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The application of thermal methods for determining chemical composition of carbonaceous aerosols: A review

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Thermal methods of various forms have been used to quantify carbonaceous materials. Thermal/optical carbon analysis provides measurements of organic and elemental carbon concentrations as well as fractions evolving at specific temperatures in ambient and source aerosols. Detection of thermally desorbed organic compounds with thermal desorption-gas chromatography/mass spectrometry (TD-GC/MS) identifies and quantifies over 100 individual organic compounds in particulate matter (PM) samples. The resulting mass spectra contain information that is consistent among, but different between, source emissions even in the absence of association with specific organic compounds. TD-GC/MS is a demonstrated alternative to solvent extraction for many organic compounds and can be applied to samples from existing networks. It is amenable to field-deployable instruments capable of measuring organic aerosol composition in near real-time. In this review, thermal stability of organic compounds is related to chemical structures, providing a basis for understanding thermochemical properties of carbonaceous aerosols. Recent advances in thermal methods applied to determine aerosol chemical compositions are summarized and their potential for uncovering aerosol chemistry are evaluated. Current limitations and future research needs of the thermal methods are included.

Keywords: Carbonaceous aerosol, thermal desorption, organic carbon, organic compounds, organic markers, carbon speciation.

Introduction

Airborne particulate matter (PM) has adverse effects on human morbidity and mortality,[1−4] visibility,[5,6] climate change,[7] and materials.[8] These effects have sparked interest in the chemical and physical properties of PM, with increasing interest in its organic matter (OM) composition. The OM fraction is complex, comprising thousands of chemical constituents from numerous organic compound classes, such as aromatics (i.e., polycyclic aromatic hydrocarbons [PAHs]), alcohols alkanes (i.e., n-alkanes, hopanes, and steranes), and carboxylic acids (i.e., alkanolic acids).[9−12] Various compounds within these classes are recognized as biologically toxic.[13−15] Many are also used as organic markers in source/receptor models for source apportionment.[16−23]

Large numbers of samples are needed to relate ambient carbonaceous materials to pollution sources and to assess their environmental and health consequences. This demands fast, simple, and sensitive analytical methods. Solvent extraction (SE) followed by gas chromatography/mass spectrometry (GC/MS) analysis has been the most widely used approach for PM collected on filters. Despite some documented advantages of using SE-GC/MS methods (e.g., selectivity, feasibility), it is labor- and time-consuming, which limits the number of samples that can be analyzed. It also requires large sample deposits (>1 mg organic carbon)[24] that are not normally acquired in speciation networks.

Simple and fast thermal methods are used to determine thousands of organic and elemental carbon (OC/EC) in ambient and source aerosols collected on quartz-fiber filters each year.[16,25−30] Similar analytical simplicity can also be expected for analysis of individual organic compounds using more specific detection methods for the thermally evolved organic compounds.

The term thermal extraction (TE) refers to the direct removal of OM from the aerosol matrix by heating the
sample; it has been used interchangeably with the term thermal desorption (TD). TD is a technique by which relatively volatile analytes trapped on a solid adsorbent (such as Tenax) are released at high temperatures, and then analyzed. TD has been used to measure volatile organic compounds (VOCs) from soil, water, and air.\textsuperscript{[31–43]} Since the 1970s, TD has been applied to aerosol samples\textsuperscript{[43]} for molecular composition.\textsuperscript{[35,44–47]} TD has also been combined with semi-continuous and continuous instrumentation that measures organic compounds in picograms collected over time frames of seconds.\textsuperscript{[48,49]}

The current knowledge of thermal stability of organic compounds as a function of chemical structures is reviewed herein, providing a chemical basis for understanding thermochemical properties of aerosol organic compounds and matrix effects during thermal analysis. Recent TD advancements and applications are summarized, the potential for uncovering aerosol chemistry is evaluated, and current limitations and future research needs of thermal methods are addressed. This paper complements the review of Hays and Lavrich,\textsuperscript{[24]} which focused on molecular marker species identified and quantified by off-line TD-GC/MS techniques.

**Thermal desorption mechanisms**

**Vaporization**

Vaporization is a conversion process by which a chemical in solid or liquid form is changed to the gas state by heating or reducing pressure. Most substances change their physical states in the order of solid to liquid to gas with increasing temperature. A few sublimate, or change directly from solid to gas. The molecules in solid or liquid states bind with the intermolecular forces, which are fundamentally electrostatic interactions (ionic interactions, hydrogen bond, dipole-dipole interactions) or electrodynamic interactions (Van der Waals force).\textsuperscript{[50]} Vaporization is an endothermic process in which molecules gain kinetic energy as temperature increases. When molecular kinetic energy exceeds the enthalpy change of vaporization ($\Delta vH$), which is the energy required to overcome intermolecular forces in the solid or liquid, individual molecules escape and enter the gas state.\textsuperscript{[50]}

This temperature is the boiling point at a constant pressure. Methane has a low standard enthalpy change of vaporization ($\Delta vH^\circ = 8.19$ kJ mol$^{-1}$) because of weak Van der Waals forces between its molecules (Sears et al., 1982). These forces result from formation of momentary dipoles in uncharged non-polar compounds.\textsuperscript{[51]} Higher $\Delta vH$ are measured for formic acid and methanol ($\Delta vH^\circ = 19.9$ kJ mol$^{-1}$ and 37.4 kJ mol$^{-1}$, respectively) since the molecules bind with strong hydrogen (H) bonds.\textsuperscript{[52,53]} The bond is an attractive interaction between an electronegative atom (e.g., oxygen [O] and nitrogen [N]) and an H atom bonded to another electronegative atom.\textsuperscript{[54]} This explains why polar organic alcohols and acids have higher $\Delta vH$ than alkanes with equivalent carbon numbers.

Apart from heating, vaporization occurs at reduced system pressures. The boiling point of a substance is the temperature at which its vapor pressure equals the pressure of its environment.\textsuperscript{[50]} When pressure is reduced, vaporization takes place at a lower temperature. The boiling point of the substance decreases while the pressure decreases such that:

$$\frac{1}{T_B} = \frac{R}{\Delta vH} \cdot \ln \frac{P}{P_o} + \frac{1}{T_o}$$

(1)

where $T_B$ is the boiling point in K under pressure $P$, $R$ is the ideal gas constant ($8.3143$ m$^3$ Pa$^{-1}$ K$^{-1}$ mole$^{-1}$), and $T_o$ is the given temperature boiling point in K under the standard pressure $P_o$.\textsuperscript{[50]} In a mixture, the vapor pressure of a solute is reduced, leading to boiling point elevation of the solute. According to Raoult’s Law, the vapor pressure reduction is proportional to the mole fraction of the solute in the mixture. Deviations from Raoult’s Law are often observed as the interaction between solute and solvent is not ideal.

**Thermal stability of organic molecules**

The thermal stability of an organic molecule is a combination of its thermodynamic and kinetic stability. The finite strength of chemical bonds puts an upper limit on the vibrational energy that molecules may possess without bond rupture, i.e., decomposition. The Boltzmann energy distribution law among molecules dictates that at any temperature a portion of the molecules will possess energy greater than the bond energy. The thermal degradation rate ($k$) of a molecule is expressed as:

$$k = A \ e^{-E/RT}$$

(2)

$A$ is the frequency factor related to a critical mode of vibration in the molecules and has the same dimension as $k$. For first order kinetics, $A$ is in units of 1/sec. $E$ is the activation energy supplied to the molecules to cause decomposition. For decomposition to occur, $E$ needs to be greater than the dissociation energy of the weakest bond in the molecule; the weakest bond strength determines the upper limit of its thermal stability, if there are no other lower-energy decomposition pathways.\textsuperscript{[55]} Simple hydrocarbons, such as alkanes, decompose through rupture of a C–C bond, with the formation of free radicals;\textsuperscript{[56,57]} however, the functional groups of many organic molecules can lead to the rearrangement of pathways and lower the thermal decomposition temperature.\textsuperscript{[58]} The rearrangement pathways take place at temperatures far below the temperature required for straightforward bond rupture.

Thermal stability of a molecule is primarily determined by its chemical structure.\textsuperscript{[58,59]} According to Eq. 2, chemical structures that minimize $A$ and maximize $E$ lower the rate of $k$, thereby increasing stability of the molecules at a given temperature. Polybonding, in which an atom is bonded to
more than one other atom in the molecule, has the effect of decreasing $A$, as collision energy can be dissipated over more than one path (e.g., the thermal stability of graphite). The thermal stability of many inorganic solids is also related to this factor, rather than to their high bond strength. More specifically, the structural features of compounds that favor high thermal stability include: (i) all bonds in the molecule having high dissociation energies; (ii) no easy paths to decomposition; (iii) resonance structure; and (iv) substituents that enhance resonance stabilization. Resonance structure moieties have the effect of increasing $E$ in Eq. 2, hence increasing thermal stability.\[58\]

Aromatic compounds have high thermal stability because of their resonance structure. For example, naphthalene in the vapor phase (at 1 atm) is thermally stable up to 620°C.\[59\] Nine PAHs (i.e., anthracene, phenanthrene, fluoranthene, chrysene, pyrene, triphenylene, benz[a]-anthracene, benzo[a]pyrene, and dibenz[a,h]anthracene) are thermally stable beyond 475°C.\[60\] In comparison, alkyl-PAHs have lower thermal stability. This follows from the introduction of lower dissociation energy bonds (i.e., alkyl –C–C bonds) than the bonds in the aromatic rings. Madison and Roberts\[60\] observed slight thermal decomposition for 1-methyl naphthalene at 475°C. For the same reason, alkanes in general have lower thermal stability than PAHs. Hydrocarbons containing alkyl chains have been found to remain stable to about 350°C.\[55\] Table 1 lists the chemical and physical properties of major organic classes and markers in aerosols.

Thermally stable molecules lack easy paths to decomposition.\[59\] Polar functional groups, such as –NH$_2$, –OH, –COOH, often provide lower energy decomposition in which bonds are broken and formed simultaneously (e.g., the loss of HX), and therefore are less thermally stable. For example, thermal decomposition of alcohols involves the unimolecular elimination of water to form alkenes.\[61\] Schwarz et al.\[62\] showed that polyhydroxylated compounds like sugars (e.g., mannitol, dulcitol, sorbitol, arabinol, xylitol, and ribitol) are stable only up to 200–250°C. Thermal stability of esters is lower than hydrocarbons. Esters of alcohols with β-hydrogen (e.g., methyl esters of fatty alcohols) are stable up to only ~285°C.\[55\]

As shown in Eq. 2, temperature (T) is the most important external factor affecting thermal stability. In addition, at a given temperature, decomposition generally occurs under high, rather than low, vapor pressure conditions due to greater collision frequencies.\[58\]

The presence of other molecules can lead to higher or lower stability by preventing or opening thermal degradation/reaction pathways, respectively. For example, in the petroleum industry, it has been known that the thermal stability of alkanes can be improved in the presence of hydrogen donors, e.g., tetralin.\[63\] This is achieved by interruption of the radical chain reaction through the H-donating action.

### Pyrolysis

Pyrolysis converts an organic compound to one or more different compounds by thermal energy in an inert environment (absence of oxygen or catalysts).\[64\] Carbonization happens in extreme pyrolysis to form EC.\[64,65\] Above a particular temperature, organic molecules gain sufficient vibrational energy to rupture their bonds and form free radicals that subsequently reform other lower molecular-weight compounds or combine with higher molecular-weight compounds.\[66–71\] Saturated alkanes break down C–C and C–H bonds to radicals that form smaller alkenes, alkanes, and hydrogen.\[72–74\] Simple aromatic compounds (e.g., benzene and toluene) produce aryl radicals, which attack other hydrocarbon molecules to give bi- and polyaryls.\[75–78\] The reaction causes loss of H and X (any leaving group [e.g., F, NH$_2$, OH]) from a compound with a configuration of H-C-C-X and results in formation of a C≡C bond.\[79–82\]

This “elimination” also occurs by loss of small molecules such as N$_2$, CO, CO$_2$, or SO$_2$, leading to formation of reactive intermediates such as arynes, diradicals, carbenes, or nitrenes.\[80,82\] Cleavage of particular C–C bonds in a carbon chain or ring always happens in pyrolysis. This includes transfer of hydrogen during fragmentation that occurs by a cyclic process.\[83–85\] Pyrolysis can involve isomerization without elimination or fragmentation. These processes occur by way of intermediates such as di-radicals from pericyclic reactions.\[86–88\]

### Thermochemical properties of carbonaceous aerosols

Carbonaceous materials can be thermally released to the gas phase either in chemically unaltered or altered forms. For carbonaceous aerosol, EC is thermally resistant, requiring oxidation to evolve into the gas phase in the form of CO or CO$_2$. OC is comprised of tens of thousands of organic compounds with diverse chemical structures. Depending on the chemical nature, some organic compounds are volatilized into the gas phase unaltered while others are thermally labile, leading to degradation products released to the gas phase. As discussed earlier, oxygenated compounds are prone to thermal conversion during TD. n-Alkanols in a GC injection port at 250–350°C yielded n-aldehydes, and 1-alkenes.\[89,90\] Llevogluconan partially degrades to levogluconone at 300°C.\[49\] Cholesterol spiked onto a quartz-fiber filter during TD-GC/MS analysis partially converted to cholesterol-3,5-diene. Thermal degradation products could be mistaken for compounds originally present in suspended particles. This highlights the importance of removing the thermally labile constituents or converting them to less sensitive functional groups before applying TD.

Thermal behaviors might be modified by other components coexisting in the particles. For example, n-alkanoic
Table 1. Chemical and physical properties of major organic classes and markers in aerosols[149]

<table>
<thead>
<tr>
<th>Organic Classes</th>
<th>Subgroups</th>
<th>Useful Marker Compounds</th>
<th>Molecular Weight</th>
<th>Melting Point (°C)</th>
<th>Boiling Point (°C)</th>
<th>Vapor Pressure at 25°C (mmHg)</th>
<th>Description (Bonds)</th>
<th>Thermal Stability</th>
<th>Amenity to Thermal Desorption</th>
<th>Amenity to Solvent Extraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aromatic PAHs</td>
<td>fluoranthene (C_{16}H_{10})</td>
<td>202.6</td>
<td>110.8</td>
<td>375</td>
<td>1.23E-08</td>
<td>aromatic ring, C—H</td>
<td>High</td>
<td>Yes</td>
<td>Yes</td>
<td></td>
</tr>
<tr>
<td></td>
<td>chrysene (C_{18}H_{12})</td>
<td>228.3</td>
<td>255.8</td>
<td>448</td>
<td>6.23E-09</td>
<td>aromatic ring, C—H</td>
<td>High</td>
<td>Yes</td>
<td>Yes</td>
<td></td>
</tr>
<tr>
<td></td>
<td>benzo[e]pyrene (C_{20}H_{12})</td>
<td>252.3</td>
<td>178.0</td>
<td>492</td>
<td>5.70E-09</td>
<td>aromatic ring, C—H</td>
<td>High</td>
<td>Yes</td>
<td>Yes</td>
<td></td>
</tr>
<tr>
<td></td>
<td>benzo[a]pyrene (C_{20}H_{12})</td>
<td>252.3</td>
<td>176.5</td>
<td>495</td>
<td>5.70E-09</td>
<td>aromatic ring, C—H</td>
<td>High</td>
<td>Yes</td>
<td>Yes</td>
<td></td>
</tr>
<tr>
<td></td>
<td>indeno[1,2,3-cd]pyrene (C_{22}H_{12})</td>
<td>276.3</td>
<td>162.5</td>
<td>536</td>
<td>5.70E-09</td>
<td>aromatic ring, C—H</td>
<td>High</td>
<td>Yes</td>
<td>Yes</td>
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</tr>
<tr>
<td></td>
<td>benzo[g]h[pi]erylene (C_{23}H_{12})</td>
<td>276.3</td>
<td>278.3</td>
<td>500</td>
<td>1.00E-10</td>
<td>aromatic ring, C—H</td>
<td>High</td>
<td>Yes</td>
<td>Yes</td>
<td></td>
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<tr>
<td></td>
<td>picene (C_{22}H_{14})</td>
<td>278.4</td>
<td>366-367</td>
<td>518-520</td>
<td>3.73E-09</td>
<td>aromatic ring, C—H</td>
<td>High</td>
<td>Yes</td>
<td>Yes</td>
<td></td>
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<tr>
<td></td>
<td>coronene (C_{24}H_{12})</td>
<td>300.4</td>
<td>438</td>
<td>525</td>
<td>3.29E-11</td>
<td>aromatic ring, C—H</td>
<td>High</td>
<td>Yes</td>
<td>Yes</td>
<td></td>
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<tr>
<td>Alkanes</td>
<td>n-Alkanes</td>
<td>n-nonacosane (C_{29}H_{60})</td>
<td>408.8</td>
<td>63.7</td>
<td>440.8</td>
<td>3.24E-14</td>
<td>C—C, C—H</td>
<td>High</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td></td>
<td>n-triacontane (C_{30}H_{62})</td>
<td>422.8</td>
<td>62.8</td>
<td>449.7</td>
<td>2.74E-15</td>
<td>C—C, C—H</td>
<td>High</td>
<td>Yes</td>
<td>Yes</td>
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<td>n-hentriacontane (C_{31}H_{64})</td>
<td>436.8</td>
<td>67.9</td>
<td>458</td>
<td>1.40E-16</td>
<td>C—C, C—H</td>
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<td>Yes</td>
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<td>n-dotriacontane (C_{32}H_{66})</td>
<td>450.9</td>
<td>69</td>
<td>467</td>
<td>8.49E-18</td>
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<td>High</td>
<td>Yes</td>
<td>Yes</td>
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<tr>
<td></td>
<td>n-tritriacontane (C_{33}H_{68})</td>
<td>464.9</td>
<td>71–73</td>
<td>485.3</td>
<td>4.02E-19</td>
<td>C—C, C—H</td>
<td>High</td>
<td>Yes</td>
<td>Yes</td>
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<tr>
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<td>n-tetratriacontane (C_{34}H_{70})</td>
<td>478.9</td>
<td>72.6</td>
<td>496.9</td>
<td>1.67E-20</td>
<td>C—C, C—H</td>
<td>High</td>
<td>Yes</td>
<td>Yes</td>
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<tr>
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<td>n-pentatriacontane (C_{35}H_{72})</td>
<td>493</td>
<td>75</td>
<td>490</td>
<td>5.39E-22</td>
<td>C—C, C—H</td>
<td>High</td>
<td>Yes</td>
<td>Yes</td>
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<td>n-hexatriacontane (C_{36}H_{74})</td>
<td>507</td>
<td>74–76</td>
<td>520.1</td>
<td>1.34E-23</td>
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<td>High</td>
<td>Yes</td>
<td>Yes</td>
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<td>Hopanes</td>
<td>17α(H)-22,29,30-trisnorhops (C_{37}H_{50})</td>
<td>370.7</td>
<td>112.8</td>
<td>387.8</td>
<td>2.09E-06</td>
<td>cyclic ring, C—C, C—H</td>
<td>High</td>
<td>Yes</td>
<td>Yes</td>
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<td></td>
<td>17α(H),21β(H)-30-norhopane (C_{38}H_{50})</td>
<td>398.7</td>
<td>124.4</td>
<td>407.7</td>
<td>5.19E-07</td>
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<td>High</td>
<td>Yes</td>
<td>Yes</td>
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<td>17α(H),21β(H)-hopane (C_{36}H_{52})</td>
<td>412.8</td>
<td>127.1</td>
<td>412.3</td>
<td>3.91E-07</td>
<td>cyclic ring, C—C, C—H</td>
<td>High</td>
<td>Yes</td>
<td>Yes</td>
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<td>17α(H),21β(H)-22R-homohopane (C_{36}H_{54})</td>
<td>426.8</td>
<td>133.8</td>
<td>423.9</td>
<td>1.71E-07</td>
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<td>High</td>
<td>Yes</td>
<td>Yes</td>
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<td>Steranes</td>
<td>aaaa 20R-cholestane (C_{27}H_{48})</td>
<td>372.7</td>
<td>115.5</td>
<td>392.5</td>
<td>8.79E-06</td>
<td>cyclic ring, C—C, C—H</td>
<td>High</td>
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<td>Yes</td>
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<td>aaaa 20R 24R-methylcholestane (C_{28}H_{50})</td>
<td>386.7</td>
<td>122.9</td>
<td>405.2</td>
<td>9.19E-07</td>
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<td>High</td>
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<td>Yes</td>
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<td>aaaa 20R 24R-ethylcholestane (C_{29}H_{52})</td>
<td>400.7</td>
<td>130.5</td>
<td>417.9</td>
<td>3.84E-07</td>
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<td>High</td>
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<td>Yes</td>
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<td>Esters</td>
<td>dimethylphthalate (C_{10}H_{10}O_{4})</td>
<td>194.2</td>
<td>0-2</td>
<td>282</td>
<td>1.65E-03</td>
<td>aromatic ring with —COO-R, C—C, C—H</td>
<td>Fair</td>
<td>Yes</td>
<td>Yes</td>
<td></td>
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<td>diethyl phthalate (C_{12}H_{14}O_{4})</td>
<td>222.2</td>
<td>-40.5</td>
<td>295</td>
<td>1.65E-03</td>
<td>aromatic ring with —COO-R, C—C, C—H</td>
<td>Fair</td>
<td>Yes</td>
<td>Yes</td>
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<td>di-n-butyl phthalate (C_{16}H_{22}O_{4})</td>
<td>278.3</td>
<td>-35</td>
<td>340</td>
<td>7.30E-05</td>
<td>aromatic ring with —COO-R, C—C, C—H</td>
<td>Fair</td>
<td>Yes</td>
<td>Yes</td>
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<td>dibutyl phthalate (C_{18}H_{30}O_{4})</td>
<td>312.4</td>
<td>-35</td>
<td>370</td>
<td>8.25E-06</td>
<td>aromatic ring with —COO-R, C—C, C—H</td>
<td>Fair</td>
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<td>Yes</td>
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<td>bis(2-ethylhexyl)phthalate (C_{24}H_{38}O_{4})</td>
<td>390.6</td>
<td>-50</td>
<td>386.9</td>
<td>9.75E-06</td>
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<td>Fair</td>
<td>Yes</td>
<td>Yes</td>
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<tr>
<td>Alcohols/Sugars</td>
<td>Molecular Formula</td>
<td>Melting Point (°C)</td>
<td>Boiling Point (°C)</td>
<td>Vapor Pressure (mb)</td>
<td>Functional Groups</td>
<td>Toxicity</td>
<td>Reactivity</td>
<td></td>
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<td>glycerol (C₃H₈O₃)</td>
<td>92.1</td>
<td>17.8</td>
<td>290</td>
<td>1.68E-04</td>
<td>-OH, C—C, C—H</td>
<td>Low</td>
<td>No</td>
<td>Yes</td>
<td></td>
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<td>xylitol (C₅H₁₀O₃)</td>
<td>152.1</td>
<td>95-97</td>
<td>216</td>
<td>1.96E-03</td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>levoglucosan (C₆H₁₀O₅)</td>
<td>162.1</td>
<td>170-180</td>
<td>313.8</td>
<td>3.47E-07</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>glucose (C₆H₁₂O₆)</td>
<td>180.2</td>
<td>83</td>
<td>380.7</td>
<td>1.82E-08</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>fructose (C₆H₁₂O₆)</td>
<td>180.2</td>
<td>85.4</td>
<td>341</td>
<td>3.11E-07</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>mannitol (C₆H₁₄O₅)</td>
<td>182.2</td>
<td>167</td>
<td>290-295</td>
<td>1.31E-09</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>sorbitol (C₆H₁₄O₅)</td>
<td>182.2</td>
<td>93-97</td>
<td>389.7</td>
<td>4.92E-09</td>
<td></td>
<td></td>
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<td></td>
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<td></td>
</tr>
<tr>
<td>sucrose (C₁₂H₂₂O₁₁)</td>
<td>342.3</td>
<td>190-192</td>
<td>591.6</td>
<td>5.15E-17</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>cholesterol (C₂₇H₄₆O)</td>
<td>386.7</td>
<td>148.5</td>
<td>360</td>
<td>7.79E-10</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>Carboxylic Mono- and oxalic acid (C₂H₂O₄)</td>
<td>90</td>
<td>189</td>
<td>190</td>
<td>2.34E-04</td>
<td>—COOH, C—C, C—H</td>
<td>Low</td>
<td>No</td>
<td>Yes</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Malonic acid (C₃H₄O₄)</td>
<td>104.1</td>
<td>135.6</td>
<td>140</td>
<td>1.50E-03</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>Succinic acid (C₄H₆O₄)</td>
<td>118.1</td>
<td>183-185</td>
<td>235</td>
<td>7.86E-06</td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>Adipic acid (C₆H₁₀O₄)</td>
<td>146.1</td>
<td>152</td>
<td>337</td>
<td>7.30E-02</td>
<td></td>
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<td></td>
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<td></td>
</tr>
<tr>
<td>Pimelic acid (C₇H₁₂O₄)</td>
<td>160.2</td>
<td>103-105</td>
<td>272</td>
<td>2.08E-05</td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Suberic acid (C₈H₁₄O₄)</td>
<td>174.2</td>
<td>144</td>
<td>230</td>
<td>1.69E-08</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Palmitic acid (C₁₆H₃₂O₂)</td>
<td>256.4</td>
<td>62</td>
<td>271.4</td>
<td>1.20E-05</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Oleic acid (C₁₈H₃₄O₂)</td>
<td>282.3</td>
<td>13-14</td>
<td>460</td>
<td>5.46E-07</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Stearic acid (C₁₈H₃₆O₂)</td>
<td>284.5</td>
<td>69.3</td>
<td>361</td>
<td>7.22E-07</td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

*a* Melting point was estimated with Gold and Ogle Method (using EPI Suite™ developed by the U.S. Office of Pollution Prevention Toxics and Syracuse Research Corporation [SRC]).

*b* Boiling point was estimated with Adapted Stein and Brown Method (using EPI Suite™ developed by the U.S. Office of Pollution Prevention Toxics and Syracuse Research Corporation [SRC]).

*c* Vapor pressure was estimated with Modified Grain Method (using EPI Suite™ developed by the U.S. Office of Pollution Prevention Toxics and Syracuse Research Corporation [SRC]).

*d* Boiling point reported at the pressure of 100 mmHg.

*e* Boiling point reported at the pressure of 15 mmHg.

*f* Vapor pressure reported at the temperature of 18°C.
acids (C12-C20) and nitriles (C14-C32) were measured in the TD-GC/MS analysis of ambient aerosols collected in Augsburg, Germany.\[91\] Five nitriles were also reported in aerosols of a forest site in Germany.\[92\] These amides and nitriles are actually thermal reaction products from analogous acids and ammonium nitrate (NH4NO3) coexisting in the aerosol samples.\[93\] Yu et al.\[94\] observed changes in the thermal evolution pattern of levoglucosan in the presence and absence of ammonium bisulfate (NH4HSO4). The presence of transition metal catalysts (e.g., Fe, Cu) in aerosols can also affect the conversion of OM during heating.

Matrix effects are little understood and may vary from sample to sample. On-line instruments using TD minimize thermal decomposition due to reduced pressure and lower aerosol loading in the analysis zone.\[95,96\] Laser desorption has been employed for on-line MS-based instruments (e.g.,\[95,96\]). However, it experiences fluctuations in desorption/ ionization conditions which lead to large pulse-to-pulse variation in ion signals that impede quantification.

**Variations among thermal methods**

Figure 1 shows a conceptual diagram of various TD methods applied to aerosol samples. Thermal conditions can be adjusted to extract the desired analytical information, and differ among methods. In aerosol carbon analyzers, the thermal conditions are targeted to evolve OC and EC separately without preserving the original forms of organic compounds. The detection of a single product (i.e., CO2 or CH4) after catalytic oxidation is sufficient to achieve the analytical objective.\[22,25–29\] Long-term databases have been compiled with the data (e.g., http://vista.cira.colostate.edu/improve/, http://www.epa.gov/ttn/amtic/speciepg.html, http://www.atmospheric-research.com/studies/SEARCH/index.html, http://www.arb.ca.gov/airways/CRPAQS/default.htm).

For TD, thermal conditions are optimized for fast and complete vaporization of target compounds in their unaltered forms, along with a sensitive detection system for individual organic compounds (e.g., MS, GC/MS, GC/FID). Thermal conditions can also be selected to evolve non-volatile and insoluble organic compounds as their pyrolysis products, and the parent compounds' identities are inferred from their thermal degradation products as in the application of pyrolysis GC for the determination of rubbers and plastics. TD coupled with a suitable detection system has the potential to become a simple and routine tool for the determination of organic aerosol chemical composition. With perfection of the equipment, procedures, and data processing methods, it would be possible to obtain data on currently acquired or archived samples with little additional cost and effort than is currently expended on OC and EC measurement.

**Off-line thermal desorption analyses of filters**

**TD-MS**

Schuetzle et al.\[44,45\] and Cronn et al.\[97\] first collected particles on glass-fiber filters and impaction plates, then introduced them directly into a high-resolution MS utilizing a temperature-programmed insertion tube (solid probe), which was heated from 20 to 400°C at 20–30°C/min under a vacuum of 10−9 atm. Compounds were selectively removed from the aerosol matrix according to their volatility. The TD-MS-generated mass thermograms, i.e., the intensity of each ion current peak as a function of time or temperature. Compound identification was based on: (i) a major characteristic ion and the temperature at which this signal was detected; (ii) one or two additional ions at the same temperature; and (iii) the plausibility of the existence of the component in the aerosol by vapor pressure calculation.

![Fig. 1. Conceptual depiction of various thermal methods as applied to aerosols.](image-url)
Cronn et al.\cite{97} identified alkanes, alkenes, aromatics (i.e., alkyl benzenes, substituted naphthalenes, and PAHs), amines (i.e., alkyl piperidines), alcohols (i.e., phenol), and carboxylic acids. Schuetzle et al.\cite{45} identified a number of peroxides in aerosols collected in Pasadena, California, suggesting low probability of decomposition of organic compounds with the TD under high vacuum conditions. Nevertheless, there were signs of matrix effects and possible thermal decomposition. For example, C$_3$-C$_7$ dicarboxylic acids were found while C$_2$ dicarboxylic acid was not found, inconsistent with results from other studies that showed oxalic acid is more abundant than the higher dicarboxylic acids.\cite{98,99} This failure to detect oxalic acid in southern California reflects thermal decomposition. The matrix effect was demonstrated by the observation that four tested compounds (i.e., naphthalene, phenol, glutaric acid, and phenanthrene) spiked onto aerosol loaded substrates required 44–152°C higher temperatures to vaporize than those spiked onto a particle-free brass disk.\cite{45} This is the effect of boiling point elevation due to reduction of vapor pressure of the substances in a mixture. The effect was more prominent for two polar compounds (phenol and glutaric acid) with hydrogen bonding.

Since TD takes place in a vacuum, organic compounds are vaporized at reduced temperatures. This in turn extends analytical feasibility to compounds of lower thermal stability (e.g., peroxides) and higher molecular weight. Perry et al.\cite{100} reported 12-ring hydrocarbons using TD-GC/MS in soot as compared to a 7-ring PAH (coronene) using GC. However, organic compounds with similar thermal and mass fragmentation behaviors cannot be resolved by TD-MS.

**TD-GC/MS**

With capillary GC, organic compounds in aerosol samples are separated according to their physical (boiling point) and chemical (polarity) properties before quantification by MS. Chromatographic separation prior to FID or MS detection minimizes interferences from coexisting species. As shown in Figure 2, two configurations exist for off-line TD-GC/MS, with TD carried out either in an external oven or inside the GC injection port. A brief summary of these units is given below; details can be found in Hays and Labrich.\cite{24}

External TD units use either conventional resistive heating\cite{101–103} or Curie point heating\cite{104,105} to thermally extract organic compounds. The in-injection port TD also has several variants. Falkovich and Rudich\cite{106} used a microvial to hold the filter strip inside a GC liner. Wauters et al.\cite{107} and Ho and Yu\cite{108} adapted a conventional GC liner without any modifications. Helmig et al.\cite{92} altered the carrier gas lines, while Blanchard and Hopper\cite{109} modified the GC injector with a small T-connector, a three-way valve, and a needle valve. Zimmermann and co-workers\cite{91,110,111} automated the insertion of a GC injection-liner, preloaded with filter pieces, and the closing of the injector port.

The Curie point TD device uses radio frequencies to induce eddy currents in a ferromagnetic foil, in which filter strips are positioned, to heat the sample to the Curie point temperature of the foil. At the Curie point, the ferromagnetism of the metal changes to paramagnetism so that the foil remains at that constant temperature. The Curie point devices offer rapid heating. This might reduce decomposition as a result of volatilization being kinetically favored relative to the competitive decomposition processes.\cite{112}

External TD units require a transfer line and a connector to the GC injector and consequently may lose organic compounds when the material of the transfer line is not inert or the line has cold spots. A contaminated line of inert material (due to deposition over time) can also become active. The line has to be inert and heated uniformly to a temperature above the desorption temperature. Residue (e.g., polar substances) may be trapped between the TD unit and the GC/MS, causing carryover.\cite{46,103} TD performed in the GC injector is simple and eliminates the need for an external oven and transfer line. It requires no modifications or only a minor rearrangement of carrier gas lines or an injector cap. This development not only reduces the carryover, but also offers maximum transfer efficiency.

TD-GC/MS differs from SE-GC/MS primarily in the principle of extracting individual organic compounds (i.e., by heat or solvent) from the filter. GC/MS analyses of the extracts are the same. Table 2 compares attributes of the two methods.

The SE methods are better known for their selectivity, feasibility, and for sample extract derivatization, fractionation, and clean-up. Solvent extracts generally pair better with off-line analytical instrumentation (e.g., ion chromatography [IC] and high performance liquid chromatography [HPLC], both transfer samples with liquid mobile phases) than TD, which has resulted in an expanded list of non-polar and polar organic compounds.\cite{12,21,113,114} TD-GC/MS applied to aerosols has been largely limited to non-polar PAHs and n-alkanes. Unlike SE in which only a small portion of the extract (typically a few percent) is injected, the entire sample mass from a filter portion is transferred to the TD-GC/MS. As a result, TD is at least an order of magnitude more sensitive than SE and requires considerably less sample mass. This attribute is particularly important when only micrograms of aerosols are available as on a 25 mm to 47 mm-diameter filter from speciation samplers.\cite{143,115} The high sensitivity of TD improves temporal resolution of organic compounds. Since TD requires a small fraction (0.3–5.0 cm$^2$) of the filter for analysis,\cite{106,108,116} it can be applied to remnants of archived quartz-fiber filters after ionic and carbon analyses without additional sampling.

**TD with two-dimensional GC-time-of-flight/MS (TD-GC×GC-TOF/MS)**

Since the greater part of organics remain unresolved by TD-GC/MS, TD paired with comprehensive two-dimensional
Fig. 2. Conceptual diagrams of different off-line thermal desorption-gas chromatography/mass spectrometry (TD-GC/MS) approaches for: (a) external TD or Curie point pyrolysis-GC/MS: (i) desorbent refocusing with a cryogenic trap inside TD unit; (ii) desorbent refocusing onto GC column head; and (iii) desorbent refocusing with a cryogenic trap in front of GC column; (b) In-injection port TD-GC/MS: (iv) desorbent refocusing onto GC column head, and (v) desorbent refocusing with a cryogenic trap in front of GC column; and (c) Direct TD GCxGC-TOF/MS: desorbent refocusing with a cryogenic trap in front of the second GC column.

GC and time-of-flight (TOF)/MS (Fig. 2c) has been used to provide additional resolution. The compounds are first separated by boiling points with a non-polar stationary phase column. As the compounds elute from this first column, they are refocused onto a shorter (1 m) polar stationary phase column for further separation according to polarity. Using this approach, Welthagen et al. detected ~15,000 compounds for particles collected in Germany, including categories of: alkanes (i.e., \(n\)-alkanes, steranes, hopanes), alkenes (i.e., terpenes), aromatic (i.e.,
Table 2. Attributes of thermal desorption and solvent extraction methods for the analysis of organic compounds in aerosols collected on filters.

<table>
<thead>
<tr>
<th>Variables</th>
<th>Thermal Desorption</th>
<th>Solvent Extraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Extraction Theory</td>
<td>- Thermal behavior of analytes (e.g., boiling point, volatility).</td>
<td>- Solubility of analytes in extraction solvent or solvent mixture (normally binary or tertiary).</td>
</tr>
<tr>
<td>Sample Size and Loading</td>
<td>- Small punches (0.3–5.0 cm$^2$) of filter depending on the design of thermal desorption unit and sample loading;</td>
<td>- Requires $&gt;50$ g 1 µg OC;</td>
</tr>
<tr>
<td></td>
<td>- Can use remnants of archived quartz-fiber samples from existing networks;</td>
<td>- Combining samples (&gt;60 cm$^2$) into composites may be needed for low loading samples;</td>
</tr>
<tr>
<td></td>
<td>- Requires $&gt;1$ µg OC;</td>
<td>- High collection flow rates (e.g., 100–1,000 L min$^{-1}$) are required to increase the sample loading.</td>
</tr>
<tr>
<td>Sample Deposit Homogeneity</td>
<td>- Essential since only a fraction of filter is used.</td>
<td>- Not relevant if entire filter is used for extractions.</td>
</tr>
<tr>
<td>Solvent Consumption</td>
<td>- Low, only few microliters (µL) internal standard containing solvent used per sample.</td>
<td>- High, ranging from 10 to 300 mL per sample;</td>
</tr>
<tr>
<td>Sample Pretreatment</td>
<td>- Spiking with internal standard, a few minutes labor</td>
<td>- Common solvents used: dichloromethane (DCM), methanol, 1-butanol, acetone, and n-hexane;</td>
</tr>
<tr>
<td>Analysis Time$^b$</td>
<td>- 1 to 2 labor hours per sample.</td>
<td>- Generally $&gt;90%$ cannot be recycled.</td>
</tr>
<tr>
<td>Analytical Instrument</td>
<td>- Mass spectrometer (MS);</td>
<td>- Complicated steps (i.e., single or multiple volume reductions, extract transfer, and sample filtration);</td>
</tr>
<tr>
<td></td>
<td>- Gas chromatography/flame ionization detector (GC/FID);</td>
<td>- 1 to 20 hours labor per sample.</td>
</tr>
<tr>
<td></td>
<td>- Gas chromatography/mass spectrometer (GC/MS).</td>
<td>- A few to tens of hours.</td>
</tr>
<tr>
<td>Sample Introduction Volume</td>
<td>- 100%.</td>
<td>- GC/MS</td>
</tr>
<tr>
<td>Sample Contamination</td>
<td>- Low probability;</td>
<td>- GC/FID</td>
</tr>
<tr>
<td></td>
<td>- Potential carryover (usually negligible), transfer loss, molecular arrangement, or breakdown as temperature $\geq 350^\circ$ C;</td>
<td>- High performance liquid chromatography (HPLC);</td>
</tr>
<tr>
<td></td>
<td>- Fragmentation of thermally labile compounds.</td>
<td>- Ion chromatography (IC);</td>
</tr>
<tr>
<td>Sensitivity and Minimum Detection Limits (MDLs)</td>
<td>- High sensitivity;</td>
<td>- Capillary electrophoresis (CE).</td>
</tr>
<tr>
<td>Suitability of Filter Matrix</td>
<td>- n-Alkanes: 0.41 to 4.36 ng/ sample$^{-1}$;</td>
<td>- 0.5 to 25% of the solvent extract.</td>
</tr>
<tr>
<td></td>
<td>- PAHs: 0.08 to 2.40 ng/ sample$^{-1}$;</td>
<td></td>
</tr>
<tr>
<td></td>
<td>- Filters that can remain intact at TD temperatures, e.g., quartz-fiber or Teflon-impregnated glass-fiber (TIGF) filters.</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Calculation based on the detection limits of the organic compounds reported in the thermal desorption method. $^{[103]}$

$^b$ Including sample pre-treatment and analytical separation.

$^c$ Data from Ho and Yu. $^{[108]}$

alkyl-benzenes, substituted aromatics, heterocyclic aromatics, PAHs, oxygenated-PAHs, branched-PAHs), aldehydes, ketones (i.e., n-alkane-2-ones), carboxylic acids, nitriles (i.e, alkyl nitriles), and esters. $^{[91]}$ These methods can also identify oxygenated compounds (e.g., aldehydes, ketones, and carboxylic acids) ascribable to secondary organic aerosols (SOA). $^{[117,118]}$ Many of the oxygenated species (e.g., 2-hexenal, furan) identified by Hamilton et al. were fairly volatile (vapor pressure $>10^{-2}$ atm at 20°C). The presence of these volatile species needs further evaluation. It is possible that some of the oxygenated species detected are TD products of thermally labile compounds that were originally present in the aerosols. Using GC×GC-TOF/MS to quantify organic compounds shows TD-potential. $^{[91]}$
**Pyrolysis-TD-GC/MS**

The two most common pyrolysis techniques are Curie point and controlled temperature programming pyrolysis. Pyrolysis is often used as a form of sample pretreatment for mass spectrometric investigations of complex materials.\[119\]

Pyrolysis-TD-GC/MS uses higher TD temperatures (often exceeding 400°C) than TD-GC/MS.\[104,119,120\] As a result, pyrolysis-TD-GC/MS produces many more evolved products. Pyrolysis of resuspended soil samples at 740°C resulted, pyrolysis-TD-GC/MS produces many more evolved compounds.\[119\] Five times more than were obtained with TD for the same sample at 315°C.

During pyrolysis, vaporized compounds include both volatile molecules (in the sample) and volatile fragments produced from cracking of non-volatilized molecules. The vaporized compounds are then collected, separated, and identified by GC/MS. In pyrolysis, polar compounds, either indigenous or those formed during thermal degradation, can readily undergo reactions such as decarboxylation and dehydration, consequently losing the functional group information. To overcome this, reactive pyrolysis mixes a derivatizing reagent with the sample to preserve the polar functional group information and also to improve their detection.\[121\] Tetramethylammonium hydroxide (TMAH) and hexamethyldisilazane (HMDS) are the common methylation and silylation reagents, respectively, for thermally assisted derivatization.\[121\]

Pyrolysis-TD-GC/MS has characterized biopolymers (e.g., lignins), soil particles, sediments, and other matrices containing macromolecules (e.g.,\[122,123\]). Subbalakshmi et al.\[124\] identified aerosol pyrolysis products and linked them to their parent molecules: (i) methoxyphenols originating from lignin; (ii) furans, aldehydes, and ketones from carbohydrates; (iii) pyrrole and indoles from proteins; and (iv) hydrocarbons from lipid structures. Fabbri et al.\[121\] applied conventional and reactive pyrolysis at 700°C to PM10 from an industrial area of Bologna, Italy, providing information on precursors (e.g., carbohydrates, lipids, synthetic rubbers, and conifer resins). Blazso et al.\[120\] used thermally assisted methylation and silylation in their pyrolysis-TD-GC/MS analysis of size-segregated aerosol samples from a forest and semi-remote site in tropical Brazil, identifying fatty acids, alkanedioic acids, hydroxybenzoic acids, levoglucosan, and other compounds of polysaccharide origin.

With pyrolysis-TD-GC/MS, the chemical nature of the sample is inferred from the molecular structure of its thermal degradation products. Compounds detected can be pyrolysis or evaporation products from one or more parent molecules. Identification of parent compounds requires extensive mapping to their pyrolysis products. Quantitative analysis is hindered by the presence of the large number of compounds detected and the effects of aerosol loading. However, pyrolysis-TD-GC/MS has the advantage of obtaining structural information for polymeric and insoluble organic compounds, which could not be otherwise obtained by conventional SE- or TD-GC/MS.\[119,125,126\] Pyrolysis-TD-GC/MS also provides a rapid screening tool, since no sample pretreatment is required.

**Parameters for aerosol analysis with TD-GC/MS and pyrolysis-TD-GC/MS**

Table 3 compares experimental parameters for 30 studies using TD-GC/MS and/or pyrolysis-TD-GC/MS. Important parameters include: (i) type of sample; (ii) sample preparation; (iii) TD unit; (iv) analytical instrument; (v) TD temperature program; (vi) TD time; (vii) desorbet refocusing pathway; (viii) GC column; (ix) GC initial temperature; (x) GC oven temperature program; and (xi) total analysis time. The quantitative significance of different parameter selections has not yet been determined.

TD temperature ramping and holding times varied by sample type, experimental objective, analytical equipment and operation, which affected the analysis times. Both isocratic and gradient heating were applied in resistively heated TD devices, whereas rapid induction heating (~3s) was used in Curie point pyrolysis. TD of aerosols in off-line ovens and inside the GC injection port is completed in a matter of minutes, or seconds in the case of Curie point pyrolysis. Isocratic desorption temperatures of 250–320°C have been used in a few studies (e.g.,\[46,92,109,116,127–129\]). For gradual heating, temperatures varied from ambient (~25°C)\[103–105,130,131\] to 175°C\[102\]. Temperature ramping in TD varied from 12°C min\(^{-1}\) to 700°C min\(^{-1}\), with holding times ranging from 0 to 10 min. These temperatures and holding times were optimized to ensure complete extraction and to minimize pyrolysis.\[46\]

The desorption temperature is directly related to the volatility and thermal stability of the targeted analytes. At desorption temperatures < 275°C, the analytes are not completely extracted, especially for less volatile compounds such as PAHs and n-alkanes.\[108\] Temperatures higher than 340°C may cause thermally labile compounds to decompose or pyrolyze.\[132\]

Helium (He) is the typical carrier gas. Hays and Lavrich\[124\] suggested that the flow rate of He over the sample in the desorption unit may influence the desorption efficiency. Commercial TD units can be adjusted to different flows and maintain a stable gas stream into the GC column and the detector. However, the relationship between He gas flow and desorption efficiency has not been studied.

Thermally desorbed organic compounds are usually cryo-focused, then heated and separated on an analytical column by their boiling points and polarities. Table 3 shows that initial temperatures in the GC oven vary from −60°C\[46,123\] to 70°C\[118\] with the most common selection at 30–50°C. Higher initial temperatures may volatilize some of the OM during sample loading. Studies using higher initial temperatures did not quantify VOCs adsorbed onto the particles. Ramping rates in the GC oven vary from
## Table 3. Summary of key parameters for TD-GC/MS and pyrolysis-GC/MS.

<table>
<thead>
<tr>
<th>Reference</th>
<th>Sample Type</th>
<th>Sample Preparation</th>
<th>TD Unit</th>
<th>Analytical Instrument</th>
<th>TD Temperature Program</th>
<th>TD Time</th>
<th>Desorbert Refocusing Pathway</th>
<th>GC Column</th>
<th>Initial GC Oven Temperature Program</th>
<th>Total Analysis Time</th>
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<tbody>
<tr>
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<tr>
<td>1. TD-GC/MS with Resistively Heated external oven</td>
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<tr>
<td>Greaves et al. [14, 17]</td>
<td>Aerosol sample and NIST SRM 1649</td>
<td>A 3 cm diameter piece of quartz filter was punched and placed on the top of a glass fist of a fritted glass sampling tube. The filter was firmly held on the position during sampling. The filter after collection was then directly analyzed by TE.</td>
<td>A cylindrical aluminum block containing a heating cartridge connected to a thermocouple</td>
<td>HP 5892A GC/MS in EI mode</td>
<td>Cold trapping onto capillary column head</td>
<td>Ultra Performance fused silica capillary (25 m × 0.20 mm × 0.25 µm) Ultra-2 (25 m × 0.25 mm × 0.25 µm)</td>
<td>Isotropic desorption at 254°C</td>
<td>NIST SRM standard: −50°C to −60°C</td>
<td>Ambient sample: −60°C to −2°C at 20°C min⁻¹, then to 300°C at 8°C min⁻¹, NIST standard: 20°C to 180°C at 20°C min⁻¹, then to 300°C at 8°C min⁻¹</td>
<td>Ambient sample: 55.5 min NIST standard 45.5 min</td>
</tr>
<tr>
<td>Volkamp et al. [16]</td>
<td>NIST SRM 1649</td>
<td>NIST urban dust was weighed, transferred into a glass-lined stainless steel GC liner containing glass wool and spiked with internal standards</td>
<td>External oven mounted on the top of the GC/MS system</td>
<td>HP 5890 GC/Fisons MD 800 MS, scan range 40–530 amu</td>
<td>Cryogenic refocusing at −196°C during TE, ramped to 300°C in 20 s</td>
<td>Phenomenex ZB-5 (25 m × 0.25 mm × 25 µm)</td>
<td>175–300°C at 5°C min⁻¹, held at 300°C for ~7.5 min.</td>
<td>15 min</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Waterman et al. [16]</td>
<td>NIST SRM 1649a</td>
<td>NIST urban dust standard (1-5 mg) were weighed and sealed into a glass tube filled with 120 mesh glass beads.</td>
<td>Same as above</td>
<td>HP 5890 GC/Fisons MD 800 MS, scan range m/z 40 to 520</td>
<td>Isotropic desorption at 300°C</td>
<td>Phenomenex ZB-5 (25 m × 0.25 mm × 25 µm)</td>
<td>0.17°C</td>
<td>10 min</td>
<td></td>
<td></td>
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<tr>
<td>Waterman et al. [16]</td>
<td>NIST SRM 1649a</td>
<td>NIST urban dust standard (1-5 mg) were weighed and sealed into a glass tube filled with 120 mesh glass beads.</td>
<td>Same as above</td>
<td>HP 5890 GC/Fisons MD 800 MS, scan range m/z 40 to 520</td>
<td>Isotropic desorption at 300°C</td>
<td>Phenomenex ZB-5 (25 m × 0.25 mm × 25 µm)</td>
<td>0.17°C</td>
<td>2 min</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sihui et al. [150]</td>
<td>Aerosol on glass fiber filters from combustion of alternative diesel fuel</td>
<td>Filter was sealed in a TD tube.</td>
<td>A stainless steel tube (0.035 cm O.D.) placed in a GC oven</td>
<td>HP 5890 GC/Fisons MD 800 MS, scan range m/z 40 to 520</td>
<td>Isotropic desorption at 300°C</td>
<td>Phenomenex ZB-5 (25 m × 0.25 mm × 25 µm)</td>
<td>30–300°C at 20°C min⁻¹</td>
<td>13.5 min</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hays et al. [103, 110, 131]</td>
<td>Aerosol collected from residential wood combustion, residential oil furnace and fireplace appliance.</td>
<td>A punch of filter was removed, spiked with internal standards and placed into a glass desorption tubes</td>
<td>A glass tube placed in an external oven (TD52, Gerstel Inc.)</td>
<td>HP 5890 GC/Fisons MD 800 MS, scan range m/z 50 to 500 amu</td>
<td>Isotropic desorption at 300°C</td>
<td>HP-5MS (30 m × 0.25 mm × 0.25 µm)</td>
<td>25–300°C at 12°C min⁻¹</td>
<td>~ 23 min</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2. Curie Point TD-GC/MS</td>
<td>Jeon et al. [105]</td>
<td>High-volume PM10 ambient samples collected along the U.S. / Mexico border</td>
<td>A 1.5 × 18 mm² filter strip was cut and positioned inside a glass fractionation tube lined with a ferromagnetic foil</td>
<td>HP 5890 GC/5792 MSD</td>
<td>Curie point pyrolyzer</td>
<td>HP-5MS (25 m × 0.20 mm × 0.33 µm)</td>
<td>Isotropic desorption at 300°C</td>
<td>50°C to 320°C at 3–15°C min⁻¹</td>
<td>50°C to 320°C at 3–15°C min⁻¹</td>
<td>U</td>
</tr>
</tbody>
</table>
| Neusser et al. [131] | Ambient aerosol collected during the 2nd Aerosol Characterization Experiment | The filter strips were wrapped in a Pyrofoil with a Curie point of 590°C and placed into the pyrolyzer. | Curie point pyrolyzer | Fisons Trio 1000 GC/MS system | Cold trapping onto capillary column head | Chrompack CP-Sil-5 CB (30 m × 0.25 mm × 0.1 µm) | Isotropic desorption at 300°C | 50°C | 50°C for 2 min, 50–280°C at 10°C min⁻¹, held at 280°C for 10 min | 35 min | (Continued on next page)
<table>
<thead>
<tr>
<th>Reference</th>
<th>Sample Type</th>
<th>Sample Preparation</th>
<th>TD Unit</th>
<th>Analytical Instrument</th>
<th>TD Temperature Program</th>
<th>TD Time</th>
<th>Desorbent Refocusing Pathway</th>
<th>GC Column</th>
<th>Initial GC Temp.</th>
<th>GC Oven Temperature Program</th>
<th>Total Analysis Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>Helmig et al.[92]</td>
<td>Aerosol samples collected on glass-fiber filters at a forest site</td>
<td>GC injector port, with modified septum cap.</td>
<td>Carlo Erba Mega 5100 GC / VG 250-70 SE MS, scan range: 45-400 amu</td>
<td>Cold trapping onto capillary column head</td>
<td>SE54 (15 m × 0.23 mm)</td>
<td>15 min</td>
<td>50°C</td>
<td>47 min</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NIST SRM 1649</td>
<td>Aerosol samples collected on quartz-and glass-fiber filters in Ontario</td>
<td>Micro-scale sealed vessel placed inside the injector port.</td>
<td>HP 3900 GC/Fisons MD500 MS, scan range: 40-500 amu</td>
<td>Cold trapping onto capillary column head</td>
<td>GC-MS capillary column (25 m × 0.25 mm)</td>
<td>50°C</td>
<td>45°C</td>
<td>82.5 min</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Blanchard and Hopp [109]; Blanchard et al.[120]</td>
<td>Aerosol samples collected on quartz-and glass-fiber filters in Ontario</td>
<td>A GC injection port was added with three minor components, including a small T-connector, 3-way valve, and needle valve.</td>
<td>HP5900 GC/5972A MS in EI mode</td>
<td>Cold trapping onto capillary column head</td>
<td>HP-5MS (30 m × 0.25 mm × 0.25 µm)</td>
<td>50°C</td>
<td>40°C</td>
<td>71 min</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Falkovich, Rudich, Graham et al.[112]; Falkovich et al.[113]</td>
<td>Ambient aerosol samples collected on Teflon-impregnated glass-fiber filters in Hong Kong and on quartz-filters at Nanning, China.</td>
<td>NIST standard or small piece of filter sample was loaded into a disposable microvial (15 mm ID × 12 mm long). The sample vials are placed by the vial holder in the GC liner.</td>
<td>Direct Sample Introduction (DSI) device (ChromatoProbe, Varian Co.).</td>
<td>Cold trapping onto capillary column head</td>
<td>DB-5MS column (30 m × 0.25 µm)</td>
<td>40°C</td>
<td>40°C</td>
<td>64.2 min</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Ho and Yu[104]; Yang et al.[114]</td>
<td>Ambient aerosol samples collected on Teflon-impregnated glass-fiber filters in Hong Kong and on quartz-filters at Nanning, China.</td>
<td>Conventional GC injection port.</td>
<td>HP 3900 GC/5791 MSD, scan range: 50-650 amu</td>
<td>Cold trapping onto capillary column head</td>
<td>HP-5MS (30 m × 0.25 mm × 0.25 µm)</td>
<td>30°C</td>
<td>30°C</td>
<td>41.5 min</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4. TD-GC × GC-MS: Welch et al.[106]; Schnelle-Kreis et al.[111]</td>
<td>Ambient samples in Augsburg, Germany</td>
<td>The filter strip was directly inserted into the direct thermal desorption (DTD) liner and subsequently loaded into a cold injection port</td>
<td>Injection port Optic III with autoinjector (ATAS-GL, Veldhoven, NL).</td>
<td>Cold trapping onto capillary column head</td>
<td>BPX5 (50 m × 0.22 mm × 0.25 µm) followed by BPX50 (1.5 m × 0.10 mm × 0.05 µm)</td>
<td>60°C</td>
<td>GC×GC (2-D): 60°C</td>
<td>175 min</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 3. Summary of key parameters for TD-GC/MS and pyrolysis-GC/MS. (Continued)
<table>
<thead>
<tr>
<th>Hamilton et al. [117]</th>
<th>PM$_{2.5}$ aerosol collected in London.</th>
<th>The filter strip (with 10µg loading) was inserted into the GC liner and directly introduced into the GC injector.</th>
<th>Conventional GC injection port.</th>
<th>The same as above, scan range: 20 to 330 amu</th>
<th>40–300 ◦C at a 20 ◦C/min$^{-1}$</th>
<th>13 min</th>
<th>Cold trapping onto capillary column head</th>
<th>HP-5 (10 m × 0.18 mm × 0.18 µm) followed by DB17 (1.66 m × 0.1 mm × 0.1 µm)</th>
<th>40 ◦C for 5 min, increased to 230 ◦C at 3.5 ◦C/min$^{-1}$, held at 270 ◦C for 10 min.</th>
<th>93.7 min</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hamilton et al. [118]</td>
<td>Secondary organic aerosol formed during the photo-oxidation of toluene with OH radicals.</td>
<td>The same as above.</td>
<td>The same as above.</td>
<td>The same as above.</td>
<td>12.5 min</td>
<td>Cold trapping onto capillary column head</td>
<td>The same as above</td>
<td>70 ◦C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>William et al. [49]</td>
<td>In-situ aerosol samples collected in Berkeley, CA.</td>
<td>The aerosols were collected into the collection-TE cell with conventional GC injection port.</td>
<td>Collection-TE cell</td>
<td>Agilent 6890 GC/5973 MSD, scan range: 29–550 amu</td>
<td>50–300 ◦C at 30–40 ◦C/min$^{-1}$</td>
<td>10 min</td>
<td>Cold trapping onto capillary column head</td>
<td>Rtx-5MS (30 m × 0.25 mm × 0.25 µm)</td>
<td>45 ◦C</td>
<td>59 min</td>
</tr>
<tr>
<td>Voorhees et al. [126]</td>
<td>PM$<em>{0.5}$ and PM$</em>{0.1}$ collected on quartz fiber in pristine regions of Colorado.</td>
<td>Filters were first extracted in sequence with methanol, dichloroethane, acetone, and hexane. The resulting insoluble material was introduced to a tube furnace.</td>
<td>A tube furnace directly interfaced to an GC/MS</td>
<td>Extrel Simulscan GC/MS, scan range: 35–430 amu</td>
<td>550 ◦C for 10 min</td>
<td>10 min</td>
<td>Cold trapping onto capillary column head</td>
<td>DB-5 (25 m × 0.25 mm)</td>
<td>35 ◦C</td>
<td>31.7 min</td>
</tr>
<tr>
<td>Subbulakshmi et al. [128]</td>
<td>Ambient aerosol collected on glass-fiber filters collected in Jakarta, Indonesia.</td>
<td>The aerosols were collected into the collection-TE cell with conventional GC injection port.</td>
<td>A pyroinjector.</td>
<td>Agilent6890 GC/5973 MS, scan range: 50–550 amu</td>
<td>450 ◦C for 1 min</td>
<td>1 min</td>
<td>Cold trapping onto capillary column head</td>
<td>BP-5 (30 m × 0.22 mm × 1.0 µm)</td>
<td>40 ◦C</td>
<td>63.5 min</td>
</tr>
<tr>
<td>Fabbri et al. [21]</td>
<td>PM$_{2.5}$ collected on glass-fiber filters in an industrial area, Italy.</td>
<td>The aerosols were collected into the collection-TE cell with conventional GC injection port.</td>
<td>A pyroinjector.</td>
<td>Varian 3400 GC/Saturn II ion trap MS, scan range: 45 to 400 amu</td>
<td>700 ◦C for 10 s</td>
<td>10 s</td>
<td>Cold trapping onto capillary column head</td>
<td>SPB-5 (30 m × 0.32 mm × 0.25 µm)</td>
<td>50 ◦C</td>
<td>57 min</td>
</tr>
<tr>
<td>Blazso et al. [20]</td>
<td>PM$_{2.5}$ collected on quartz fiber filters and size-segregated aerosol samples collected on Al foils in Brazil.</td>
<td>The aerosols were collected into the collection-TE cell with conventional GC injection port.</td>
<td>A pyroinjector.</td>
<td>Agilent 6890 GC/5973 MS, scan range:</td>
<td>400 ◦C for 20 s</td>
<td>20 s</td>
<td>Cold trapping onto capillary column head</td>
<td>HP-5 (30 m × 0.25 mm)</td>
<td>50 ◦C</td>
<td>30.3 min</td>
</tr>
<tr>
<td>Labuhn et al., 2006</td>
<td>PM$_{3.7}$ of resuspended soil collected on quartz-fiber filters.</td>
<td>The aerosols were collected into the collection-TE cell with conventional GC injection port.</td>
<td>A pyroinjector.</td>
<td>Agilent 6890 GC/5973 MS, scan range:</td>
<td>740 ◦C for 10 s</td>
<td>10 s</td>
<td>Cold trapping onto capillary column head</td>
<td>Rtx-5MS (30 m × 0.25 mm × 0.25 µm)</td>
<td>50 ◦C</td>
<td>25.5 min</td>
</tr>
</tbody>
</table>

*Total analysis time could not be determined because of insufficient experimental details.*
1.5°C min⁻¹[110] to 100°C min⁻¹,⁷⁹ with the most common in the range of 5–20°C min⁻¹.

**Intercomparison between TD- and SE-GC/MS.**

Hays and Lavrich[24] tabulated compound GC classes from several TD-GC/MS studies. These include alkanes (i.e., n-alkanes, steranes, and hopanes), alkenes, aromatic (i.e., PAHs and furans), alcohols (i.e., phenols), amines, amides, esters (i.e. phthalates), carboxylic acids, aldehydes, ketones, and carboxylic acids. The quantification of PAHs by TD-GC/MS has been evaluated with Standard Reference Material (SRM) 1649 (dusts collected in the urban Washington, DC area in 1976–77 and sieved to <125 µm) from the National Institute of Standards and Technology (NIST).⁴⁶,¹⁰²,¹⁰⁶,¹³³,¹³⁴ SE- and TD-GC/MS results were compared for PAHs and alkanes by Jeon et al.,¹⁰⁵ and Ho and Yu.¹⁰⁸

These two methods agreed within a factor of 2.5 for the majority of PAHs and alkanes. Hansen et al.⁹⁰ characterized the TD recoveries of three alcohols (tridecanol, octadecanoic, and eicosanoic acid), two PAHs (9-fluorenone and pyrene), and three source markers (nicotine, guaiacol, vanillin) at a TD temperature of 250°C. Only the two PAHs showed better than 75% recoveries, guaiacol, vanillin) at a TD temperature of 250°C. Only the two PAHs showed better than 75% recoveries with <55% for other compounds. Jeon et al.¹⁰⁵ showed good correlation between SE- and TD-GC/MS for hopanes and steranes (R² = 0.998), PAHs (R² = 0.978), n-alkanes (R² = 0.975), and phenols (R² = 0.940) with the exception of n-alkanoic acids (R² = 0.731). Neususs et al.¹⁰⁶ also demonstrated agreement within 130 ± 30% for PAHs between SE- and Curie point TD-GC/MS, except for the lower concentrations of indeno[1,2,3]pyrene and benzo[g,h,i]perylene by the TD method. Neususs et al.¹⁰⁴ suggested that transfer losses of the less volatile compounds might be the cause. Poor comparisons are probably due to partial decomposition during the TD process.

**Continuous and semi-continuous TD aerosol measurement systems**

TD has been applied in several first-generation semi-continuous and continuous instruments, typically coupled with MS.⁶⁸ Semi-continuous instruments integrate aerosol sample collection with TD-GC/MS-FID analysis⁴⁹ particle beam/MS (PB/MS)⁴³,¹³⁵,¹³⁶ and chemical ionization/MS (CI/MS).¹³⁷,¹³⁸ Figure 3 shows conceptual diagrams of these instruments.

**TD-GC/MS-FID**

Williams et al.⁴⁹ developed an in situ Thermal desorption Aerosol GC (TAG)/MS-FID to achieve 30-min average organic speciation. As shown in Figure 3a, TAG impacts particles into a thermal desorption cell (TDC) after a PM₂ cyclone and humidifier (to increase adhesion and minimize bounce). TD occurs under He in the TDC, which is temperature-programmed at 100°C to purge water from the system and then at 300°C to remove organic compounds followed by GC/MS-FID analysis. Desorbed analytes are focused onto the head of a GC column with the oven temperature set at 45°C. During the chromatographic separation step and subsequent MS or FID detection, the system is switched back to the sampling mode. Williams et al.⁴⁹ concluded that a sampling time of 30 min (<1 m³ of air in several cases) in urban environments (i.e., Berkeley, CA) provides sufficient sample to speciate >100 organic compounds. With the current design, TAG provides <50% collection efficiency for particles smaller than ~65 nm, thereby underestimating ultrafine organic constituents.

**Thermal desorption-particle beam/mass spectrometer (TD-PB/MS)**

TD-PB/MS identifies and quantifies organic species in chamber-produced SOA and diesel engine nanoparticles.¹³⁵,¹³⁶,¹⁴⁰ As shown in Figure 3b, particles are drawn into a high-vacuum chamber (6.6 × 10⁻¹¹ atm), focused onto a narrow, low-divergence particle beam using aerodynamic lenses followed by impaction onto a metal (Mo) foil. The particles are either continuously vaporized by resistively heating the foil to a set temperature (e.g., 165°C, 250°C) for real-time analysis or heated using a linear temperature ramp as low as 1°C/min to achieve compound separation by volatility.¹³⁵ In both temperature ramping methods, the vapors are continuously mass-analyzed using a quadrupole MS. Optimal separation of target compounds is achieved by adjusting the temperature ramping rate. With the linear-ramping temperature-programmed Thermal decomposition mode, separation was demonstrated for compounds having vapor pressures exceeding a factor of five. Mass spectra of the individual components are inferred from the time-dependent spectra for compound identification. Size-dependent chemical composition can also be obtained by passing the incoming aerosol through a differential mobility analyzer.¹³⁵

TD-PB/MS provides higher time resolution and allows study of aerosol chemistry dynamics than is possible with GC/MS analysis of filter samples. Sampling artifacts due to vapor adsorption on or particle volatilization from the filter are much reduced.¹⁴⁰ Both laboratory experiments and theoretical calculations indicate that little evaporation occurs in the ~0.2 sec transit time from the TD-PB/MS inlet to the vaporizer for alkanes down to ~C₁₅–C₁₇. Analytical artifacts caused by thermal decomposition are lower. TD of unstable compounds, which can occur on a GC column, is reduced because vaporization during TD-PB/MS occurs in a vacuum (~1.3 × 10⁻⁵ atm).¹³⁹ Thermally labile species such as α-alkoxylalkyl hydroperoxides and sulfuric acid (H₂SO₄) are detectable by TD-PB/MS.¹³⁵,¹³⁶,¹⁴¹ Hydroperoxides would have dehydrated into corresponding esters during GC analysis. A vaporization temperature of 165°C was demonstrated to completely evaporate hexadecanoic acid, tridecanoic acid, and oleic acid.¹³⁹ In
Thermal methods used to study carbonaceous aerosols

Fig. 3. Conceptual diagrams of different in-situ continuous or semi-continuous thermal desorption (TD) instruments for: a) TD-GC/MS-FID or thermal desorption aerosol (TAG)/GC-MS-FID\(^\text{[40]}\); b) TD-particle beam (PB)/MS\(^\text{[139]}\); and c) TD-chemical ionization (CI)/MS\(^\text{[137]}\).

Comparison, TD with a GC inlet at 200\(^\circ\)C only removed 70\% of octadecane in ambient aerosols.\(^\text{[108]}\)

TD-PB/MS captures ultrafine particles in the range of 20–500 nm in diameter and has quantified laboratory-generated SOA and nanoparticles from diesel engine exhaust. Quantification with an estimated uncertainty of 20\% is achieved using calibration techniques that account for particle shape and transport efficiency.\(^\text{[139]}\) The application of TD-PB/MS to ambient aerosols is still untested. Neither diesel particles nor chamber-generated SOA require prior knowledge of the types of products to be expected. Extraction of single compounds from the composite of the mass spectra of many compounds, in the case of ambient aerosols, is yet to be achieved.

Thermal desorption-chemical ionization/mass spectrometer (TD-CI/MS)

TD-CI/MS is designed for real-time chemical analysis of ultrafine particles in the 6–20 nm in diameter using a high-efficiency aerosol charger.\(^\text{[137,138]}\) As shown in Figure 3c, particles are charged and collected on a Ni/Cr wire. The collected particles are heated to 300\(^\circ\)C in an ionization chamber for particle evaporation, followed by chemical ionization by N\(_2\) buffer gas ions such as H\(_3\)O\(^+\), O\(^-\), and CO\(_3\)^{2-}. The buffer gas ions are produced by \(\alpha\)-particles emitted from a radioactive material (i.e., \(^{231}\)Americium [Am]). The ions are detected with a triple quadrupole MS.

On-line TD-CI/MS has been used in selective ion monitoring mode to size and identify inorganic ions (e.g., nitrate...
[NO$_3^-$], sulfate [SO$_4^{2-}$], and ammonium [NH$_4^+$]). The instrument has the potential to identify and detect OM in particle nuclei, but this has not yet been demonstrated.

**Aerosol mass spectrometer (AMS)**

The AMS integrates high-time resolution (5 sec) sampling and sizing with MS detection of aerosol components. Particles passing through an aerodynamic lens are impacted onto a plate at 600°C in a vacuum (<1.3 x 10$^{-6}$ atm). Flash volatilization converts PM constituents from condensed phase to gaseous form, which are introduced into either a quadrupole- or TOF/MS detector. AMS also monitors inorganic components that can be evaporated, including NO$_3^-$, SO$_4^{2-}$, NH$_4^+$, chloride (Cl$^-$), and potassium (K$^+$). Much progress has been made in interpreting the ion fragments. For example, fragment ions of m/z at 57 and 44 are used to separate OM into hydrocarbon-like organic compounds (HOCs) and oxygenated organic compounds (OOCs). However, the de-convolution of single mass spectra from multiple organic compounds remains a daunting challenge.

**TD method limitations**

Not all types of substrates are suitable for high temperature desorption. Filters containing organic binders (e.g., Teflon with an operational temperature < ~320°C) would decompose during the analysis. Sampling with quartz- or glass-fiber filters are the proper choices. Compounds with similar volatilities limit the specificity of TD-MS without chromatographic separation. In addition, matrix effects associated with TD-MS analysis have been reported. Sakurai et al. found that the desorption temperature, matrix effects associated with TD-MS analysis have been reported. Sakurai et al. [140] found that the desorption temperature. They also affect the quantification of some thermally stable compounds when their degradation products are targeted for quantification. For example, n-alkanols degrade to their corresponding 1-alkenes, n-aldehydes, or possibly to n-alkane compounds. [89, 93]

**Future research directions**

On-filter derivatization techniques such as thermally assisted alkylation using tetramethylammonium hydroxide, tetrabutylammonium hydroxide, or silylation reagents are likely to be applicable to TD-GC/MS with minor filter pretreatment. On-line derivatization methods similar to those developed by Nimz and Morgan, Docherty and Ziemann, and Blokker et al. appear to be feasible for measuring organic acids and alcoholic compounds. The derivatization reaction can proceed by filter spiking with reagent or by spiking inert material in the GC injector with reagent. Care must be taken with most derivatizing reagents because of their hazardous nature and ability to damage analytical instruments.

When TD methods are established for organic compounds, one must consider the possibility of the target compound undergoing thermal decomposition or being a decomposition product of other coexisting constituents. This can be achieved by evaluating recovery through spiking the target compound onto aerosol matrices representative of the real samples. Comparison with other methods (e.g., SE-GC/MS) will also help to minimize mis-identification of thermal decomposition products as organic compounds originally present in the aerosols. Discrepancies between the independent methods need to be further examined. When a compound identified in the TD approach is absent from the analysis using an alternative method for similar samples, there must be a reason to expect that the compound in question is actually present in the aerosol sample and not an artifact, such as thermolysis product arising from the TD analytical procedure. Conversely, there should be a chemical/physical reason why a compound was not detected by one method or the other. While method comparisons for an exhaustive list of organic compounds detected by the TD methods is desired, priority should be given to those species known to be source markers or of toxicological importance.

TD-MS has the potential to analyze unaltered thermally labile compounds because TD takes place in a vacuum. This feature could be useful and should be explored for the analysis of species such as organic peroxides that have low thermal stability and are also sensitive to solvents.

As mentioned, few TD-GC/MS experiments use the temperature programming option for separating and analyzing organics. GC/MS analysis of PM evolves incrementally by decreasing GC column temperature and sample load, potentially increasing chromatographic resolution. In
addition, they might also support individual compound identification with on-line MS measurements that employ specific temperature programming. This assumes that nanogram or individual particle mass spectra can be deconvoluted mathematically from temporally integrated ion chromatograms of the same sample. Nonetheless, this is surmised as a strong argument for the field deployment of both real-time and time-integrated aerosol sampling instruments at ambient monitoring stations.

Pyrolysis-TD-GC/MS can obtain polymeric and insoluble carbonaceous materials which could not be obtained with any SE-based methods. However, work is needed to understand the relationship between parent molecules and their pyrolysis products before this unique advantage can be realized.

Summary

TD has been widely applied and proven for the determination of aerosol OC and EC for decades. The basic principles of thermal methods are now increasingly being applied with advanced analytical detection of the evolved gases, furthering our understanding of aerosol chemistry. TD is a viable and attractive alternative to liquid injection for off-line analysis of trace level organic compounds in aerosol samples. The most prominent advantages of the TD approach are dramatic reductions of time and labor for sample pre-treatment and improved sensitivity. Exploration of TD methods to cover more organic species, especially polar organics, and overcoming the possible artifacts are necessary. While TD-MS has the potential to detect species of low thermal stability and high sensitivity, pyrolysis-TD-GC/MS has the potential to extend the analytical capability to insoluble carbonaceous materials.

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References

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