Developments in direct thermal extraction gas chromatography-mass spectrometry of fine aerosols

Michael D. Hays, Richard J. Lavrich

This review examines thermal extraction gas chromatography-mass spectrometry (TE-GC-MS) applied to aerosols collected on filters. Several different TE-GC-MS systems as a group have speciated hundreds of individual organic constituents in ambient fine aerosols. Improved molecular marker source apportionment (chemical mass balance) may be one of the benefits of further developing TE-GC-MS to determine organic aerosol composition.
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1. Introduction

Thermal extraction-gas chromatography-mass spectrometry (TE-GC-MS) is emerging as a popular analytical method in aerosol science. It is being used to identify and to quantify individual organic matter constituents in combustion-source and atmospheric fine particulate matter ($PM_{2.5}$; fine aerosols; particles with aerodynamic diameters equivalent to or less than 2.5 microns). Several of these constituents cause adverse health effects. They also function as organic tracers for particulate-matter air pollution [1].

The components of specific analytical interest frame a wide array of chemical classes, including the *n*-alkanes, branched alkanes, polycyclic aromatic hydrocarbons, carbohydrates, carboxylic acids, ketones, aldehydes, esters, alcohols, steroids, amines, and nitriles.

Determining $PM_{2.5}$ composition is an important first step in understanding how $PM_{2.5}$ affects human health [2], visibility [3], and climate [4]. It will also be needed to plan appropriate PM regulatory and risk-management strategies. However, $PM_{2.5}$ chemistry is perplexing, and the $PM_{2.5}$ matrix can contain different combinations of any number of individual organic species, elemental carbon segments, geo-polymer or bio-polymer structures, and inorganic phases, which complicate analysis.

The TE-GC-MS technique has been utilized on a number of solid, semi-solid, and liquid samples, and a substantial body of research looks at TE for the analysis of volatile organic compounds in air; however, these subjects are not covered here. The specific focus of this article is the emerging off-line application of TE-GC-MS to combustion-source and ambient fine aerosols collected on filter media. TE-GC-MS is likely to become more widely utilized in this area in the near-term because it:

(i) is readily available commercially;
(ii) is fully automated;
(iii) operates inexpensively;
(iv) is quantitative;
(v) requires just micrograms of sample; and,
(vi) eliminates hazardous solvents.

It is also compliant with filter-based sample-collection methods and program quality-control plans currently in use within existing air quality-sampling networks. Method automation potentially increases laboratory throughput, which will improve sample management for large air-quality field-sampling campaigns. Moreover, the sensitivity of TE-GC-MS increases the temporal resolution of atmospheric aerosol composition and may be adequate for estimating daily human exposures to organic compounds in $PM_{2.5}$ air pollution measured by personal monitors. This makes TE-GC-MS a method of choice when using individual organic compounds to apportion ambient PM

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linked to personal exposures. The aerosol sample mass available for analysis is a principal factor when considering an off-line extraction method. TE-GC-MS is more likely to be implemented when the organic carbon (OC) mass is greater than approximately 10 μg but less than that required for use with ultrasonic, Soxhlet, or pressurized fluid solvent extraction techniques ($\geqslant$ 1 mg of OC). Small quantities of organic matter on aerosols are becoming more common due to improving combustion efficiencies and implementation of air-quality standards.

Other methods of aerosol characterization share some of the analytical attributes described above for TE-GC-MS. For example, on-line continuous and semi-continuous instruments, such as the aerosol time-of-flight mass spectrometer [5] and photoionization aerosol mass spectrometer (PIAMS) [6] have been used to identify chemical species in individually sized particles and in particle ensembles of just picograms, respectively. These instruments are also fully automated and reduce or eliminate the need for solvents and cumbersome sample preparation, while providing a real-time size measurement and MS-based separation. However, they can be expensive to procure and operate, are relatively less versatile than filter packs, and will require further development before fully speciating and quantifying many of the individual organic species in aerosols. Because both the accurate quantification of organic compounds in aerosols and the study of transient aerosol events are typically required (i.e. when studying diesel-exhaust emissions), the sampling trend has been to deploy on-line instrumentation in tandem with filter-based collection systems, to which off-line methods, such as TE-GC-MS, are later applied. However, on-line; semi-continuous GC-MS instrumentation that implements TE is also currently being developed for field use.

Regardless of the recent advent of on-line instruments (since the 1990s) and advanced extraction techniques, the detailed organic chemical speciation of source emissions and ambient aerosols has been grounded in solvent extraction (SE)-GC-MS over much of the past two decades (e.g., [7,8]). TE-GC-MS is beginning to overcome many of the significant analytical challenges associated with the SE-GC-MS methods. It has its benefits; however, there is much that needs to be learned about TE-GC-MS and its application to $PM_{2.5}$ (e.g., the use of TE is complicated by the potential for carry-over, transfer loss, or molecular rearrangement, fragmentation, or breakdown at higher extraction temperatures ($\geqslant$ 350°C)). Limitations are impaired quantitation, lost aerosol sample, more frequent TE equipment failure, and limited laboratory throughput. Of course, SE and other extraction methods are less plagued by these limitations, which must be studied closely for their effects on analytes in different aerosol matrices. Introduction of chemical-derivatization techniques and the optimization of TE parameters (such as the mass of organic carbon to be thermally extracted from aerosol samples and the extraction rate and hold temperature) are likely to limit the extent of these effects, which are mainly research-program and equipment specific.

In this article, we provide examples of recent TE-GC-MS studies that characterize individual organic matter constituents in fine ambient and emission-source aerosols. An assessment of the state of TE-GC-MS development is considered relative to the notable, recent progress made by SE-GC-MS in this area. In the process of reviewing the current state of TE-GC-MS in aerosol science, we offer an overview of the different TE hardware in use. Further objectives of investigating the advancement of TE-GC-MS in this field are to:

(i) indicate important future directions in TE-GC-MS research; and,
(ii) assist analysts needing a sound basis for decision making when adopting an extraction technology for determining the organic chemical properties of fine aerosols.

Much of the discussion covering the advancement of TE-GC-MS is framed relative to achieving source-receptor apportionment with organic markers.

We focus on designs of TE systems and investigations conducted since 1985 to determine the thermally-extracted organic compounds in PM. Since 1985, systems incorporating ovens interfaced to GC-MS equipment by transfer lines, direct sample introduction (DSI) to the GC inlet, and Curie-Point pyrolysis (CPP) techniques have been developed to extract organic compounds thermally from aerosol matter. What follows is how these different apparatus designs, heating techniques and operating conditions have affected experimental results. For sake of space, we do not refer to experiments conducted prior to 1985 that thermally extracted aerosol organic matter.

2. TE-GC-MS in aerosol research – use of TE ovens

2.1. Sample introduction

Several of the first investigations of particle organic matter composition implemented TE using an oven interfaced to the GC-MS by a transfer line [9–14]. Sample introduction to the oven, oven heating, and subsequent analyte transfer to and analyte trapping in the GC are all essential to accomplishing TE-GC-MS in this way. Certainly, new developments in TE have eliminated the oven and transfer line, and we cover these advancements. However, we first discuss the use of TE-oven systems because it helps to put these TE advancements in perspective, many of which utilize the same basic strategies and principles as those learned with oven-based technologies.

The practice of introducing aerosol sample to the TE oven has varied by investigation. Because of the

radically different filter and extraction tube geometries, introduction of the aerosol-filter sample to the tube has been a challenge. The approach of Greaves et al. [9] showed that it was possible to integrate low-volume sampling and a TE tube, whereas the independently developed TE-GC-MS system of Waterman et al. [12], which is more typical, required PM sample (1–5 mg) to be manually placed in a glass-lined stainless steel desorption tube between pre-conditioned (350°C) glass-wool plugs. The glass wool trapped aerosol and ensured even gas flow over the aerosol sample. An adjustable liner holder was required to control sample placement in the desorption oven, somewhat complicating this sample-introduction scheme. However, the unique integrated system developed by Greaves and co-workers [9] minimized sample handling and largely eliminated any difficulty associated with introducing aerosol sample to the TE tube and oven. It consisted of a quartz filter in a small concentric sampling tube and could collect micrograms of airborne PM in short intervals (~60 min; 336 L).

The use of a micro-scale sealed vessel (MSSV) for sample preparation has also been investigated [13,14]. The MSSV is a bent (170°) glass tube (3 cm × 3 mm i.d.; 40 μL internal volume), which is pre-cleaned (350°C for 30 min), filled with sample and glass beads (120 mesh), spiked with liquid standard, and then sealed. For analysis, the sealed tubes are heated (300°C) in the thermal desorption oven and then broken open with an external plunger. A potential drawback to conducting this step is that the desorption unit requires a back-purge system for flushing the oven of glass shards post analysis. In addition, the ''closed'' (high-pressure) MSSV system promoted thermal decomposition, producing relatively more volatile matter, so this sample-introduction technique is more likely to be applied as an alternative to pyrolysis rather than to quantify the individual organic constituents in aerosols.

2.2. Sample heating and extraction

TE of the aerosol sample has traditionally been conducted in ovens positioned above the GC inlet (as shown in Figs. 1 [aluminum block] and 2 [desorption double oven]). With most modern TE ovens, temperature programming is possible. The question of what extraction heating rate and hold temperature to apply is important. Both gradual and rapid heating in ovens (20°C/min) and Curie-Point devices (~1.4×10^5°C/min) have been used to extract organic matter from aerosols with hold temperatures spanning 275–590°C. The optimum extraction heating rate and hold temperature is surmised as dependent on the aerosol-matrix type, volatility and thermal stability of compounds sought, and equipment design, among other factors. Thus far, aerosol extraction has proceeded for 10–15 min at 300°C for the majority of experiments performed in TE ovens [9–14]. This

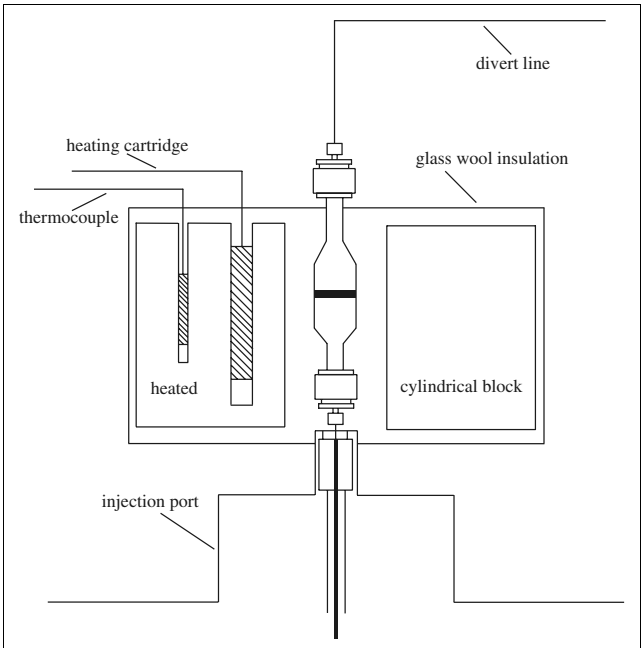

Figure 1. Schematic diagram of integrated low-volume sampling and thermal extraction (TE) analysis tube inserted in the heating assembly apparatus and interfaced to gas chromatography-mass spectrometry (GC-MS). (Reprinted with permission from [9]; © 1985 American Chemical Society).

temperature sufficiently volatilizes many of the analytes of interest without causing significant organic matter pyrolysis or charring. Use of TE ovens amenable to protracted heating rates does increase the analysis time but maintains the physical structure of the aerosol matrix intact relatively longer during compound extraction – assisting with the extraction of the heavier, higher boiling point organic compounds. Helium flow over the aerosol sample being extracted in the oven is also an important consideration, as it improves the extraction efficiency to some degree. In some TE equipment, desorbents are swept from the oven at a rate limited by the carrier gas flow, which is diverted from the inlet to the sample during extraction. However, some newer, commercially available TE-oven systems permit the analyst to adjust and control the He flow over the sample beyond that needed to maintain column flow, potentially increasing extraction efficiency.

2.3. Analyte transfer and trapping

Quantitative analyte delivery to the GC from the oven post extraction is typically achieved through a short, inert, heated capillary transfer line or short-path interface. Transfer lines are designed to minimize adhesion and adverse chemical reactions while rapidly delivering analytes to the GC. The transfer-line temperature is normally maintained constant throughout desorption and set equal to the maximum desorption temperature (~300°C). Despite the success of limiting the adsorption of neutral organic compounds on transfer lines, polar

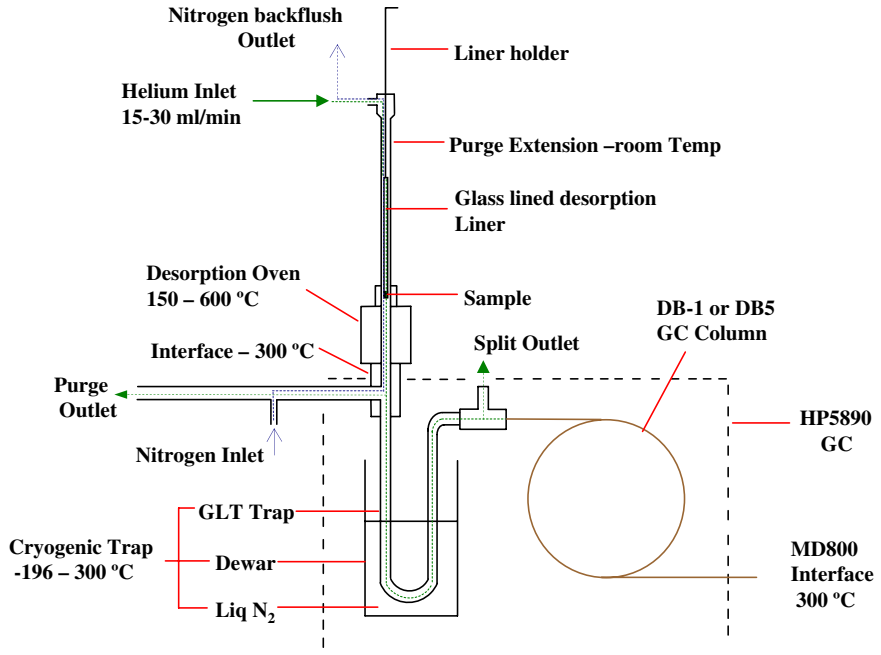

Figure 2. A thermal extraction gas chromatography-mass spectrometry (TE-GC-MS) system consisting of a desorption double oven, short-path interface, and cryogenic trap. (Reprinted with permission from [12]; © 2000 American Chemical Society).

compounds (i.e., methoxyphenols) in aerosols remain likely to adhere. Improvements in sample introduction and possibilities for in situ, thermally-assisted derivatization processes are expected to overcome this challenge in the near future. Though not always necessary, transferred compounds are normally cryofocused (−196°C – −60°C) on the analytical column [9], heatable cryogenic trap [12], or a programmable temperature vaporization (PTV) inlet [15]. The trap and PTV inlet are typically ballistically heated upon completion of the TE. This step ensures that the analytes are transferred to the column in plug form. A GC-MS analysis normally follows the successful transfer of analytes from the TE oven.

2.4. Validation with standard reference materials

Airborne PM samples, standards, and National Institute of Standards and Technology (NIST) Standard Reference Material (SRM) 1649 have all been studied by oven-based TE-GC-MS methods. SRM 1649, a dust (sieved to <125 μm) collected in the urban Washington D.C. area (1976–77) [16], has been particularly useful to TE-GC-MS validation efforts. PAH compounds are of specific interest due to their toxicity, and the SRM 1649 has NIST-certified PAH concentration values reported as a mass fraction of the PM. Certified values such as these, determined with Soxhlet-SE-GC methods, can be compared to those values obtained using TE-GC-MS by viewing Table 1. TEs of the NIST SRM 1649 (34–386 μg) generated PAH concentrations that showed no statistical difference ($\alpha = 0.05$) from those certified by NIST (see [9] and the NIST SRM 1649 [1982] column in Table 1). However, a calculated f statistic ($\alpha = 0.05$) indicated a significant difference in variability between these data sets. The TE method performed less effectively in this respect due to the lack of homogeneity in the low microgram quantities used during the TE of NIST SRM. Using ~3 mg of the SRM 1649a and phenanthrene-d_{10} as an internal standard, Waterman et al. [12] quantified nanogram quantities of PAHs in the urban dust with seven of the eight TE-GC-MS-determined PAH values showing no statistical difference ($\alpha = 0.05$) from the NIST-certified PAH concentrations (Table 1).

Linearity tests with TE-GC-MS further demonstrated that the total integrated chromatogram area increased linearly ($r^2 = 0.948$) with the SRM sample mass (1–5 mg) [12]. The even/odd carbon-number predominance and carbon maximum of *n*-alkane homologues have helped to apportion tropospheric aerosols; thus, their accurate quantification is important. Over the 1–5-mg mass range, linearity was confirmed for individual C_{20}–C_{33} *n*-alkane homologues ($r^2 = 0.931$–0.993) and for 10 PAHs (phenanthrene, pyrene, fluoranthene, benz[*a*]-anthracene, chrysene, benz[*b*]fluoranthene, benz[*e*]pyrene, benz[*a*]pyrene, benz[*ghi*]perylene, and indeno[*1,2,3-cd*]pyrene). The PAH r^2 range was 0.973–0.997. The TE-determined PAH in NIST SRM 1649a was also investigated with the MSSV, the results of which are given in Table 1 [13,14]. The entire suite of organic compounds identified or quantified by these ([12,13] discussed immediately above) and other TE-GC-MS studies is summarized in Table 2. A total of 216

Table 1. PAH concentrations in NIST SRM 1649 and 1649a

	Study/SRM analyzed					
Ref.	**[9]**	**[12]**	**[13]**	**[19]**	**NIST 1982**	**NIST 1998**
Compound (μg/g)	**1649**	**1649a**	**1649a**	**1649a**	**1649**	**1649a**
Phenathrene	4.9 (1.3)	4.621 (0.124)	4.557 (0.245)	4.05 (0.13)	4.5 (0.3)	4.14 (0.37)
Fluoranthene	7.3 (2.7)	6.67 (0.178)	6.400 (0.285)		7.1 (0.5)	6.45 (0.18)
Pyrene	6.0 (2.1)	5.055 (0.199)	4.562 (0.621)	4.61 (0.24)	7.2 (0.2)	5.29 (0.25)
Benz[*a*]anthracene	2.8 (1.1)	2.859 (0.191)	2.389 (0.314)	2.2 (0.40)	2.6 (0.3)	2.21 (0.073)
Chrysene	3.8 (1.1)	3.655 (0.228)	3.657 (0.367)		3.6 (0.2)	3.049 (0.06)
Benzo[*b*]fluoranthene	7.1 (1.9)*	6.201 (0.780)	6.432 (1.085)		8.2 (0.4)*	6.45 (0.64)
Benzo[*k*]fluoranthene						1.913 (0.031)
Benzo[*e*]pyrene	3.1 (1.8)	3.592 (0.652)	3.908 (0.872)		3.3 (0.2)	3.09 (0.19)
Benzo[*a*]pyrene	2.2 (1.4)	2.789 (0.922)	2.471 (0.688)		2.9 (0.5)	2.509 (0.087)
Perylene	0.9 (1)				0.84 (0.09)	0.646 (0.075)
Indeno[1,2,3-*c,d*]pyrene	4 (9)				3.3 (0.5)	3.18 (0.72)
Benzo[*g,hi,i*]perylene	5 (9)				4.5 (1.1)	4.01 (0.91)

Additional notes: Standard deviations in parenthesis. All concentrations reported as μg analyte/g NIST SRM. NIST-certified concentrations determined using solvent extraction GC-MS and LC-FL analyses. SRM 1649 was issued in 1982 and reissued in 1998 as SRM1649a. The extraction equipment or vessel corresponding to [9,12,13], and [19] are: integrated sampling and desorption tube; glass-lined stainless steel desorption tube and double oven; MSSV; and, DSI, respectively.
*Reported as benzo[*b* and *k*]fluoranthenes.

organic chemical species were either identified or quantified in the 11 TE-GC-MS studies included in this review. Within Table 2 is a designation indicating whether a specific organic compound was identified or quantified and which particular TE-GC-MS study provides that information. We refer often to Table 2 throughout the remainder of the review.

2.5. Comparisons with other methods

The comparison of TE-GC-MS with other methods is highly relevant to its verification. Greaves et al. [9] quantitatively compared TE and SE methods by running a high-volume sampling device in parallel with the low-volume TE sampling tube. Airborne PM collected on quartz was used for SE, which was conducted by ultrasonic agitation with methylene chloride. Quantitative comparisons showed the TE and SE methods agreed within a factor of 2.5 for the majority of PAHs and alkanes. Half of these compounds agreed within a factor of 1.25. The PAH and alkane concentration ranges reported for the low-volume sampling/TE of airborne PM were 0.06–7.8 ng/m^3 and 0.3–15 ng/m^3, respectively. Subsequent TE of solvent-extracted filter sections (as well as solvent extraction of thermally extracted filter sections) indicated that the TE method more efficiently removed the PAH (~5–10%) and alkane (by 20% on average) compounds.

Hansen et al. [10] compared the analytical performances of supercritical fluid extraction (SFE) and the sampling and TE tube/apparatus of Greaves et al. [9]. Comparative analyses were accomplished using ambient aerosol samples (Boulder, CO, USA) and blank matrix-standard spikes. The standard matrix spike included organic compounds emitted into the atmosphere from various PM sources. The vast majority of these standard compounds were polar (alcohols, acids, methoxyphenols, and oxy–PAH). We note that the PAH quantified in the NIST SRM characterize less than 1% wt/wt of the urban dust; elucidating the importance of considering the full suite of organic compounds found in aerosols when comparing methods. Individually identified compounds within the suite have diverse uses. For example, organic acids are studied to indicate aerosol age and understand diurnal and geographical emission patterns [17], and methoxyphenols formed pyrolytically from lignin precursor are used to trace wood smoke in the atmosphere [18].

The research objective of Hansen et al. [10] was to evaluate whole sampling and analysis techniques and to determine the organic composition of tropospheric aerosols on a time-scale relevant to meteorological changes (on the order of minutes to hours). In achieving these objectives, more was learned about the TE technique. Compared with SFE, TE recoveries of C_{13}–C_{28} primary alcohols and C_9–C_{20} carboxylic acids were poor (<30% recovery). Analysis of mass spectra showed that the parent alcohols had undergone thermochemolysis-based dehydration, yielding alkenes. The dehydration of C_9–C_{28} alcohols by TE was noticed in the ambient sample as well. Unique organic tracers of wood smoke (guaiacol) and cigarette smoke (nicotine) were also poorly recovered (44%) by TE; nevertheless, TE did identify wood-smoke specific molecules (retene, guaiacol, and vanillin) in the airborne PM (Table 2). Both SFE and TE were judged to be similarly effective at removing *n*-alkanes, carboxylic acids, furanones, and PAH from

Table 2. Organic species identified or quantified in aerosols by TE-GC-MS investigations

Compounds	Study		Compounds	Study	
	identified	quantified		identified	quantified
PAH					
Benzo[*b*]fluoranthene	[19]	[9,12,13,29,30]	Chrysene	[10]	[9,12,13,19,24,27,29,30]
Benzo[*k*]fluoranthene		[9,29,30]	Benzo[*a*]anthracene	[10]	[9,12,13,19,24,27,29,30]
Benzo[*j*]fluoranthene		[27]	Naphthalene	[9,19]	
Alkylbenzofluoranthenes	[9]		Methylnaphthalenes	[9]	[24]
Benzo[*a*]pyrene	[19]	[9,12,13,24,27,29,30]	Dimethylnaphthalenes		
Benzo[*e*]pyrene		[9,12,13,24,27,29,30]	Acenaphthylene	[19]	[30]
Indeno[1,2,3-*c,d*]pyrene	[12]	[9,27,29,30]	Acenaphthene	[19]	[24,30]
Indeno[1,2,3-*c,d*]fluoranthene		[27]	Methylanthracenes	[9]	[24]
Dibenzo[*a,h*]anthracene	[9]	[29,30]	Methylfluoranthenes	[9]	
Benzo[*g,h,i*]perylene	[10,12,19]	[9,27,29,30]	Acepyrene		[24]
Coronene			Retene	[10]	[27,29]
Fluorene	[19]	[24,29,30]	Alkylpyrenes	[9]	
1-methylfluorene			Perylene		[9,27,30]
Phenanthrene		[9,12,13,19,24,27,29,30]	Alklylbenzopyrenes	[9]	
Alkylphenanthrenes	[9]	[24]	Acephenathrylene		[24]
Anthracene	[9]	[19,24,29,30]	Phenylnaphthalenes		[24]
Fluoranthene	[10,28]	[9,12,13,19,24,27,29,30]	Dibenzo[*def, mno*]chrysene		[24]
Pyrene	[28]	[9,10,12,13,19,24,27,29,30]	Dibenzopyrenes		[24]
***n*-alkanes**					
n-decane		[11]	*n*-tetracosane	[10,28]	[9,11–13,19,24,27,29,30]
n-undecane		[11]	*n*-pentacosane	[10,28]	[9,11–13,19,24,27,29,30]
n-dodecane		[11]	*n*-hexacosane	[10,28]	[9,11–13,19,24,27,29,30]
n-tridecane		[11]	*n*-heptacosane	[10,28]	[9,11–13,19,24,27,29,30]
n-tetradecane		[11]	*n*-octacosane	[10,28]	[9,11–13,19,24,27,29,30]
n-pentadecane	[10]	[9,11]	*n*-nonacosane	[10,28]	[9,11–13,19,24,27,29,30]
n-hexadecane	[10]	[9,11]	*n*-triacontane	[10,28]	[9,11–13,19,24,27,29,30]
n-heptadecane	[10]	[9,11]	*n*-hentriacontane	[10,28]	[9,11–13,19,24,27,29,30]
n-octadecane	[10]	[9,11,27,30]	*n*-dotriacontane	[10,28]	[9,11,12,19,24,27,29,30]
n-nonadecane	[10]	[9,11,27,30]	*n*-tritriacontane	[10,28]	[9,11,12,19,24,27,29,30]
n-eicosane	[10]	[9,11–13,24,27,29,30]	*n*-tetratriacontane	[10,28]	[9,30]
n-heneicosane	[10]	[9,11–13,24,27,29,30]	*n*-pentatriacontane		[30]
n-docosane	[10,28]	[9,11–13,24,27,29,30]	*n*-hexatriacontane		[30]
n-tricosane	[10][28]	[9,11–13,24,27,29,30]			
Branched alkanes					
b-C_{21}		[11]	b-C_{26}	[10]	
b-C_{22}	[10]	[11]	b-C_{27}	[10]	
b-C_{23}	[10]		Pristane	[9]	
b-C_{24}	[10]		Phytane	[9]	
b-C_{25}	[10]				
Alkenes					
Nonadecene		[11]	Nonacosene	[10]	
Alcohols and phenols					
Decanol		[11]	Guaiacol	[10]	
Dodecanol		[11]	Vanillin	[10]	[27]
Tetradecanol		[11]	2-ethoxy-1-propanol	[10]	
Pentadecanol		[11]	4-acetyl-2-methoxyphenol		[27]
Hexadecanol		[11]	2-(2-butoxyethoxy)-ethanol	[10]	[27]
Pentacosanol	[10]		Hexacosanol	[10]	
Octacosanol	[10]		Pentachlorophenol	[19]	
2-(2-(methoxyethoxy) ethoxyethanol		[27]	1-(2-hydroxy-3-methoxy-4-methylphenyl-ethanone		[27]

(*continued on next page*)

Table 2 (*continued*)

Compounds	Study			Study	
	identified	quantified		identified	quantified
2-methyl-2,2-dimethyl-1-(2-hydroxy-1methylethyl) propyl propanoate		[27]	2-methyl-3-hydroxy-2,4,4-trimethylpentyl propanoate		[27]
1-(4-hydroxy-3,5-dimethoxyphenyl) ethanone		[27]	Phenol	[19]	
Esters					
Nonanoic acid, methyl ester		[11]	Hexanedioic acid esters	[28]	
Decanoic acid, methyl ester		[11]	Undecanoic acid, methyl ester		[11]
Tetradecanoic acid, methyl ester	[10]	[27]	Pentanoic acid, methyl ester		[11]
Heptadecanoic acid, methyl ester		[11]	Hexadecanoic acid, methyl ester	[10]	[11]
Tetradecyl acetate		[11]	Hexadecyl acetate		[11]
Hexadecanoic acid, methylethyl ester	[28]		Octadecanoic acid, 2-methylpropyl ester	[28]	
Hexadecanoic acid, isopropyl		[27]	Methyl dehydroabietate		[27]
Propanoic acid esters		[27]			
Carboxylic acids					
Acetic acid	[9]		Tridecanoic acid	[9]	[27]
Propanoic acid	[9]		Tetradecanoic acid	[9,10,19]	[24,27]
Butanoic acid	[9]		Pentadecanoic acid	[9,19]	[24,27]
Pentanoic acid	[9]		Hexadecanoic acid	[9,10,28]	[19,24,27]
Hexanoic acid	[9,10,19]		Heptadecanoic acid	[9]	
Heptanoic acid	[9,10,19]		Octadecanoic acid	[9,10,19]	[24,27]
Octanoic acid	[9,10]	[19]	Eicosanoic acid	[10]	
Nonanoic acid	[9,10,19]	[27]	Benzoic acid	[9]	[27]
Decanoic acid	[9,10,19]	[27]	Hexadecenoic acid	[9]	
Undecanoic acid	[9,10,19]		Octadecenoic acid	[9,24]	
Dodecanoic acid	[9,10]	[19,24,27]	Octadienoic acid	[28]	
Phthalates					
Dimethyl phthalate	[9,28]		Methylpropyl phthalate	[10,28]	
Diethylphthalate	[9,19,28]	[27]	Phthalic anhydride	[9]	
Dibutyl phthalate	[9,19,27]		Phthalide	[9]	
Diisobutyl phthalate	[9]		Diisoonyl phthalate	[28]	
Dioctyl phthalate	[9]		Benzybutylphthalate	[19]	
Di-2-ethylhexyl phthalate	[9,10,19,28]	[27]	Methylethyl phthalate	[10]	
Ketones and aldehydes					
Octanal		[11]	Benzaldehyde	[9,10]	
Nonanal	[10]	[11,27]	Trimethylbenzaldehyde		[27]
Decanal		[11]	Camphor	[10]	[11]
Dodecanal		[11]	Trimethyl-2-pentadecanone	[10]	[11,27]
Tridecanal		[11]	Sabina ketone		[11]
Tetradecanal		[11,27]	Isophorone		[11,19]
Pentadecanal		[11]	Piperitone		[11]
Hexadecanal		[11]	2-dodecanone		[11]
Heptadecanal		[11]	2-tridecanaone		[11]
Octadecanal		[11]	2-heptadecanone	[10]	[11]
9-fluorenone	[9,10]	[24]	1,4-dimethyl-3-cyclohexenyl-ethanone		[11]
9,10-anthracenedione		[24,27]	3-hexen-2-one		[27]
Xanthone	[9]		1H-phenalen-1-one		[27]
Methylacetophenone	[9]				
Furans			Hydro-methyl-benzofuranones		[27]
Methylfurans	[9]		Isobenzofuranone	[19]	
Dihydromethylfurans	[9]		Benzofuran	[19]	
Furaldehyde	[9]				

Table 2 (*continued*)

Compounds	Study		Compounds	Study	
	identified	quantified		identified	quantified
N-containing					
3-methyl-2-butaneamine	[10]		Dimethylquinolines	[19]	
Hexadecanenitrile	[28]		Methylisoquinoline	[19]	
Octadecanenitrile	[28]		N,N-dibutylformamide		[27]
Eicosanenitrile	[28]		2,4-dinitrotoluene		[19]
Octacosanenitrile	[28]		Azobenzene		[19]
Triacontanenitrile	[28]		Carbazole		[19]
1-methyl-2-pyrrolidinone		[27]	2,5-pyrrolidinedione		[19]
Quinoline		[19,27]	Phthalimide		[19]
Isoquinoline	[19]	[27]	Acridine	[19]	
Methylquinolines	[19]		Indol	[19]	
Steranes and hopanes					
22,29,30-trisnorneohopane		[27]	22S-17α(H),21β(H)-30-bishomohopane	[27]	
22,29,30-trisnorhopane		[27]	22R-17α(H),21β(H)-30-bishomohopane	[27]	
17α(H),21β(H)-29-norhopane		[27]	20S-13β(H),17α(H) diacholestane	[27]	
17α(H),21β(H)-hopane		[27]	20R-13β(H),17α(H) diacholestane	[27]	
17β(H),21β(H)-hopane		[27]		[27]	
17β(H),21α(H)-hopane		[27]	20R-5α(H),14β(H),17β(H) cholestane	[27]	
22S-17α(H),21β(H)-30-homohopane	[27]		20S-5α(H),14β(H),17β(H) cholestane	[27]	
22R-17α(H),21β(H)-30-homohopane	[27]				
Amyrins					
β-amyrin		[27]	α-amyrin acetate	[27]	
α-amyrin		[27]			

the aerosols collected at the Boulder site. However, because this judgment was made qualitatively, further study will be required before concluding that these compounds are satisfactorily analyzed by TE and SFE methods. The TE method effectively removed branched aromatics from the PM matrix as well. More than 90% of the extractable organic matter was determined to be removed in one step by both techniques. Early eluting chromatographic peaks of thermal extracts were plausibly assigned to thermally degraded compounds.

The TE equipment used by Greaves et al. [9] and Hansen et al. [10] was later improved by Veltkamp et al. [11], who used a newly designed septumless injection port, which eliminated any contamination associated with the Grob-type injection port used in the previous studies. They again applied their TE technique to determine the organic composition of 2–5-h ambient PM samples collected in Colorado. More than 50 individual organic species were quantified in the Colorado PM (see Table 2) and incorporated into a principal component analysis model to achieve a factor analysis-based source apportionment.

2.6. Quality-control considerations

Setting proper quality-control criteria is critical to achieving a reliable TE-GC-MS analysis. The high sensitivity of TE has required development of means to control organic contamination. Greaves et al. [9] showed that high-temperature annealing (600°C) adequately removed organic contaminants from their sampling media and extraction equipment, whereas the work of Waterman et al. [12] showed pre-conditioning at 350°C is adequate. Required conditioning time has generally correlated inversely to conditioning temperature. Memory effect or analyte carry-over due to shortened extraction times or less than optimal extraction temperature-program parameters can negatively influence quantitation efforts. A strategy for examining these effects includes re-heating the sample/assembly after the initial extraction and checking the GC-MS profile for consistency. Analyte peaks should not appear in chromatograms of the subsequent extractions of aerosol. Their appearance indicates carry-over, which can be treated by using either a higher extraction temperature or a longer hold time. Carry-over has been

observed to be largely negligible in most TE-apparatus types and for most TE methods developed to study aerosols [9,19]. A means for ensuring that the extraction temperature of the tube equals the set temperature of the oven is also essential, as past work has shown that these temperatures can differ [9].

Conversion (degradation or formation) of organic constituents in aerosol is a serious concern during TE experiments; this difficulty is universal to TE and not isolated to any one type of TE apparatus. Converted substituents can be sufficiently volatilized and detected by GC-MS, and thus potentially interfere or co-elute with the organic substances being targeted for quantitation. If it is a target analyte being formed or degraded, an erroneous concentration estimate is certain to result. The quantitative recovery of standard spikes can partly alleviate this concern. There has been no appreciable thermal degradation or formation of the widely studied PAH and *n*-alkane substances in TE oven systems and this can be confirmed with SRM 1649. However, Greaves et al.[9] did observe a surprising number of early eluting volatile organic compounds in the TE chromatograms of an ambient aerosol collected in Colorado. These compounds were plausibly thermal decomposition by-products or artifacts or were perhaps formed from secondary atmospheric reactions and desorbed directly from the aerosol.

As mentioned, the ''closed'' (high-pressure) MSSV system promoted thermal decomposition and produced relatively more volatile matter. It also reduced the UCM in the chromatogram. UCM is the raised baseline feature in gas chromatograms of $PM_{2.5}$; the potential toxicity of the UCM makes it an important environmental concern [20]. A total ion chromatogram of thermally-extracted $PM_{2.5}$from residential wood combustion exhibiting the UCM feature is given in Fig. 3, which shows the large fraction of chromatogram area ascribable to the UCM hump. Extended heating of the MSSV (72 h at 300°C) further deconvolved UCM, but thermally degraded resolved matter as well. This latter condition will probably limit the use of extended MSSV heating for further identifying the UCM composition. By comparison, the lower pressure ''open'' TE systems are likely to minimize thermal breakdown of the molecular desorbates by immediately flushing them from the oven. The ''open'' thermal method is thus an obvious choice for analysis of the organic constituents in aerosols. Rapid aerosol-sample heating perhaps minimizes pyrolysis and maximizes compound volatilization. This thinking underlies the application of CPP for determining aerosol composition, the topic of Section 3.

As the results of the studies with NIST SRM show, the TE-GC-MS method can be accurate and precise. Additionally, ambient sample pairs (collected in parallel) analyzed for both PAH and alkane compounds were not significantly different (as shown by a two-sided *t* test with $\alpha = 0.05$) [9]. Regardless of these past successes of TE-GC-MS, future validation efforts will require working over an extended range of organic compound classes.

2.7. Composition of carbonaceous aerosols

Carbonaceous aerosols are known to contain thousands of individual organic chemical constituents. As mentioned, an exhaustive rendering of these species is required for understanding the health implications and toxicity of aerosols and for use in source apportionment and attribution. References [9–13] designate the studies performed using TE ovens. Data in Table 2 indicate that oven-based TE-GC-MS systems were able to account for organic species from all the listed chemical classes, with the exception of the steroid biomarkers. For example, Table 2 shows that, with their integrated device, Greaves et al. [9] identified monocarboxylic acids (C_2–C_{18}), furans, chlorinated aromatics, *n*-alkanes (C_{13}–C_{34}), phthalates, aromatic hydrocarbons, and various oxygenated compounds in ambient PM collected at their sampling site (Boulder, Colorado, USA). Several of the oxygenated molecules detected (e.g., camphor, benzaldehyde and

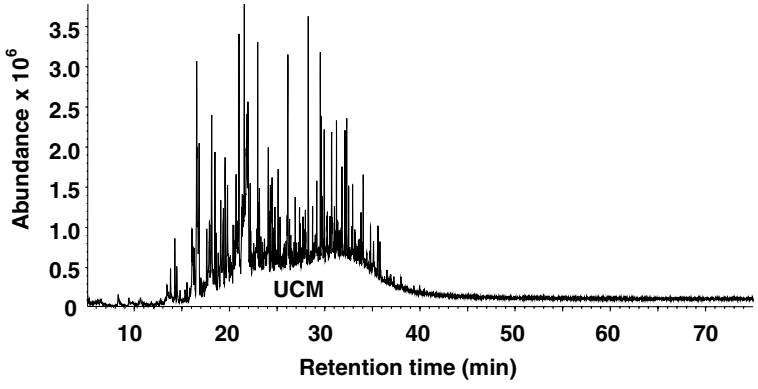

Figure 3. A total ion chromatogram of thermally-extracted $PM_{2.5}$ from residential wood combustion. Note the large area ascribable to the unresolved complex mixture (UCM) hump.

nonanal) are considered important to the understanding of biogenic plant emissions and the formation of secondary organic aerosols [21].

3. Application of Curie-Point pyrolysis (CPP)

CPP-GC-MS has been used extensively to analyze and to fingerprint non-volatile organic matter and polymeric substituents [22]. It has also been employed to extract and analyze insoluble and semi-volatile organic compounds from source and atmospheric PM [23,24]. CPP is performed by depositing a PM filter sample on a ferromagnetic foil or wire. The sample is flash heated (~0.2 s) by induction in a radio-frequency field, and analytes are then transferred to the GC-MS. The metal composition (Co, Fe, Ni) of the foil alloy determines the precise Curie-Point temperature (160–1040°C). CPP-GC-MS analysis has been performed with and without the use of cryogenics. The work of de Leeuw et al. ([25], and references therein]) characterized environmental polymers and showed that sufficiently volatile non-polymeric organic material was evaporated intact from the pyrolysis wire. This result validated CPP for TE use and justified Neususs et al. [24] applying CPP-GC-MS to characterize ambient PM.

Neususs and colleagues [24] demonstrated the reproducibility of CPP-GC-MS for measuring particulate organic matter collected on quartz-fiber filters. PAH concentrations in solvent and thermal extracts of an ambient PM sample were compared to assess accuracy. Agreement between the methods was observed, but the CPP method only partially recovered indeno[*1,2,3-cd* pyrene] and benz[*ghi*]perylene due to transfer loss. The CPP method systematically detected most of the PAH at slightly higher levels. This result was due either to better CPP system efficiency or possibly to the pyrolytic formation of PAH. An Fe/Ni alloy with a Curie Point of 590°C was used in this effort. Thermal-optical analyses of some aerosols have shown evidence of charring at temperatures as low as 300°C. Lignin chars that formed near these temperatures have been shown to contribute to PAH formation [26]. Flash heating the sample could also denature the aerosol matrix and obstruct the complete extraction of certain analytes. Repeated heating cycles on the same sample indicated no carry-over. Neususs et al. [24] found that only micrograms of PM sample were required for CPP-GC-MS analysis. They therefore went on further to develop CPP-GC-MS by characterizing the PAH and *n*-alkane components in size-resolved atmospheric aerosols. The determination of PM composition by particle size is important because PM deposition in the human respiratory tract is size dependent and harmful physiological response is expectedly a function of this composition. Jeon et al. [27] also used CPP to conduct TE experiments. Their technique was an intra-injector one, and is therefore described below, where intra-injector methods are covered.

4. Application of direct sample introduction (DSI) and GC inlet extractions

The examination of TE-GC-MS applied to aerosols would be incomplete without discussion of DSI techniques. Several research groups have practiced intra-injector or DSI TE methods to determine atmospheric aerosol composition [19,27–30]. This approach is unique in that device installation requires only minor modification to the GC, and TE is performed directly in the inlet, eliminating the transfer line and peripheral oven, and reducing organic compound loss.

To study aerosol composition, Falkovich and Rudich [19] applied the DSI device first established by Jing and Amirav [31] for pesticide analysis. This device made it possible to introduce aerosol sample in a disposable microvial into the GC liner of a PTV inlet (Fig. 4). Vial and liner sizes were optimized on the basis of substrate and sample geometry and sample mass. Use of the PTV inlet allowed for an open split vent (1:100) and high inlet pressure (32 psi, 4.5 mL/min) during sample introduction and TE, respectively. As mentioned earlier, extraction efficiency increases with carrier gas flow over the sample.

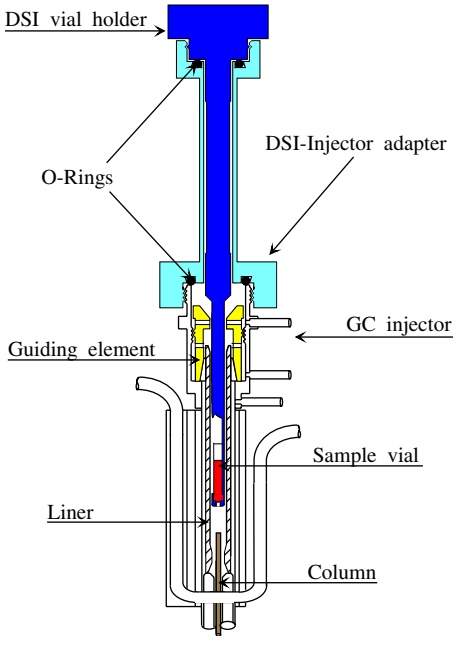

Figure 4. A direct sample introduction (DSI) device for thermal extraction. (Reprinted with permission from [31]; © 1997 American Chemical Society).

In the same vein, Jeon et al. [27] developed an intra-injector technique that combined DSI and Curie-Point technology. They analyzed 2-h ambient sample filters inside a customized GC inlet, which contained a glass tube lined with ferromagnetic foil (Curie-Point temperature = 315°C) (Fig. 5).

Other studies utilizing DSI techniques revealed several instances where it had also been possible simply to transfer quartz-filter sections to GC injection liners and perform TE [28–30]. With the advent of robotic liner replacement, the earlier criticisms regarding the time-consuming exchange of samples in such systems have become less valid. For the DSI studies mentioned, TE hold temperatures ranged from 275–350°C, and desorbed compounds were routinely trapped on-column (30–50°C) without the use of cryofluid. Clearly, the arrival of DSI techniques has greatly simplified the TE-GC-MS apparatus.

Analyte concentrations similar to those determined with oven-based TE methods were observed when DSI-method validation was carried out using SRM 1649a [19], though DSI detected a relatively larger array of compounds in the SRM 1649a (including monocarboxylic acid, cycloalkane, furan, furanone, pyridine, quinoline, pyrrole, indole, benzene and phenol derivative, phthalate, PAH, N-containing non-aromatic, and multifunctional compounds). Replicate DSI analyses of 0.5-mg SRM 1649a samples reproduced peak-retention times and responses to within 1% and 11%, respectively. NIST-certified and DSI technique-determined values for phenanthrene, pyrene, and benz[a]anthracene correlated to within 15%.

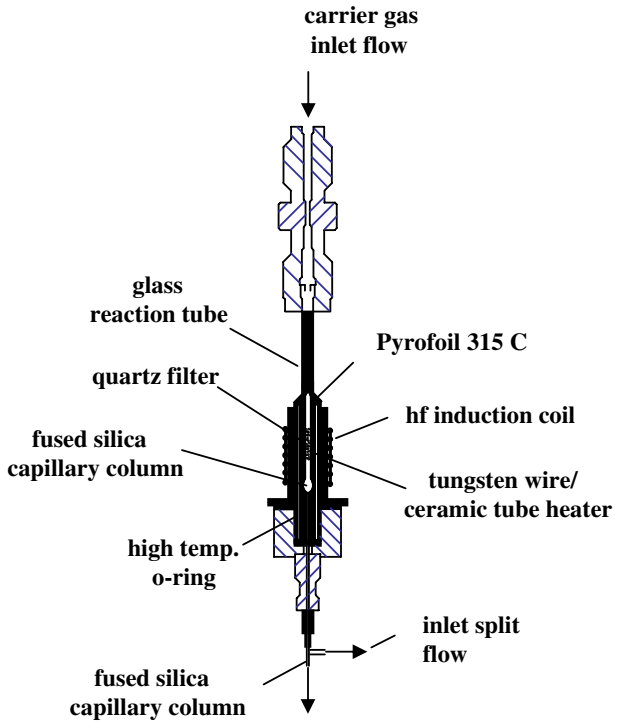

Figure 5. An intra-injector, Curie-point pyrolysis design for thermal extraction. (Reprinted with permission from [27]; © 2001 Air & Waste Management Association).

We continue to stress the importance of comparing TE results to results obtained with other methods. The DSI technique detected traces of PAH in Soxhlet-extracted SRM 1649a, indicating higher recoveries for the DSI technique. Further comparisons between SE and the DSI TE method agreed (r^2 = 0.940–0.998; by compound class) [27]. However, the methylated *n*-alkanoic acids in solvent extracts corresponded poorly with the underivatized parent forms detected by TE (r^2 = 0.731). This result reinforces the need for implementation of in situ derivatization techniques for TE-GC-MS analysis of aerosols.

In studying the relationship between TE and SE, Ho and Yu [30] showed that the TE method was more sensitive than SE due to its higher sample-utilization rate. For example, they showed that TE was 9–500 times and 12–120 times more sensitive than SE for the PAH and *n*-alkane classes, respectively. They also observed relatively fewer sample contaminants with the TE method. We would add that this latter result appears valid even when practicing SE with doubly-distilled solvents. The DSI method of simply introducing filter sections to the GC inlet correlated well with SE for the PAH (r^2 = 0.95) and *n*-alkanes (r^2 = 0.94). The TE efficacy for the *n*-alkane (m = 1.11) and PAH (m = 1.26) was greater; the methods never deviated more than 40% from one another using these compounds.

Intra-injector techniques capably extended the range of compound classes identified and quantified by oven-based TE-GC-MS methods. Jeon et al. [27] presented the most comprehensive list of organic compounds identified to date (Table 2). It was the first and only TE-GC-MS study to observe the presence of sterane and hopane molecules in ambient PM. These molecules have been treated as tracers for mobile emission sources and have been used in attempts to determine the split between diesel and gasoline emissions from vehicles during source apportionment and attribution [32,33]. They are also putatively associated with lung toxicity [34].

N-alkanes (C_{18}–C_{33}), *n*-alkanoic acids (C_9–C_{18}), amyrins, PAH and aromatics, phthalates, aliphatic alcohols and phenols, N-containing species, aldehydes and other oxygenated compounds were also detected by the intra-injector, Curie-Point device (Table 2; [27]). DSI-GC-MS analysis of size-segregated air samples collected in Tel Aviv showed azaarenes, PAH and monocarboxylic acids present. Helmig et al. [28] qualitatively identified monocarboxylic, alkenoic and dialkanoic acids in forest, urban, and indoor air. PAH, *n*-alkanes, fatty acid esters, and nitriles were also identified in these samples (Table 2; [28]).

Carry-over, pyrolysis, and reactions with the DSI technique were for the most part negligible. Chromatograms of standards (*n*-alkanes, polychlorinated biphenyls, and pesticides) spiked on glass-fiber filters and then thermally extracted at 320°C were observed to be identical to those obtained with direct liquid injections [28]. Ho and Yu [30] showed for DSI that an extraction temperature of 275°C was sufficient for extracting PAH and *n*-alkanes from spiked quartz filters. However, quartz filters – besides being difficult to handle – can apparently promote the pyrolysis of long-chain hydrocarbons, even when using slower extraction heating rates as a pyrolysis-avoidance measure [19]. The relatively high extraction temperature of 350°C used in this study perhaps contributed to the observed pyrolysis, but *n*-alkane extraction from pre-fired aluminum foil substrates at 350°C was shown to be relatively effective [19]. (Aluminum foil is a common medium used in impactor devices, which segregate particle matter by size in stages.) The evidence suggests that both temperature and substrate type can affect recoveries and the interactions between the substrate and organic constituents. The substrates used for aerosol-sample collection should thus be selected in tandem with the TE-GC-MS method to be applied and the target analytes sought. Throughout the selection process, analysts should also be aware that heat-transfer rates vary by substrate (e.g., quartz, glass, or aluminum foil).

In reflecting on the above results with DSI, it should be noted that (a) the work of Ho and Yu has not been verified against actual aerosol-sample matrices, and (b) the work of Falkovich and Rudich has implications for resolving the chemical composition of aerosols by size. The inadequate current understanding of how the different substrates and aerosol matrices affect TE-GC-MS analysis is certainly an area suitable for future study.

Replicate TE-DSI analyses for ambient samples showed suitable repeatability for all compounds except for the *n*-alkanoic acids [27]. Ho and Yu [30] calculated limits of detection (LODs) of 0.41–4.36 ng and 0.08–2.40 ng for *n*-alkanes and PAHs, respectively. They needed an extraction time of just 7.5 min to limit band broadening and analysis time. However, their initial inlet temperature of 100°C led to volatility losses during sample loading. This high initial temperature was used in exchange for shorter total analysis times.

Falkovich and Rudich [19] showed that chemical standards in a suite comprising 64 chemical compounds from several classes [including PAH, phenols, organic acids, furans, and azaarenes (see [19]; Table 2)] exhibited a wide dynamic range (~0.6–40 ng; $r^2 = 0.970$–1.00). The reproducible TE and quantification of the underivatized C_6–C_{16} monocarboxylic acids in PM was accomplished. However, the LODs (4–16 ng) for the C_6–C_{16} acid subset increased with carbon number, and the higher molecular weight and more polar dicarboxylic acids typically measured in PM were not observed. Also, compounds with boiling points closer to the lower sample-introduction temperature were potentially volatilized and escaped through the split vent using the DSI method. This was because the sample split vent was open and the inlet left above room temperature for the sample-introduction step. The actual extraction of aerosol was performed in splitless mode with the split vent closed.

Molecular marker-source apportionment has been an aim of several of the TE-GC-MS studies implementing DSI. Generally, the application of TE-GC-MS for this aim has encountered mixed levels of success. For example, one multivariate analysis performed showed that the level of molecular detail provided by the TE analysis was sufficient to apportion ambient (2 h) PM samples collected at the U.S./Mexico border [27], identifying the predominant primary sources as vehicular emissions, biomass combustion, kiln operations, vegetative debris, and waste burning. However, another study of Canadian aerosols showed that the use of just the ambient PAH and *n*-alkane data for source apportionment resulted in illogical collinear source profile pairs (i.e., meat cooking and paved road dust) [29]. These results confirm the need for highly detailed analysis for $PM_{2.5}$ apportionment. However, under all of the applied TE-GC-MS conditions, quantification of only PAH and *n*-alkanes is certain; data on heteroatomic and polar molecules in aerosols analyzed by TE-GC-MS have been relatively scant. Review of the state of the science currently underlying the source apportionment of ambient aerosols suggests that TE-GC-MS methods require advancement. The specific areas requiring development and the analytical strategies for achieving these advancements are given below.

5. TE-GC-MS for molecular marker-source apportionment

Analytically measured organic marker concentrations in source emissions and in ambient PM are the primary input to the chemical mass balance (CMB) apportionment model. Achieving source apportionment and attribution with CMB is an impetus for developing TE-GC-MS for the determination of organic aerosol composition. The acceptance of TE-GC-MS for this aim, to some extent, will rely on its favorable comparison to SE methods. Agreement with SE will permit compositional TE data to be modeled with and added to emissions and air-quality repositories currently grounded in SE. As discussed, SE-GC-MS has been successfully implemented in several source-apportionment investigations (e.g., [32,33,35]). Its success is largely due to its applicability to such a wide range of organic markers and compound classes [33,36]. We identify the key research areas in

which improvements are necessary if TE-GC-MS is to become an essential tool for source apportionment research.

5.1. Expanding the classes of compounds that can be quantified with TE-GC-MS

As evidenced by the information in Table 2, the main preference to date has been to use TE-GC-MS to quantify the concentrations of PAH and *n*-alkane constituents in fine aerosols. The concentrations of TE-GC-MS-determined PAH and *n*-alkane species did corroborate those determined by SE-GC-MS; but alone these compound classes will not support all source-apportionment scenarios under study. The future development of TE-GC-MS methods must include the quantification of an expanded set of organic tracers. For example, the robust analysis of polar organic molecules is desirable in aerosol characterization, and several key molecular markers are polar in nature. Organic acids have been used to estimate aerosol age, understand regional air-quality issues and atmospheric chemistry, for source reconciliation, and as tracers for biomass combustion [18,37,38]. Levoglucosan and cholesterol have been used as tracers of burning cellulose and meat cooking, respectively. Several polar lignin pyrolysis products (i.e. methoxyphenols) are used to attribute biomass burning to ambient PM.

Quantifying many of these polar organic compounds in aerosols has traditionally required derivatizing them in solvent extracts. By comparison, direct TE-GC-MS methods have identified and quantified relatively fewer acids (*n*-C_8–C_{18} versus *n*-C_4–C_{30} for SE) and have not yet quantitatively recovered levoglucosan or cholesterol in PM samples. Moreover, dialkanoic, alkenoic, and several diterpenoic and aromatic acids were among those missing from the TE-GC-MS analyses of aerosols, but they are commonly identified by SE-GC-MS. Also, the full set of SE-GC-MS-identified methoxyphenols used for tracking and apportioning biomass burning aerosols has not been measured by TE methods [39]. The quantitative development of TE-GC-MS analysis for polar organic molecules in fine aerosols will be required to advance TE beyond its traditional use as a screening method. Next, we reveal a possible strategy for the successful analysis of these compounds by TE-GC-MS.

On-line chemical derivatization protocols, such as thermochemolysis, may hold promise for TE-GC-MS. Preliminary research has indicated that the silylation procedure used to neutralize and quantify levoglucosan and cholesterol in solvent extracts is compatible with TE-GC-MS [40]. A diazomethane reagent has effectively methylated fatty acids in solid-phase microextraction (SPME) fibers [41] and in solvent extracts of $PM_{2.5}$ [8] and may also be suitably integrated with TE-GC-MS methods. Pyrolysis-based thermochemolysis has esterified fatty acids in solids using tetramethylammonium hydroxide [42]. This process requires heating conditions comparable to those arrived at when using TE-GC-MS for determining organic aerosol composition. Surely the emergence of TE-GC-MS methods for $PM_{2.5}$ stands to benefit from these well-established in situ derivatization techniques.

5.2. Characterization of primary source emissions

The trend so far has been to develop TE-GC-MS for only organic aerosols collected at ambient monitoring stations. Source-receptor models also require quality chemical measurements of source composition to operate properly [43]. The source variability and analytical uncertainty in PM-emission chemistry are factored into the CMB model framework (i.e. individual chemical species measured with lower uncertainties have a larger influence on the final model-approximated source attributions). Compared with SE, automated TE-GC-MS methods could significantly improve the measurement precisions of organic compounds in PM-source emissions. Evaluating the $PM_{2.5}$ chemical composition at the source and the receptor using the same analytical method will also free the source-contribution estimates from any systematic bias. The focus of future TE-GC-MS research should therefore include the development of source-emission profiles for use in apportionment studies and the investigation of any matrix or any analytical biases due to primary source aerosol emissions. The consequences of all this will be:

(i) improved approximations of source contributions to ambient aerosols;
(ii) better resolution of contributions among similar sources of emissions (i.e. agricultural, wildfire, and residential wood burning); and,
(iii) accurate estimates of human exposure to anthropogenic and biomass-burning sources.

Further understanding of the TE-GC-MS method and verification of its applicability to source aerosols can be accomplished with the standard addition method and by continuing to compare TE-analysis results to those of other methods, such as SE and SFE-GC-MS. The future integration and use of TE-GC-MS-obtained chemical-source signatures with SE-GC-MS-based emissions inventories will require confirmation. In other words, the accuracies of TE-GC-MS and SE-GC-MS measurements for organic compounds in source aerosols will need to be verified as analogous or else used independently. While using TE-GC-MS, improved knowledge of sterane and hopane emission factors for mobile sources must be gained. Amyrins, phytosterols, and other organic tracer species must also be further studied by TE-GC-MS with the intent to use these compounds in source-receptor apportionment research. Added size-segregated chemical data for source aerosols similar to that provided by Hays et al. [15] are also necessary. This knowledge of aerosol composition by particle size will contribute to the design

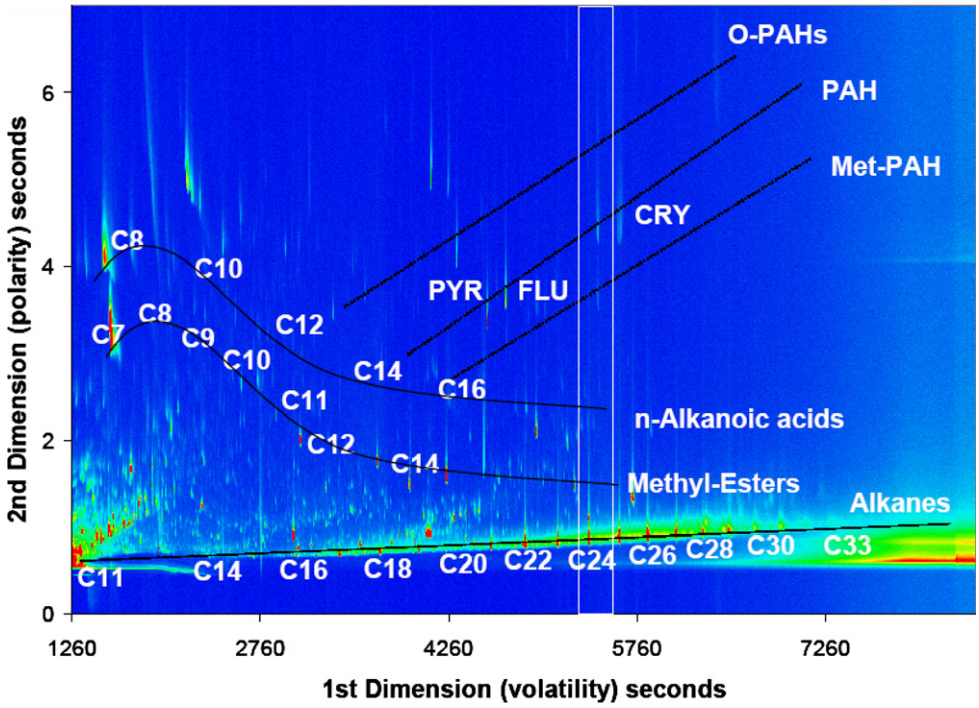

Figure 6. A 2-D chromatogram of a winter aerosol collected in Augsburg, Germany. (Reprinted with permission from [46]; © 2005 Wiley-VCH Verlag GmbH & Co KG).

and the application of future pollutant-dispersion and exposure models.

5.3. Search for new organic molecular markers

Finally, an expanded search for rare molecular markers and the development of methods that deconvolve UCM using TE-GC-MS must ensue. Welthagen and colleagues [44], Hamilton et al. [45], and Schnelle-Kreis and co-workers [46] have initiated some of this research by coupling TE to multi-dimensional separation and time-of-flight MS techniques. A 2-D chromatogram of a winter aerosol collected in Augsburg, Germany, is shown Fig. 6, which clearly illustrates the ability of 2-D methods to resolve UCM further and potentially to isolate thousands of individual organic components in the PM mixture. Future research in this area should significantly advance our comprehension of the complex chemical composition of aerosols.

6. Summary and conclusions

Future air regulations, the reductions in emissions that they cause, and the shorter temporal scales needed for epidemiology and health studies have created an interest in more sensitive analytical measurements of the chemical composition of aerosols. For organic compounds in aerosols, the investigations conducted to date have indicated that TE-GC-MS potentially serves this interest. Several differently configured TE-GC-MS systems have successfully analyzed individual organic constituents in fine aerosols. The individual species identified and quantified in each study were probably limited to the TE equipment used, the aerosol-sampling method, the standards available, the aerosol matrix, and the specific air-mass characteristics. Extraction heating rates, and hold times and temperatures must be optimized for the compounds sought and the aerosol matrix.

For the PAH and *n*-alkane compounds quantified in ambient aerosols, TE-GC-MS methods have adequately replicated SE-GC-MS results. The TE-GC-MS analysis of source aerosols was identified as an important future research area, as it pertains to successful molecular marker-source apportionment. The development of in situ derivatization methods for polar organic compounds in aerosols will also be critical to the advancement of TE-GC-MS research. Several well-established derivatization methods currently in use are likely to be compatible with TE-GC-MS. They typify logical starting points for accomplishing simultaneous derivatization and analysis of organic markers with TE-GC-MS.

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