% diphenyl/95% dimethylsiloxane; 30 m long × 0.25 mm I.D. × 0.25 μm film thickness; J&W Scientific, Folsom, CA, USA) was used to separate the eluting compounds. The carrier gas was ultra-high purity (99.9999%) helium (He) at a constant flow of 1.0 cm³ min⁻¹. Organic compounds desorbed from the filter at <275 °C were transferred by a pure He carrier gas flow. The MS detector was operated in scan mode from 50 to 650 amu at 230 °C and 70 eV for electron ionization. Identification was achieved by comparing the mass spectra and retention times of the chromatographic peaks with those of authentic standards. More than 500 samples were analyzed between July 2008 and April 2009.

3. Results and discussion

3.1. Injection port cleanliness

Replicate calibration standards were analyzed after the analyses of 100, 200, and 500 filter samples. The gold-plated seal (inlet base seal, located at the bottom of the GC injection port) was not replaced during these analyses, but the ion source was cleaned after analyses of 100 samples and the autotune program was run daily. Fig. 1 shows that the decrease in signal from the first to 500th sample was 28–43% for n-alkanes, 33–45% for hopanes and steranes, 28–56% for PAHs, and 38–78% for phthalates, – after 500 TD-GC/MS analyses. Apparent cumulative decrease in signal response after the analysis of 100, 200, and 500 samples may be caused by non-volatile organics, coarse particles, and fiber debris that are not blocked by the glass wool in the TD tube. Most of these contaminants are unable to enter into the capillary column due to their size, but they may decompose inside the injection port and can adhere to the gold-plated seal. In addition, polar organics such as fatty acids and alcohols can activate the injection port surface and are not quantified using the direct TD method (Chow et al., 2007a). Non-volatile and polar organics can adsorb and interact with the compounds being quantified. The signal decreased more for the heavier compounds (with higher boiling points) owing to longer residence times in the heated injection port. The average signal decrease was $40 \pm 12\%$ for homologous n-alkanes (n-$C_{>30}$), compared to $30 \pm 11\%$
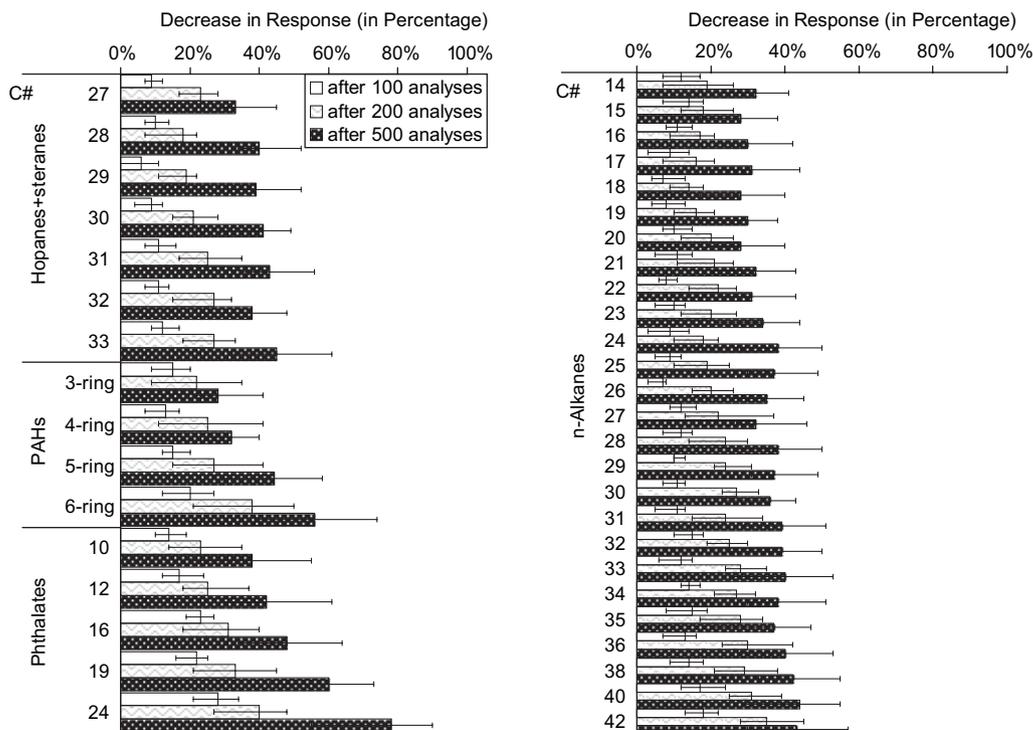
Fig. 1. Decrease in signal response for non-polar organic compounds in analysis of 100, 200, and 500 replicate calibration standards without replacing the gold-plated seal in the GC injector.

for n-C$_{<20}$. For five-aromatic ring PAHs (e.g., benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[e]pyrene, benzo[a]pyrene, and perylene) the signal decreased by $44 \pm 12\%$, compared with a $32 \pm 9\%$ decrease for four-ring PAHs (e.g., benzo[a]anthracene and chyrene). The largest decreases were found for phthalates, which contain alkyl aryl ester functional groups. Since no peaks were detected in the blank calibration samples, the mean blank signal was approximated from the intercept and standard error of the peak area ratio for a blank sample.

Tables 1 and 2 compare LODs for non-polar organic compounds determined using clean and contaminated (after analysis of 500 samples) gold-plated seals in the injection port, demonstrating LOD degradation of 14–76% with the unmaintained seal. LOD deterioration is most severe for the six phthalates ($56 \pm 15\%$). A clean gold-plated seal is important for the splitless TD process because the analytes have a long residence time in the injection port. Weekly inspection and replacement of this seal after 50–100 TD analyses is recommended to minimize sensitivity changes due to adsorption by the contaminant materials. The injection port septum and O-ring should be replaced at weekly (or more frequent) intervals along with cleaning of the inner wall. In some cases, higher background and ghost peaks were found after heavily loaded samples were analyzed. A high background degrades the accuracy of chromatographic peak integration and thus affects quantification of the targeted compounds. The ghost peaks potentially cause over-estimation of some abundant compounds such as n-alkanes and phthalates. The use of IScan overcome the loss of sensitivity in the system but could not solve the background and ghost peak issues. Such contamination and carry-over can be avoided by routine periodic maintenance of the GC injection port.

3.2. GC column head condition

Fig. 2 compares chromatographic separation of five-ring PAHs for prepared samples. Peak co-elution of six PAHs was observed with the unmaintained column head after >100 TD analyses. The GC capillary column head acts as a cryogenic or cold trap to re-concentrate the organic vapor desorbed during the TD process. Its condition affects analyte separation and peak resolution in the chromatogram, especially for isomers. A clean column head is especially critical for the in-injection port TD because the 12.5 min required for complete sample vaporization (from 50 to 275 °C; i.e., thermal desorption time) exceeds the few seconds at an isocratic high temperature (e.g., >250 °C) in the liquid injection approach. Non-volatile organic compounds from aerosol samples can condense or adsorb in the column head, but they may not be efficiently released at the maximum column operation temperature (i.e., 300–320 °C for a DB-5 GC column). The accumulated residue

Table 1
Comparison of limits of detection (LODs)[a] for n-alkanes and hopanes determined with a new and used gold-plated seal in the GC injector.

Organic Compounds	MW	Quant Ion [a]	LOD (new gold-plated seal)	LOD (gold-plated seal used for 500 analyses)	LOD Change (+)
n-Alkanes					
n-tetradecane (n-C14)	198	57	4.56	5.45	20%
n-pentadecane (n-C15)	212	57	4.12	4.87	18%
n-hexadecane (n-C16)	226	57	3.82	4.35	14%
n-heptadecane (n-C17)	240	57	3.14	3.66	17%
n-octadecane (n-C18)	254	57	1.27	1.64	29%
n-nonadecane (n-C19)	268	57	0.98	1.24	27%
n-icosane (n-C20)	282	57	1.23	1.45	18%
n-heneicosane (n-C21)	296	57	1.52	1.87	23%
n-docosane (n-C22)	310	57	1.25	1.52	22%
n-tricosane (n-C23)	324	57	1.87	2.44	30%
n-tetracosane (n-C24)	338	57	0.98	1.24	27%
n-pentacosane (n-C25)	352	57	0.83	1.09	31%
n-hexacosane (n-C26)	366	57	1.52	1.87	23%
n-heptacosane (n-C27)	380	57	0.87	1.27	46%
n-octacosane (n-C28)	394	57	0.76	1.07	41%
n-nonacosane (n-C29)	408	57	1.28	1.76	38%
n-triacontane (n-C30)	422	57	1.09	1.55	42%
n-hentriacotane (n-C31)	436	57	1.11	1.62	46%
n-dotriacontane (n-C32)	450	57	1.43	1.89	32%
n-tritriactotane (n-C33)	464	57	1.29	1.87	45%
n-tetratriactoane (n-C34)	478	57	0.99	1.42	43%
n-pentatriacontane (n-C35)	492	57	1.20	1.56	30%
n-hexatriacontane (n-C36)	506	57	0.67	0.97	45%
n-octatriacontane (n-C38)	534	57	0.87	1.18	36%
n-tetracontane (n-C40)	562	57	1.28	1.77	38%
n-dotetracontane (n-C42)	590	57	1.32	1.87	42%
Hopanes					
22,29,30-trisnorneophopane (Ts)	370	191	0.27	0.34	26%
22,29,30-trisnorphopane (Tm)	370	191	0.31	0.43	39%
αβ-norhopane (C29αβ-hopane)	398	191	0.23	0.31	35%
αα- + βα-norhopane (C29αα- + βα-hopane)	398	191	0.22	0.33	50%
αβ-hopane (C30αβ-hopane)	412	191	0.25	0.36	44%
βα-hopane (C30βα-hopane)	412	191	0.28	0.41	46%
αβS-homohopane (C31αβS-hopane)	426	191	0.29	0.42	45%
αβR-homohopane (C31αβR-hopane)	426	191	0.18	0.25	39%
αβS-bishomohopane (C32αβS-hopane)	440	191	0.17	0.25	47%
αβR-bishomohopane (C32αβR-hopane)	440	191	0.22	0.32	45%
22S-trishomohopane (C33)	454	191	0.18	0.25	39%
22R-trishomohopane (C33)	454	191	0.19	0.28	47%

[a] Quantification Ion for MS detection.

Table 2
Comparison of limits of detection (LODs)[a] for steranes, PAHs and phthalates determined with a new and used gold-plated seal in the GC injector.

Organic Compounds	MW	Quant Ion[a]	LOD (new gold-plated seal)	LOD (gold-plated seal used for 500 analyses)	LOD Change (+)
Steranes					
ααα 20S- + βαα 20R-cholestane	372	217	0.23	0.29	26%
αββ 20R-cholestane	372	218	0.25	0.32	28%
ααα 20R-cholestane	372	217	0.28	0.36	29%
αββ 20R 24S-methylcholestane	386	218	0.22	0.28	27%
ααα 20R 24R-methylcholestane	386	217	0.28	0.40	43%
ααα 20S 24R/S-ethylcholestane	400	217	0.21	0.28	33%
αββ 20R 24R- + βαα 20R 24R-ethylcholestane	400	218	0.23	0.35	52%
ααα 20R 24R-ethylcholestane	400	217	0.22	0.31	41%
PAHs					
Acenaphthylene	152	152	1.43	1.82	27%
Acenaphthene	154	154	2.02	2.63	30%
Fluorene	166	166	1.07	1.39	30%
Phenanthrene	178	178	0.82	1.12	37%
Anthracene	178	178	0.76	0.98	29%
Fluoranthene	202	202	0.62	0.83	34%
Pyrene	202	202	0.54	0.72	33%
benzo[a]anthracene	228	228	0.66	0.84	27%
Chrysene	228	228	0.56	0.74	32%
benzo[b]fluoranthene	252	252	0.65	0.91	40%
benzo[k]fluoranthene	252	252	0.45	0.64	42%
benzo[a]fluoranthene	252	252	0.67	0.97	45%
benzo[e]pyrene	252	252	0.43	0.61	42%
benzo[a]pyrene	252	252	0.65	0.91	40%
perylene	252	252	0.72	0.99	38%
indeno[1,2,3-cd]pyrene	276	276	1.04	1.54	48%
dibenzo[a,h]anthracene	278	278	0.87	1.33	53%
benzo[ghi]perylene	276	276	1.01	1.52	50%
picene	278	278	0.87	1.29	48%
coronene	300	300	1.21	1.87	55%
dibenzo[a,e]pyrene	302	302	1.13	1.81	60%
Phthalates					
dimethylphthalate	194	163	6.12	8.32	36%
diethyl phthalate	222	177	4.12	5.89	43%
di-*n*-butyl phthalate	278	149	3.02	4.56	51%
butyl benzyl phthalate	312	149	4.77	7.66	61%
bis(2-ethylhexyl)phthalate	390	149	6.42	11.28	76%
di-*n*-octyl phthalate	390	149	6.24	10.65	71%

[a] The limit of detection (LOD) is the minimum amount of non-polar organic compound that generates the minimum distinguishable signal plus 3 times the standard derivation of the blank signals.

engages the polymer coating on the inner wall of the capillary column, thereby reducing adsorption efficiencies during the TD process and causing peak broadening and overlap. After sample analysis, black residues can sometimes be seen in the column head. In addition to the regular column head cutting, a short (e.g., 1 m) pre-column with the same diameter and phase as the working capillary column can be installed. The pre-column should be replaced after analysis of 50 samples. More frequent replacement may be needed when heavily loaded samples are analyzed.

3.3. High polar compound abundances

Few polar organic compounds desorb from the filter at 275 °C, and those that do are poorly separated in TD-GC/MS by the common

Peak Identification:
a: benzo[b]fluoranthene; b: benzo[k]fluoranthene; c: benzo[a]fluoranthene; d: benzo[e]pyrene; e: benzo[a]pyrene; f: perylene
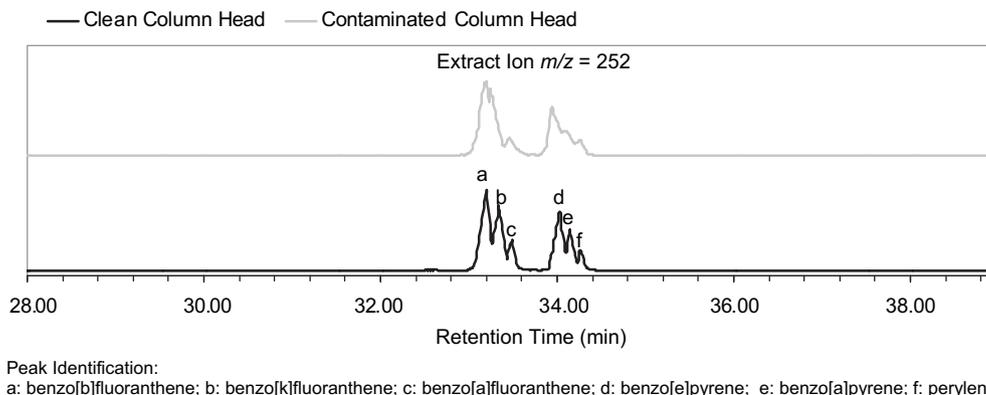
Fig. 2. Comparison of ion chromatograms ($m/z = 252$) for six five-ring PAHs using a clean vs. unmaintained (e.g., no replacement after >100 TD analyses) column head.

stationary-phase capillary columns (e.g., DB-1 or DB-5 GC column). However, some polar organic compounds that do desorb may elute with some of the targeted non-polar organic compounds. For example, n-hexadecanoic acid (C_{16}) can overlap with n-tetradecane (n-C_{14}) and pentadecane (n-C_{15}), and n-octadecanoic acid (C18) can overlap with n-heptadecane (n-C_{17}). Desorbed fatty acids from samples containing meat cooking and wood burning contributions (McDonald et al., 2000, 2003, 2006) can potentially overload the ion source, reducing the signal and biasing the n-alkane concentrations. Since it is difficult to remove polar organic compounds from the hot gas stream (e.g., with absorbent), precautions against potential interferences must be taken when high levels of polar organics are suspected. An application of two dimensional GC is a solution to prevent the peak overlaps (Ma et al., 2010).

3.4. MS ion source maintenance

The MS ion source (e.g., ion focus lens, repeller, and ion source body) is subject to contamination during the in-injection port TD process since there is no pre-treatment of the samples, so frequent ion source cleaning is also necessary. Similar to the normal GC/MS application, anomalous increases of electron multiplier voltage (EMV) and presence of undesirable fragments in the MS autotune report indicate that ion source cleaning is required.

4. Conclusion

Owing to its simplicity and applicability to existing samples, the in-injection port TD-GC/MS method is becoming more widely used to identify and quantify non-polar organic compounds in atmospheric filter samples. Because the method is applied to large numbers of samples, the GC/MS system must be cleaned after every batch of 50–100 samples. Cleaning is needed for the injection port and gold seal, the column head where the eluted compounds are pre-concentrated, and the ion source. The use of a pre-column can also reduce column head contamination. Increases in LODs and reduction in signal response are most severe for samples with high polar organic compound contents.

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