



Evaluation of an in-injection port thermal desorption-gas chromatography/mass spectrometry method for analysis of non-polar organic compounds in ambient aerosol samples

Steven Sai Hang Ho^{a,1}, Jian Zhen Yu^{a,b}, Judith C. Chow^{a,c,*}, Barbara Zielinska^a, John G. Watson^{a,c}, Elber Hoi Leung Sit^b, James J. Schauer^d

^a Division of Atmospheric Sciences, Desert Research Institute, Reno, NV 89512, USA

^b Department of Chemistry, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong, China

^c Institute of Earth and Environment of the Chinese Academy of Sciences, Xian, China

^d Department of Civil Engineering and the Wisconsin State Laboratory of Hygiene, University of Wisconsin-Madison, Madison, WI 53706, USA

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ABSTRACT

Thermal desorption coupled with gas chromatography/mass spectrometry (TD-GC/MS) is an alternative to solvent extraction (SE)-based GC/MS (SE-GC/MS) for the analysis of non-polar organic compounds in filter or impactor-collected aerosols. TD-GC/MS has no sample pretreatment and requires a small filter aliquot for detecting individual organic compounds. The performance of an in-injection port TD-GC/MS is evaluated for polycyclic aromatic hydrocarbons (PAHs), *n*-alkanes, iso-/anteiso-alkanes, hopanes, steranes, branched alkanes, cyclohexanes, alkenes, and phthalates in standards and ambient air samples. Replicate analysis for 132 organic compounds showed relative standard deviations <10%, with the majority <5%. Accuracy for 15 PAHs, determined with NIST standard reference material (SRM) 1649a urban dust, was within ±5% of the certified values. TD-GC/MS and SE-GC/MS method comparisons for 14 Hong Kong ambient samples agreed within 11% for 106 non-polar compounds. For 19 Tong Liang, China samples, agreement was within 13% for 23 PAHs.

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1. Introduction

Organic species account for a large fraction of air particulate matter (PM), especially in PM_{2.5} [1]. They are important for human health [2], visibility [3], and soiling [4]. Aerosol organic matter (OM) is a mixture of many compounds from a wide range of compound classes [5]. Many of these compounds have been identified and quantified by solvent extraction (SE) followed by gas chromatography/mass spectrometry (GC/MS) [6–11]. These analyses have been useful for source apportionment using chemical mass balance (CMB) receptor models [12–15]. Analytical methods using the SE approach require large sample sizes (several mg of PM_{2.5} collected on a filter) and lengthy and laborious pre-analysis treatment (i.e., solvent extraction, volume reduction, and, in some cases, sam-

ple pre-cleaning), thereby limiting the practical number of samples that can be analyzed. Possible contamination also arises from using a large quantity of solvents.

Thermal desorption (TD) has recently emerged as an alternative to SE in the GC/MS analysis of PM non-polar organic compounds [5,11,16–24]. In TD-GC/MS, transfer of analytes from the collection substrate to the GC system is accomplished by heating a small portion of the sample in either an external TD device connected to the GC or inside the GC injector in a flow of inert gas. Analytes are thermally extracted into the vapor stream and focused on the GC injection liner or the head of the GC column. The TD approach avoids contamination from solvent impurities, requires little sample preparation (<1 min), and uses sample quantities of ~10 µg in organic carbon mass [22]. The TD-GC/MS method requires a much smaller filter sample size (0.3–5 cm²) than the SE-GC/MS approach (~203 cm²) when the same 24-h high-volume filter sample is analyzed [24]. Organic speciation can be obtained from archived filters from which portions have already been taken for other chemical analyses, without additional sampling.

Considering the various configurations implementing TD, in-injection port TD is among the most cost effective because it requires no modification to the GC instrument and no transfer

* Corresponding author at: Division of Atmospheric Sciences, Desert Research Institute, 2215 Raggio Parkway, Reno, NV 89512, USA. Tel.: +1 775 674 7050; fax: +1 775 674 7009.

E-mail address: judy.chow@dri.edu (J.C. Chow).

¹ Present address: Hong Kong Premium Services and Research Laboratory, Kowloon, Hong Kong, China.

line [23,25]. Moreover, it is capable of qualitative and quantitative analysis of polycyclic aromatic hydrocarbons (PAHs) and *n*-alkanes in aerosol samples [23]. While Ho and Yu [23] described the in-injection port TD method, a comprehensive assessment of the method's accuracy, precision, and validity has yet to be reported. This paper demonstrates that the in-injection port TD-GC/MS method is accurate, precise, and valid for the analysis of 132 non-polar organic species in the functional groups of PAHs, *n*-alkanes, iso-/anteiso-alkanes, hopanes, steranes, branched alkanes, cyclohexanes, alkenes, and phthalates. This is accomplished by comparison with the well-established SE approach for non-polar organic compounds for two sets of ambient aerosol samples. Method comparisons were reported in two previous studies [23,26], and they were limited to a small number of samples and compounds. Accuracies and precisions are quantified by replicate analyses of ambient samples and standard reference materials (SRMs).

2. Experimental

2.1. Aerosol samples

Sample information, analytical protocols, and participating laboratories are tabulated in Table 1. PM_{2.5} samples from the campus of Hong Kong University of Science and Technology (HKUST; Kowloon, Hong Kong, China) and the Fresno Supersite (Fresno, CA, USA; [27]) were used to determine the reproducibility of the TD method for 132 non-polar organic compounds. The same TD protocol was followed at HKUST and at the Desert Research Institute (DRI) laboratories [23] to evaluate method reproducibility. The Yuen Long (Hong Kong) and Tong Liang (China) samples were used to evaluate the equivalence and comparability between the TD- and SE-GC/MS methods for 106 non-polar organic compounds and 25 PAHs, respectively. The SE-GC/MS method was applied to the monthly composites of the Teflon Impregnated Glass-Fiber (TIGF) filters (DuPont, Delaware, DE, USA) at DRI's Organic Analytical Laboratory (OAL), whereas TD-GC/MS analysis was applied to individual quartz-fiber filters at DRI's Environmental Analysis Facility (EAF) [28]. Monthly averages of ten 72 h quartz-fiber samples by TD-GC/MS are compared to the corresponding monthly composite TIGF samples by SE-GC/MS.

2.2. Chemical standards

Three types of standards were used, including: (1) the National Institute of Standards and Technology (NIST, Gaithersburg, MD, USA) SRM 1649a urban dust [29]; (2) Chiron AS (Trondheim, Norway) hopanes and steranes; and (3) the Wisconsin State Laboratory of Hygiene organic standard mixtures containing PAHs, *n*-alkanes, branched alkanes, cyclohexanes, and phthalates. Among the internal standards (I.S.), [²H₁₀] phenanthrene (phe-*d*₁₀), 1-phenyldodecane, and [²H₅₀] *n*-tetracosane (*n*-tetracosane-*d*₅₀) were obtained from Aldrich (Milwaukee, WI, USA), and [²H₁₂] chrysene (chr-*d*₁₂) was obtained from Cambridge Isotope Laboratories (Andover, MA, USA). The chemical standards and I.S. were prepared in benzene/iso-propanol (50:50, Aldrich). Dichloromethane, methanol, and acetonitrile were HPLC- or GC-grade obtained from Mallinckrodt (Phillipsburg, NJ, USA), and were laboratory-distilled before use.

2.3. In-injection port TD-GC/MS

Portions (1.0 cm² for the Fresno and Tong Liang samples, and 2.9 cm² for the Hong Kong samples) of quartz-fiber filter samples were spiked with 50 ng of I.S. and cut into smaller portions

Table 1
Description of PM_{2.5} aerosol samples used in this study

Sample set	Sampling location and time	No. of samples	Sampler type	Sampling rate (l min ⁻¹)	Sampling duration (h)	Filter type	Analysis protocol	Participating laboratories ^a	Analysis objective
I	HKUST Campus, Kowloon, Hong Kong, China (summer 2004)	1	High volume	1130	24	Prefired quartz-fiber ^b	TD-GC/MS	HKUST	Method reproducibility
II	Fresno Supersite, CA, USA (spring 2004)	20	High volume	1130	24	Prefired quartz-fiber ^b	TD-GC/MS	DRI-EAF	Method reproducibility
III	Yuen Long, New Territories, Hong Kong, China (winter 2004)	14	High volume	1130	24	Prefired quartz-fiber ^b	TD- and SE-GC/MS	HKUST	TD- and SE-GC/MS method comparison
IV	Tong Liang, northeast of Chongqing, China (2002–2003)	19	MiniVol (low volume)	5	72	Teflon-impregnated glass fiber ^c	SE-GC/MS	DRI-OAL	TD- and SE-GC/MS method comparison
						Prefired quartz-fiber ^b	TD-GC/MS	DRI-EAF	

^a HKUST: Hong Kong University of Science and Technology, DRI-EAF: Desert Research Institute Environmental Analysis Facility, DRI-OAL: Desert Research Institute Organic Analytical Laboratory.

^b QAT2500-UP, Pall Sciences, Ann Arbor, MI.

^c T60A20, 47-nm diameter, Pall Sciences, Ann Arbor, MI.

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