

# Validation Studies of Thermal Extraction-GC/MS Applied to Source Emissions Aerosols. 1. Semivolatile Analyte–Nonvolatile Matrix Interactions

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In this work, we develop a novel validation approach for studying how nonvolatile aerosol matrixes of considerably different chemical composition potentially affect the thermal extraction (TE)-GC/MS quantification of a wide range of trace semivolatile organic markers. The nonvolatile matrixes of a set of source emissions aerosols are first operationally isolated by thermally clearing the aerosols of their native semivolatile organic matter. TE-GC/MS analysis is then performed in triplicate on matrixes refortified with multilevel organic compound standard suites. The spiking of empty thermal extraction tubes and blank quartz filters is introduced as experimental control and also allows for the calculation of method detection limits. For the vast majority of organic compounds fortifying the matrixes (e.g., the alkane, alkene, cycloalkane, sterane, and phthalate classes), the analytical bias observed was classified as either minor or nonexistent. Furthermore, compound recoveries were generally highly reproducible, demonstrating relative standard deviations of less than 20%. For a diesel engine exhaust sample, significant matrix effects for the six- and seven-ring polycyclic aromatic hydrocarbons (PAHs) are observed and ascribed to the high proportion of elemental carbon in the sample. Our results suggest that TE-GC/MS may underestimate inhalation exposures to PAHs (with 5 rings or more) in atmospheric aerosols replete with diesel engine exhaust (e.g., near roadways or in polluted urban air). Due to its stability and representativeness, the use of a thermally cleared particulate matter matrix for validation purposes is probably expandable to additional sample pretreatment and instrumental techniques also being applied to quantify organic molecular markers in source and atmospheric aerosols.

The chemical composition of atmospheric aerosols is governed by emissions contributions from a wide variety of natural and anthropogenic sources. Further complexity is introduced from (i) the potential chemical reactions that may occur on the atmospheric particles themselves, (ii) the formation of secondary organic aerosols from the photooxidation of volatile organic

compounds, and (iii) the dynamic equilibrium and gas- and particle-phase partitioning established for semivolatile organic compounds. Consequently, atmospheric fine aerosols typically consist of a complex mixture of hundreds if not thousands of organic compounds spanning a wide range of chemical and physical properties.<sup>1–4</sup>

The importance of a detailed understanding of the chemistry and physics of aerosols cannot be overstated. Aerosols continue to be a major component of urban smog<sup>5,6</sup> with several epidemiological studies linking aerosol mass to significant negative human health impacts.<sup>7–10</sup> Their influence on the radiation balance of the Earth, both in an indirect manner by acting as cloud condensation nuclei<sup>5,11</sup> and directly by absorbing and scattering light,<sup>12,13</sup> has been demonstrated. The surface area provided by aerosols has been implicated as the site of the heterogeneous chemical reactions linked to the depletion of ozone over Antarctica.<sup>14</sup> Atmospheric aerosols have also been shown to be the primary cause of visibility degradation in polluted areas<sup>15,16</sup> and a transport mechanism for nonvolatile material.<sup>5</sup>

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Because of the complex nature of the chemical composition of fine particulate matter (PM) coupled with the small amounts of organic carbon (OC) typically sampled from primary source emissions and ambient aerosols, great demands are placed upon the analytical method employed in their analysis. Solvent extraction-gas chromatography/mass spectrometry (SE-GC/MS) has been widely utilized to characterize the organic fraction of the fine particulate matter contained in both ambient aerosols<sup>17,18</sup> and primary source emissions.<sup>19</sup> Despite its past success, SE-GC/MS has several characteristics that may limit its usefulness in future studies of fine particulate matter. Perhaps the most detrimental aspect of the solvent extraction method is its requirement for milligrams of organic carbon, which necessitates longer air sampling times and as a result prevents the investigation of diurnal and temporally short trends required for an understanding of epidemiology, health, and atmospheric studies. Several other limitations also present challenges in solvent extraction methods including the selective and incomplete extraction of analytes, the introduction of interferents through impure solvents, and the high costs and environmentally unfriendly practice associated with the disposal of spent solvent.

Thermal extraction (TE) provides a very attractive alternative to the long-established method of solvent extraction. Several key advantages of TE have been demonstrated; the most relevant with respect to the study of fine PM is the greatly reduced organic carbon mass requirement. Because of its more efficient transfer, thermal extraction has been used routinely to analyze samples containing micrograms of organic carbon.<sup>20</sup> In side-by-side comparisons, TE-GC/MS has been shown to be comparable with SE-GC/MS,<sup>21</sup> supercritical fluid extraction GC/MS,<sup>22</sup> and the standard DNPH/HPLC method for the determination of airborne carbon-yls.<sup>23</sup> The TE-GC/MS method has adequately reproduced and recovered an array of individual species across many compound classes including alkanes,<sup>20,21,24–29</sup> polycyclic aromatic hydrocarbons (PAHs),<sup>20–22,25–27,29–31</sup> monocarboxylic acids,<sup>26,27,31</sup> alcohols and phenols,<sup>24,27</sup> aldehydes and ketones,<sup>24,26,27</sup> and phthalates.<sup>27</sup>

Thermal extraction is not without its difficulties, however. The high extraction temperatures required (typically above 300 °C) may promote molecular rearrangement, fragmentation, or breakdown of more thermally labile analytes. Incomplete extraction of lower vapor pressure or polar components may result in carryover effects. Moreover, relatively little is known about the matrix effects owing to the nonvolatile and semivolatile components of the PM. This latter challenge is further compounded by the fact that TE-GC/MS analysis has primarily been applied only to ambient PM samples. Matrix effects are of concern in analytical science because they can cause quantification inaccuracies. The accurate quantification of semivolatile organic analytes in emissions PM is of particular interest to air quality managers, regulators, and atmospheric scientists. Such thermal (or solvent) extraction data that include the effect of different source emissions matrixes are sparse if available at all, and further understanding is critical for the development and for the widespread use of the method.

The study presented here differs in a number of key ways from previous studies. First, rather than study ambient samples, we have chosen to apply TE-GC/MS to samples of source emissions. By examining a number of chemically diverse PM source samples, insights into the influence that the PM matrix may have on the thermal extraction process may be obtained. This paper is the first of two papers validating TE-GC/MS for the quantification of organic compounds in source emissions aerosols. In each effort, we attempt to isolate and investigate one of two possible types of interactions that may play a role in the quantification of semivolatile analytes in fine PM samples: a semivolatile–nonvolatile interaction and a semivolatile–semivolatile interaction in the presence of the nonvolatile matrix fraction. Here, we examine the role that the nonvolatile components in the source emissions PM have on the quantification of a suite of semivolatile analytes typically contributing to source matrixes and thus to the chemical makeup of atmospheric aerosols. We also consider several additional compound classes that are of particular relevance to the source apportionment of atmospheric PM. In particular, we have included hopanes and steranes, key biomarkers for petroleum source emissions, into our standard suite. Finally, attempts have been made to develop a validation method that is easily transferable as well as to point out conditions and compounds that may be unsuitable for the method at the present time. Following will be a second paper investigating the combined effect of the large number of semivolatile and nonvolatile matrix components on the quantification of the relatively small subset of semivolatile components targeted for analysis.

## EXPERIMENTAL SECTION

**PM Samples.** The intent was to study an aerosol sample set consisting of matrixes that are as chemically diverse as possible. Four PM samples were chosen for investigation; the sources were (i) an agricultural fire (AF), (ii) emissions from the Ground Zero area soon after the collapse of the World Trade Center (WTC) towers, (iii) diesel engine exhaust (DE), and (iv) jet engine exhaust (JE). Each PM sample and its source are described in detail below. Collectively, the sample set represents emissions from biomass burning, land area, and fossil fuel combustion sources, all of which contribute significantly to the atmospheric aerosol burden. All primary source emissions examined in this

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study were collected using pre-fired (540 °C, 12 h) quartz fiber filters (QF).

A carbon analyzer implementing a thermal–optical transmittance technique was used to provide insight into the makeup of the native PM matrixes prior to analysis as well as to illuminate any alteration (charring) of the matrix due to the thermal extraction process utilized in the analysis. Details of the operating procedure for the carbon analyzer can be found elsewhere.<sup>32,33</sup> Specifically, the technique was used for the following: (1) to determine the organic carbon/elemental carbon (OC/EC) ratio of the source PM matrix, (2) to estimate the percentage of PM analyzed, (3) to estimate the fraction of the total organic matter (OM) that evolves at the working temperature of 300 °C, and (4) to determine the level of charring that occurs at that same working temperature. In addition, the OC/EC result was used to determine the size of the filter punch used in the TE analysis. A target value of greater than 3 µg but less than 40 µg of OC was chosen for analysis. In our experience, OC levels of <3 µg made it difficult to detect target analyte, whereas OC levels of >40 µg tended to contaminate the system leading to degradation and loss of response for several compounds. Analytes that were particularly sensitive to this type of contamination included the deuterated internal standard 4,4'-dimethoxybenzophenone-*d*<sub>8</sub>, and several PAHs including benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, coronene, and the cholestanes.

**Agricultural Fire Aerosol.** This aerosol sample was taken from a simulated agricultural fire with rice straw (*Oryza sativa*, M202 variety). Field residual was gathered in Sacramento Valley, CA, and burned in a test enclosure replicating how it burns in the field (see Hays et al.<sup>34</sup> for further details). Aerosols were collected and diluted 35 times (with conditioned ambient air) using the dilution sampling system (DSS) described by Hildemann et al.<sup>35</sup> A high-volume QF positioned in the mixing chamber was used for analysis. Thermal–optical analysis revealed this matrix comprises greater than 80% w/w organic matter. It consists of predominately small organic carbon entities with molecular weights less than 1000 amu. The HR-TEM nanostructure of this sample was highly amorphous, showing significant primary particle merging.

**World Trade Center–Ground Zero Aerosol.** This source sample represents a 24-h snapshot of the emissions from the 0.06-km<sup>2</sup> Ground Zero area. It was taken on 10/19/2001 roughly 500 m northeast of Ground Zero (the World Trade Center) on the 16th floor (~50 m above street level) of the EPA Federal Building at 290 Broadway, New York, NY. Aerosol was collected using an integrated organic gas and particle sampler (URG model 3000DB) operating with a 2.5-µm cyclone inlet at a volumetric flow rate of 85 L min<sup>-1</sup> at 4 °C above ambient temperature. A 90-mm-diameter QF collected the fine aerosol used in this analysis. Further details of the sampling of the NYC aerosols, including instrumentation, collection site position, meteorology, protocol and operations, and

period are provided elsewhere.<sup>36</sup> Unlike the other emissions aerosols, the Ground Zero sample was not predominantly carbonaceous. Rather, it represented a complex mixture of sulfate (22% w/w), nitrate (8% w/w), ammonium (8% w/w), Fe (4% w/w), and inorganic elements such as Na, K, Ca, Zn, Br, Pb, and Cl (10% w/w) with some carbon [organic matter (27% w/w) and elemental carbon (5% w/w)]. Atmospheric processing of this sample during the daytime hours was a possibility owing to the open path and distance from the source to receptor. Background New York City air pollution, and ongoing fires and a range of debris cleanup activities at Ground Zero, contributed to this sample.

**On-Road, Heavy-Duty Diesel Truck Aerosol.** Aerosol emissions were collected from the exhaust of a high-mileage (>900 000 miles) 1990 Kenworth long-haul, heavy-duty diesel truck. The truck was outfitted with a series 60 Detroit diesel engine (see Brown et al.<sup>37</sup> for the engine and truck specifications). During the 188-km on-road test with an average speed of 102 km/h, the median air-to-fuel ratio was 36 and the average power output was ~117 kW. Sample exhaust was diluted (1:56) with compressed, dry, HEPA-filtered air directed to a series of three eductors (~1:20 dilution each). A PM<sub>2.5</sub> cyclone was positioned in the dilution system upstream of the quartz filter, which amassed ~4 mg of aerosol sample during the 1.7-h test. Thermal–optical analysis showed this particular sample matrix comprised predominantly elemental carbon with a small fraction of organic carbon.

**Jet Aircraft Engine Exhaust.** This fine aerosol sample was collected from the emissions of a commercial (General Electric CFM-56-2-C1) turbofan engine mounted on a Boeing DC-8 jet aircraft. Tests were conducted as part of the NASA Air Particulate Emissions eXperiments (APEX) program with the engine operating at four power (thrust) settings [7% (idle), 30% (approach), 85% (climb out), and 100% (takeoff)] typical of the landing and takeoff cycle at commercial airports. The engine had an air bypass ratio of 6. Jet propulsion fuel no. 8 (JP-8; ρ<sub>15 °C</sub> = 0.8199 g/cm<sup>3</sup>; heat of combustion 43.2 MJ/kg) was used as the base fuel. With the aircraft anchored to the ground, its engine emissions were sampled using the DSS connected to a probe positioned ~1 m downstream from the engine exit plane. The DSS dilution ratio was 1:39. Roughly 4 µg of aerosol collected on the high-volume quartz filter was used for analyses. The sample typified several integrated test cycles, which included the four power settings. Thermal–optical analysis of this sample revealed an OC/EC ratio of 2. More than half of this sample was carbonaceous, with ammonium sulfate accounting for much of the remaining aerosol mass.

**PM Injection Standards.** Two PM standard suites containing a total of 66 compounds were used. The analytes contained in these standards are those that are commonly found in the primary source emissions under investigation. The chemical classes investigated (with the number of compounds within each class given in parentheses) were as follows: the *n*-alkanes (12), branched alkanes (6), alkenes (2), PAHs (26), oxy-PAHs (3), phthalates (6), cyclohexanes (4), hopanes (1), and steranes (6). Table S1 in Supporting Information lists the specific compounds

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within each class, their concentrations in the master standard, the internal standard to which it is referenced, and the concentration level range fit to a linear calibration curve. Three dilution levels of the master standard were examined: 1:1, 1:2, and 1:5 (corresponding to levels 1, 2, and 3).

**Instrumentation.** The TE-GC/MS system used in this study has been described in detail elsewhere.<sup>38,39</sup> Briefly, the thermal extraction of the PM was accomplished with a Gerstel TDS2 system. The TDS oven was temperature programmed to ramp from 25 to 300 °C at a rate of 12 °C/min and held at 300 °C for 5 min. Significant pyrolysis of the organic components is not expected at the temperature limit of 300 °C. On the other hand though, the effective removal of semivolatile organic matter is expected to occur. The desorption was performed in splitless mode, with a helium flow of 20 mL/min. Desorbed material was directed to a heated (300 °C), inert steel, short-transfer capillary connected to a cryogenically cooled (−100 °C) programmable temperature (PTV-CIS) inlet also functioning in splitless mode. To enhance cryofocusing and to keep solid contaminants from entering the column, the inlet liner was packed with a deactivated glass wool solid support.

After desorption, the TDS oven was cooled to 25 °C, and the PTV-CIS was ballistically (720 °C/min) heated to 300 °C to transfer the sample to the chromatographic system (HP6890; Agilent Technologies). An ultralow bleed capillary column (30-m length, 0.25- $\mu$ m film thickness, 0.25-mm i.d.) with a 5% diphenyl, 95% dimethylsiloxane copolymer stationary phase was used for the analysis. A constant flow of 1.0 mL/min of ultrapure helium carrier gas was maintained. The GC oven temperature was held at 65 °C for 10 min, ramped at 10 °C/min to 300 °C, and then held constant for 41.5 min. The quadrupole mass spectrometer (5973, Agilent Technologies) was operated in scan mode (50–500 amu, 3 scans/s). Enhanced Chemstation (V.B 01.00, Agilent Technologies) software was used to control the GC/MS and for data acquisition. Gerstel MAsTer (version 1.76  $\times$  5) software monitored and controlled the TDS2 operation.

## VALIDATION STUDIES

**Method Detection Limits (MDLs).** Initial experiments were performed in order to determine the MDL of each analyte in our PM standard suite. The MDL for this study is defined as the minimum concentration of analyte that can be measured and reported with 95% confidence to be greater than zero.<sup>40</sup> To estimate the MDL for the thermal desorption technique, the PM standard suite was injected into the empty TD tube. Dilutions were made as necessary in order to achieve an instrument signal-to-noise ratio within the range of 2.5–5.0 for the particular analyte under consideration. Once the necessary dilution factor was determined, five replicate injections were made. The standard deviation of the measured concentrations for each analyte was determined and multiplied by the one-sided *t*-statistic at the 95% level, *t* (*n* − 1,  $\alpha$  = 0.05). The estimated quantitation limit (EQL), defined as the lowest concentration that can be reliably achieved within specified

limits of precision and accuracy during routine laboratory operation conditions, has been estimated for each analyte to be five times its MDL value.<sup>40</sup>

**Empty Tube and Quartz Fiber Filter: Control Experiments.** The empty thermal desorption tube (ET) represents a limiting case for this study due to its lack of a matrix. An examination of the accuracy and precision of the thermal desorption method for the empty thermal desorption tube provides an understanding of the full ability of the method to quantify analytes of interest to fine particulate matter studies. These studies provided baseline measurements of the technique's ability to provide reliable and reproducible measurements. The empty tube was also used as a method calibration medium. Similarly, we examined pretreated quartz filter blanks in an effort to isolate any potential effect quartz might have on quantitation. One such concern is the suggestion in some of the literature that *n*-alkanes crack when heated in the presence of quartz.<sup>31</sup> A comparison of the precision and accuracy of the recoveries of the *n*-alkanes from quartz with those of the empty tube will determine whether cracking has occurred at the temperature used in this study.

**Calibration.** A calibration database was created by taking the average response of three injections of the PM standards at three concentration levels in the empty thermal desorption tube. Concentration values for each analyte were determined by relating the response of the analyte to the response of a suitable deuterated internal standard and deriving appropriate response factors. Across the three-tier concentration range, we determined the precision and accuracy of the recoveries of the PM standards spiked on the representative PM and blank matrixes listed above and tested for differences in the relative GC/MS response caused by matrix effects. This approach afforded us the opportunity to study source PM without the influence of the resolved, unresolved, or unidentified semivolatile components in source PM, which can constitute as much as 90% of the GC/MS elutables, but usually less than 50% of the total PM mass.<sup>41</sup>

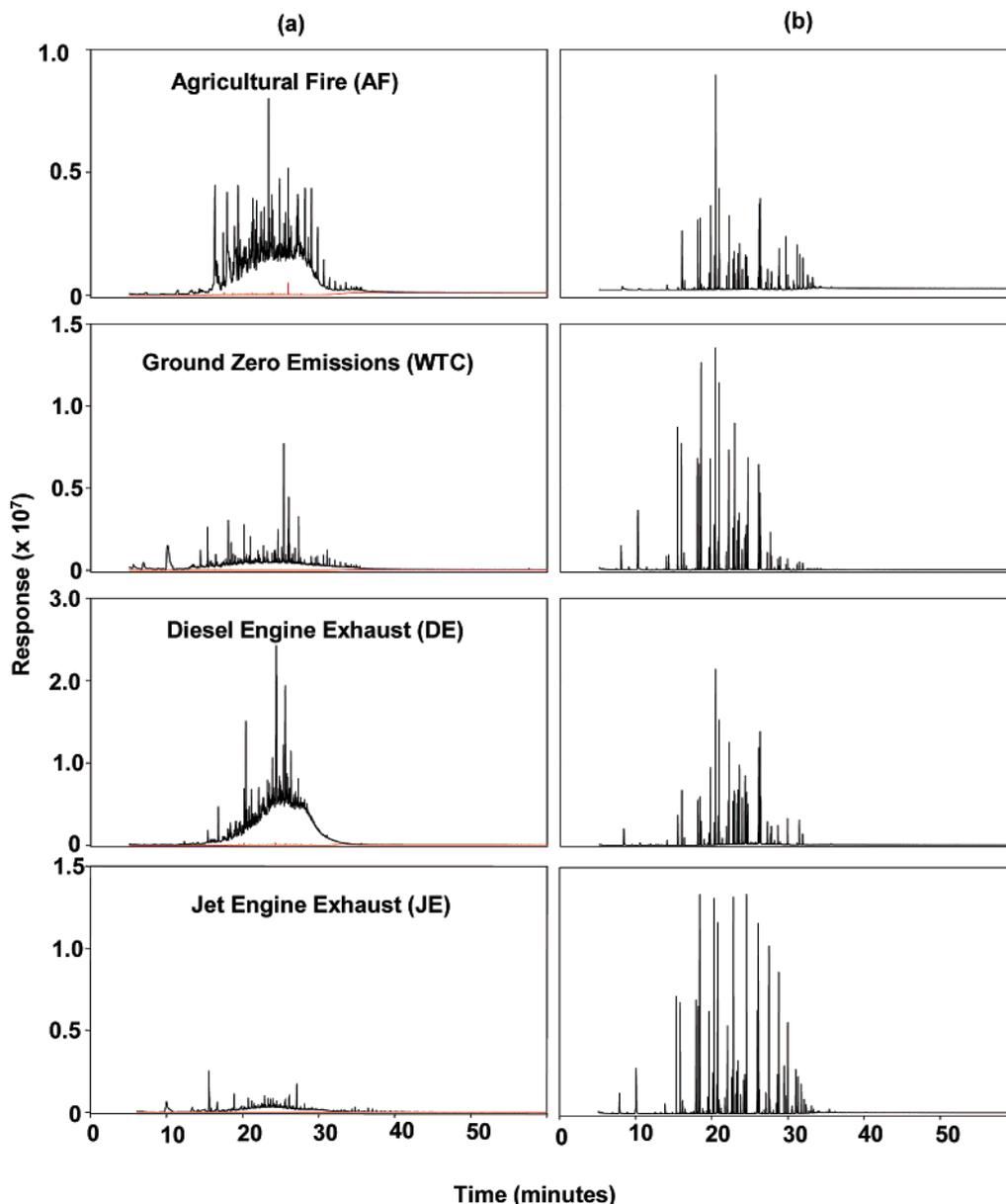
**PM Matrixes.** The black trace in Figure 1a shows the chromatographic response of the semivolatile compounds native to each PM matrix studied. In order to accurately quantify the role of the nonvolatile portion of the PM matrix in the quantification of semivolatile analytes, it was first necessary to remove these native semivolatile compounds before refortification with known concentrations of semivolatile analytes. Removal of the native semivolatile compounds was accomplished by multiple thermal extraction runs of the particular primary source emission matrix under investigation. So, we define the nonvolatile portion of the matrix operationally as the sample fraction remaining after successive thermal extraction runs at 300 °C under He. The matrix was considered nonvolatile when all the original analytes present gave MS responses that were below MDLs. The red trace in Figure 1a shows the sample responses (or lack thereof) after this removal process and confirms the removal of the native semivolatiles from the aerosols. Once this condition was met, refortification of the semivolatile portion of the PM matrix was accomplished using our PM injection standards. Figure 1b illustrates the responses occurring for the midlevel injection standard from this refortified PM matrix.

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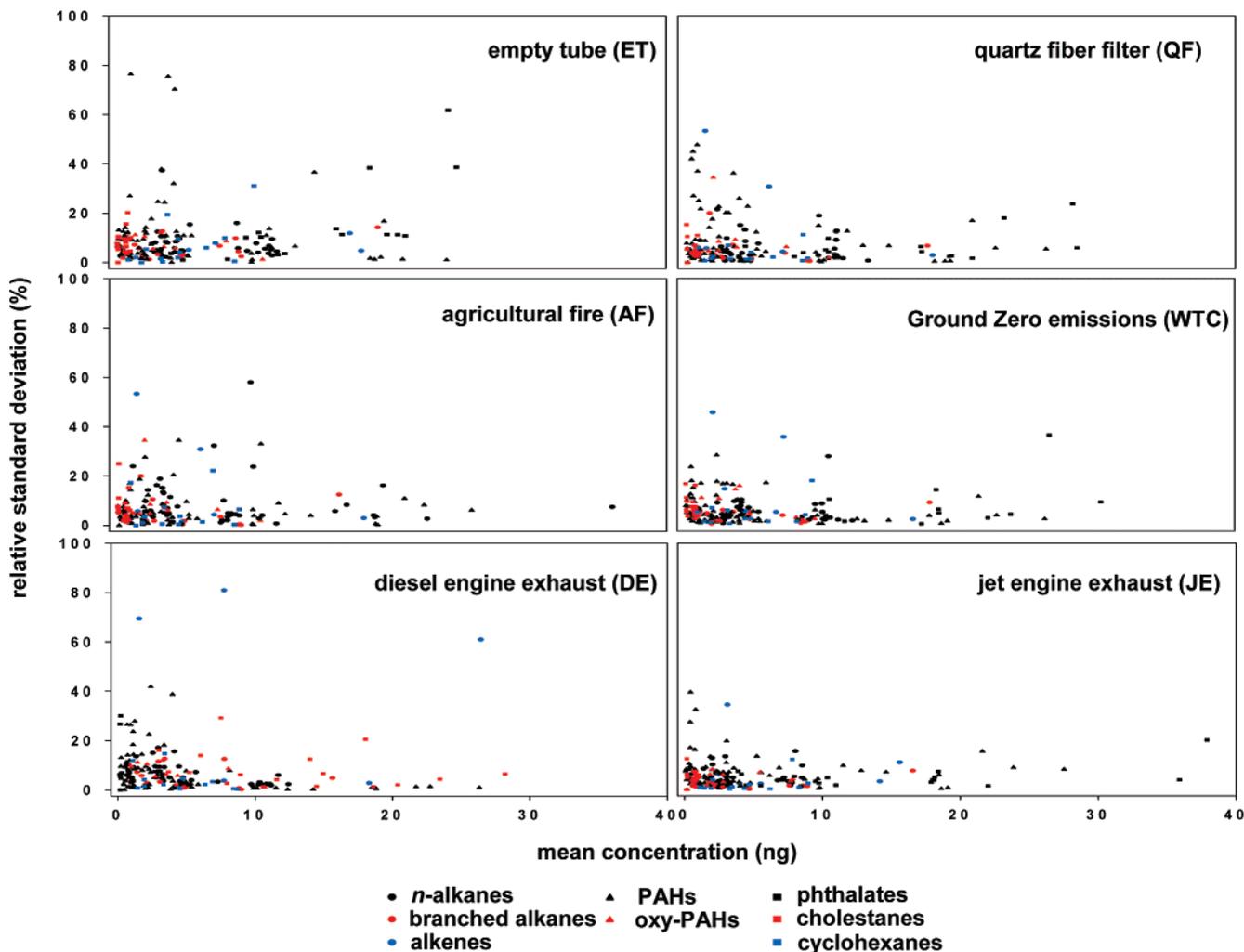
**Figure 1.** Total ion chromatograms of PM thermally extracted from each matrix. The black trace in (a) depicts native PM matrix response; red trace in (a) depicts the cleared PM matrix after multiple thermal extraction cycles. The response from injection of the midlevel concentration standard on the cleared PM matrix is shown in (b).

Despite the fact that the PM matrix has undergone numerous thermal extraction cycles (initial removal of native SVOCs and triplicate injections for each of the three standard concentration levels investigated) and has been subjected to solvent during the spiking of standards, we have made the assumption that, during this sample reprocessing period, the nonvolatile part of the PM matrix, on which the semivolatiles condense, is not significantly denatured. Insight into whether this assumption is valid may be provided by the tightness of the standard deviations of the mean values of the triplicate injections as well as the presence/absence of deviant behavior across the concentration range evaluated. Even if the test matrix structure is altered somewhat (i.e., due to pyrolysis, etc.), duplicating a better analytical model has been impractical thus far owing to the chemical, physical, and morphological complexity of source aerosols and aerosols in general.

Part 2 of this study will further explore the effect that the native semivolatile matter has on this system.

## RESULTS AND DISCUSSION

**Method Detection Limits.** Table S1 in Supporting Information gives the MDL and EQL obtained for each analyte for the empty thermal desorption tube. Also reported are the relative standard deviations (RSDs) of the five injections used in the determination of these values. In general, the method exhibits excellent sensitivity, achieving picogram level detection limits for most compounds. Several trends are evident within certain compound classes. For the *n*-alkanes used in this study, thermal desorption is most sensitive for *n*-C<sub>11</sub>–*n*-C<sub>16</sub> with detection limits less than 100 pg. Method sensitivity decreased ~4-fold for *n*-alkanes outside this range. Similar behavior has been reported being attributed to the



**Figure 2.** Precision of the thermal extraction method for each matrix investigated. The RSD, defined as the standard deviation divided by the corresponding mean multiplied by 100, is plotted versus analyte concentration for all analytes within each compound class.

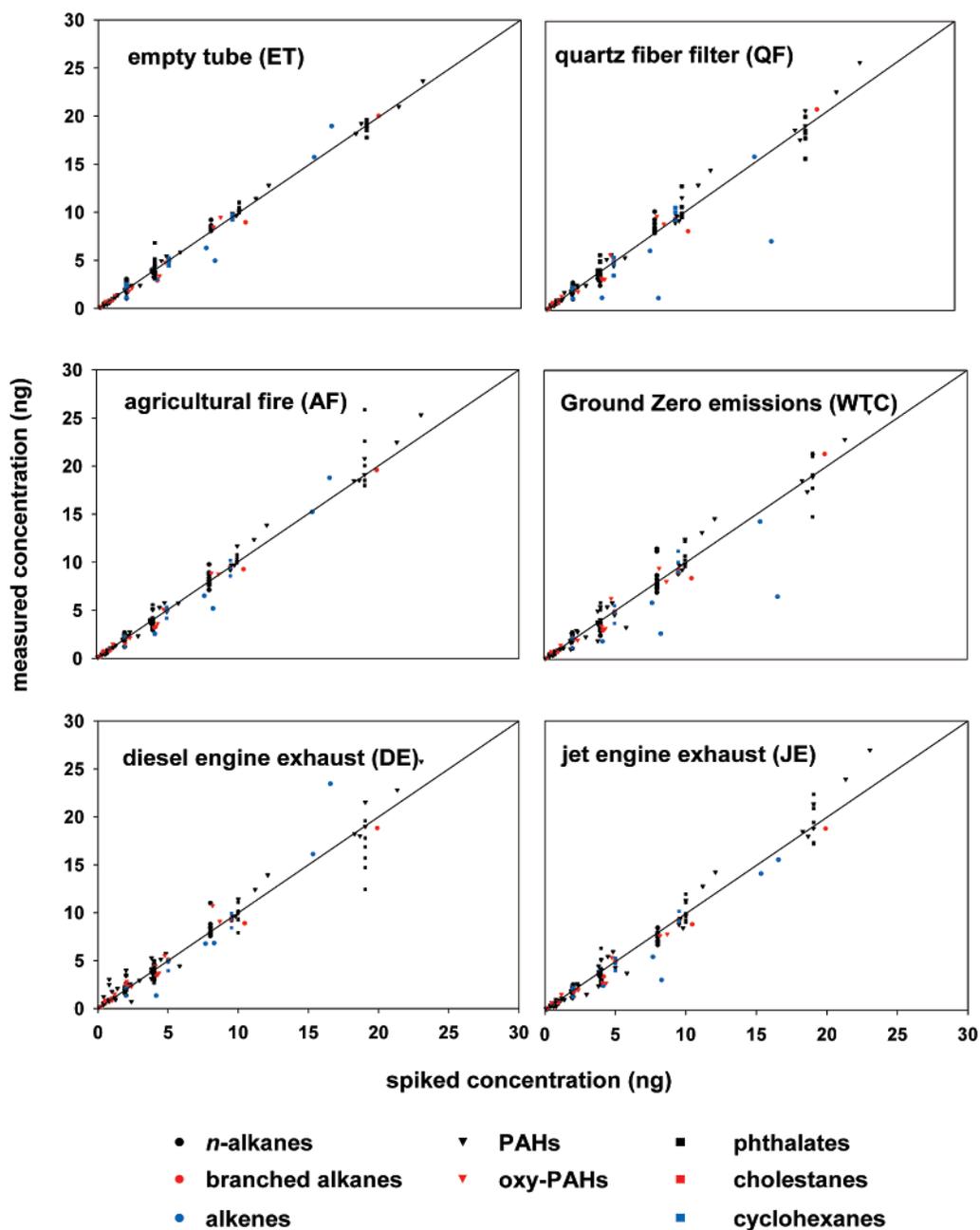
incomplete extraction of lower vapor pressure, higher molecular weight alkanes.<sup>29</sup>

Variations of the minimum detection limits within the PAHs were also observed. Although a direct relationship between boiling point and vapor pressure does not exist, a decrease in sensitivity was observed in some cases for analytes that have boiling points above the upper temperature limit used during the thermal extraction. For example, the MDL for benzo[ghi]perylene (boiling point of 500 °C) was determined to be 0.234 ng while for 1-methylnaphthalene (boiling point of 240 °C) an MDL of 0.027 ng was observed.

**Accuracy and Precision of the Control Experiments with the Empty Tube and Blank Quartz Filter.** Supporting Information Table S2 lists the mean values of triplicate injections for the recovered analyte concentrations obtained with the empty desorption tube at the midpoint injection concentration along with the corresponding value of the RSD given in parentheses. The precisions obtained with the thermal extraction method for the empty desorption tube are also illustrated in the top left panel of Figure 2. Table S3 in Supporting Information lists the percentage of analytes within each compound class at each injection concentration which have RSDs that are within 20 and 10% of their respective mean values. Based on these results, thermal extraction

in the absence of a PM matrix (i.e., for the ET and QF) was able to provide reproducible measurements for the chemical classes contained in our PM standard suite. Other than the difficulties observed for certain analytes within the PAH, oxy-PAH, and phthalate compound classes, good precision was observed for the vast majority of analytes in the injection standard. In the case of the ET, at the midlevel injection concentration, 65% of the compounds in the injection standard have RSDs whose values are less than 10% of their respective means. This number increases to 92% when the cutoff is raised to 20% of the mean value. The compounds exhibiting excellent precision (i.e., those with RSDs less than 10%) include all 7 biomarkers (6 steranes and 1 hopane), all 6 branched alkanes, both alkenes, 2 of the 3 oxy-PAHs, 3 of the 4 cyclohexanes, 8 of the 12 *n*-alkanes, 13 of the 25 PAHs, and 1 of the 6 phthalates.

For the ET at the midlevel concentration injection, five compounds had RSDs that were greater than 20%: benzo[b]-fluoranthene (38.9%), benzo[k]fluoranthene (31.8%), benzo[a]pyrene (38.6%), dioctyl phthalate (36.9%), and *n*-C<sub>24</sub> (36.9%). A closer examination of these compounds suggests the most probable cause of their poor precisions. Two of the three runs have analyte concentrations within ~10% of one another. The analyte response for the suspected errant run for each of these



**Figure 3.** Accuracy of the thermal extraction method for each matrix investigated. The recovered concentration of each analyte (mean value of triplicate injections) is compared with the spiked concentration; the solid line represents 100% recovery.

analytes was on average 50% less than the other two. A *Q*-test at the 90% confidence level performed for each of these analytes did not allow for any data points to be discarded. This is not surprising since *Q*-tests for small data sets ( $n < 5$ ) are not particularly useful. However, recalculation of the mean and standard deviation after removal of the seemingly errant injection resulted in RSDs for all five compounds of less than 10%.

The accuracy of the thermal extraction method is displayed by plotting the TE-GC/MS recoveries of the spiked analytes against the spike injection concentrations. The upper left panel in Figure 3 illustrates the accuracy observed for the ET. The solid line in the figure is the 1:1 line between the injected concentration plotted on the *x*-axis and the mean value for the recovered concentration plotted on the *y*-axis. Analytes falling on this line have 100% recovery efficiency. In the absence of PM matrix,

excellent recoveries were obtained as demonstrated by the clustering of all analytes around this 1:1 line. Numerical values of recovered and spiked analyte concentrations for the midlevel injection concentration are listed in Table S2 (see Supporting Information).

Because the primary source emissions samples utilized in this study were all collected on QF, we next applied our validation methodology to this empty matrix. As might be expected for the QF, relatively modest, if any, change in the accuracy of the method was observed. The recoveries of analytes injected on the QF matrix (Figure 3 upper right panel) with the exception of squalene were essentially identical to those observed for the ET (Figure 3 upper left panel), indicating that the QF matrix alone will probably have limited affect on quantification. The precisions obtained for the QF, listed in Supporting Information as Table S3 and displayed

**Table 1. Results Obtained from the OC/EC Analyzer**

PM sample	OC/EC	punch size (cm <sup>2</sup> )	PM mass analyzed (μg)	PM extracted as OM <sup>a</sup> (%)	nonvolatile PM matrix <sup>b</sup> (μg)
agricultural fire (AF)	36.0	0.1	45.8	37.1	28.8
World Trade Center (WTC)	6.0	0.6	21.8	7.9	20.1
jet engine exhaust (JE)	2.0	0.6	4.3	20.8	3.4
diesel engine exhaust	0.3	0.2	8.6	12.1	7.5

<sup>a</sup> PM extracted as OM—approximated using OC/EC thermogram, punch size, and filter mass loading. <sup>b</sup> Estimated on the basis of thermally evolving carbon only. Loss of inorganic nitrogen species from WTC (~16% w/w) and JE exhaust is unaccounted for here.

in Figure 2, are also essentially identical to those obtained for the ET with 85% of the compounds having standard deviations less than 10% of their respective mean values and 94% within the 20% range for the midlevel concentration injection. No differences were observed for the precision and accuracy of the recovered *n*-alkanes spiked in the empty tube and on quartz fiber filters, demonstrating that no quartz-catalyzed cracking of the *n*-alkanes occurs at the temperature utilized in this study (300 °C).

**Semivolatile–Nonvolatile Interactions: PM Matrixes (Accuracy and Precision).** With the reliability of the thermal extraction method proven for the empty desorption tube and the empty quartz fiber filter, we next turn our attention to the examination of the possible bias caused by the interaction of the semivolatiles contained in our injection suite with the nonvolatile components of each of the PM matrixes.

We first sought to determine whether the sample processing protocol (removal of native SVOCs and the subsequent solvent/standard spikes and reheating) affected the nonvolatile PM matrix system in any way. One concern was that the OC-bearing portion of the matrix would be charred or pyrolyzed while heating, yielding nonvolatile EC nonintrinsic to the matrix. EC matter can strongly adsorb certain organic compounds and thus could influence quantification efforts. We used the OC/EC analyzer to estimate the level of charring in each source PM. Integrating the increase in laser absorbance as the OM peaks evolved over temperatures of 50–300 °C (under He) provided a measure of the amount of carbon being pyrolyzed. The observed charring was minimal, with the AF matrix exhibiting the most at roughly 5% of the total PM mass analyzed. Of course this check does not address all of the possibilities relating to altering the matrix. Under the experimental conditions used here, certain inorganic components (e.g., ammonium and nitrate ions) likely volatilized from the WTC and JE aerosols where they were present. Molecular constituents of the operationally defined nonvolatile matrix that are perhaps forming, rearranging, or thermally degrading during heating will also be unaccounted for here, though there is scant evidence of these latter incidences in the literature. In the final analysis, heating the nonvolatile PM matrix to 300 °C did not appear to significantly char it or modify it by any other process, and as mentioned, a better analytical model for aerosols is currently unavailable.

Our next concern was to address whether multiple cycles of solvent/standard spiking and reheating the same PM sample deposit alter the matrix. We learned that the organic standards spiked onto the PM matrix responding nonlinearly with concentration did so reproducibly throughout the duration of cycles. This observation suggested to us that the PM matrix entity (or entities)

responsible for the nonlinearity was not in any way altered or destroyed due to our experimental design. Or if it was, the alteration of the matrix did not affect our ability to repeat the result. Likewise for those spiked organic standards with linear response, the response was quite reproducible at multiple concentrations. This observation further suggested to us that the actual process of continuously spiking and reheating the same thermally cleared aerosol deposit did not create the occurrence of a matrix effect where there indeed was not one. A limitation of this approach, though, is that variability owing to sample filter inhomogeneity is unaccounted for, as less than 1% of the total exposed filter area is typically being examined.

Table 1 summarizes the results obtained from the OC/EC analyzer. For each PM matrix, the OC/EC ratio given was used to determine the appropriate size of the filter punch needed for analysis. The PM matrixes studied represent varying levels of OC and EC and inorganic matter. The AF source matrix is predominantly made up of OC while the DE source matrix represents the other extreme, comprising predominantly EC. The WTC and JE matrixes fall within these two extremes, each comprising carbon matter entities with more inorganic material than either AF or DE. The organic matter in the AF and WTC matrixes was likely partly oxygenated due to cellulose and lignin pyrolysis and secondary organic aerosol production, respectively. Also listed in Table 1 is the fraction of OM that evolves from the PM at a working temperature of 300 °C. These values can provide even further insight into the extent the source PM matrix may be transforming during the sample (re-)processing period. We observe the AF and JE matrixes as having the highest amount of OM evolving from the PM matrix at 300 °C. However, less than half (37.1 and 20.8%) of the total PM mass thermally evolves from these matrixes. The WTC and DE matrixes have notably less OM extracted from them at 300 °C. An estimate of the nonvolatile or residual PM matrix mass given in Table 1 was obtained by subtracting the extracted OM (as measured by carbon analysis) from the total PM mass analyzed. For the WTC and JE sources, these values are likely overestimates as these matrixes contain small percentages of ammonium and nitrate ions, which may volatilize during heating but are not measured by carbon analysis. Recall that examining the interaction between targeted organic compounds and the native semivolatile matter (inorganic and organic) in the presence of the nonvolatile PM fraction is the topic of part 2 of this series.

The precisions obtained with the thermal extraction method for each of the PM matrixes are illustrated in Figure 2. As described above, evaluation of the precision is obtained by converting the standard deviations for each analyte into a percent-

age of the corresponding mean. An inspection of Figure 2 shows that for the vast majority of analytes from each of the compound classes RSDs have values less than 20%. In fact, many of the analytes have RSDs below 10%. Table S3 (Supporting Information) lists the percentage of analytes within each compound class at each injection concentration which have RSDs that are within 20 and 10% of their respective mean values. An examination of the data in the figure and table shows that thermal extraction is capable of reproducibly removing semivolatile analytes from the nonvolatile portion of each of the PM matrixes. The accuracy of TE-GC/MS applied to the analysis of semivolatile compounds contained in primary source PM has been assessed by comparison of the means obtained for each analyte at each concentration level on each source PM matrix to those obtained for the empty desorption tube. Student's *t*-test was conducted to determine whether the mean values obtained for each matrix were statistically different ( $\alpha = 0.05$ ) from those obtained for the ET.

Table S4 in Supporting Information provides by matrix the complete list of analytes for which the null hypothesis was rejected (vis-à-vis the *t*-test). What is classified as minor matrix bias due to the high precision of the TE-GC/MS measurements (see more below) was evident for roughly half of the analytes in the injection standard (per matrix, with the exception of QF and AF). From analysis, two conditions resulted in an increase in the number of analytes having means that exhibited statistical differences with respect to the ET. First, a higher percentage of EC within the PM matrix (i.e., DE and JE) tended to increase the number of analytes with means exhibiting statistical differences. In the case of the AF matrix—which comprised just 2.8% w/w EC and likely a preponderance of oxygenated organic matter—very little affect on the accuracy of the recovered semivolatile analytes was observed. Second, the greatest number of analytes displaying deviant means was generally evident at the low injection standard concentration. This trend was observed by considering all deviant analytes across all the PM matrixes at each examined level.

In the quantification of certain trace organic species in fine PM, the observation of high variability in source emissions—well beyond that needed to infer means as statistically different using the *t*-test—is not uncommon. As a result, we chose to examine more closely the organic compounds that not only failed the *t*-test but also demonstrated a greater than 20% difference between means. The 20% value represents the traditional sampling and analytical measurement uncertainty arbitrarily applied when using organic markers to develop air quality models.<sup>17</sup> Without imposing this added constraint, the *t*-test determined statistical differences between means that made little practical sense for our particular application (i.e., the quantification of trace organic species in combustion emissions). For example, the following means were obtained for octylcyclohexane at the lower injection concentration level: ET 2.5(1), AF 2.34(7), WTC 2.3(2), JE 2.32(9), and DE 2.18(8). Although the results of the *t*-test determined that the means obtained for each of the PM matrixes were statistically different from the mean obtained for the ET and the high method precision of TE-GC/MS did help identify a slight matrix bias, differences of 6–12% are considered quite minor in the quantification of semivolatile analytes in PM—especially in light of the typically high variability of combustion source emissions.

Table 2 lists the analytes for which the above conditions were met; that is (i) the Student's *t*-test determined statistically significant differences between the means relative to the empty tube and (ii) the added constraint of the means being at least 20% different was fulfilled. The compounds in Table 2 are those perceived to have experienced relatively serious matrix effects. Immediately evident is the substantial reduction in the number of analytes due to the added constraint being imposed (compare Table 2 with Table S4). Several trends, comparable to those observed when viewing Table S4, become apparent from the data in Table 2. The DE matrix has the highest percentage of the total carbon bearing EC (74.7% w/w) and the highest number of aberrant analytes (20). On the opposite end of the spectrum again is the AF matrix with only 2.8% w/w of the total carbon being EC and having only two analytes meeting both conditions i and ii above. The WTC and JE matrixes represent intermediate cases with 14.9 and 32.0% of the total carbon being EC, respectively (13 analytes for WTC and 10 for the JE were included in Table 2). The influence of the nonvolatile DE matrix on analyte response is quite interesting, considering that the mass of the DE source matrix being refortified is the third lowest (7.5  $\mu\text{g}$ ) among the group of four being studied. Ironically, the nonvolatile mass of the AF matrix being refortified is the highest.

The second trend to emerge is the identity of the analytes undergoing substantial bias during quantification of semivolatile analytes from the nonvolatile portion of the PM matrix. Across the PM matrixes investigated, the overwhelming number of analytes displaying poor recovery belong to the PAH class. The few remaining analytes were scattered across the other compound classes in the injection standard displaying a more matrix-specific distribution. For instance, serious difficulties with the quantification of phthalates and oxy-PAHs were predominately isolated to the diesel engine exhaust matrix. Except for two phthalates in the lowest concentration level injection of the jet engine exhaust matrix, no other matrixes showed significant bias toward this class of analytes. Again, the most analytes displaying deviant means was observed at the low injection standard concentration.

Closer examination of these trends reveals for the DE matrix that (i) the statistical and mean differences are generally greater for the six-member-ring PAH at the lower spike concentrations; (ii) the six-ring PAH spike concentrations are being overpredicted at all levels, and (iii) coronene, a seven-ring PAH, is being underpredicted at the higher spike concentrations. Visual evidence of these effects is given in Supporting Information as Figure S1. The overprediction of the six-member-ring PAH is likely the result of injection standard carryover owing to the adsorptive power of the DE matrix. In other words, the buildup of spiked PAH in the DE matrix causes an artificial increase in analyte response and hence concentration for each subsequent standard injection. At a single concentration level, we observe a systematic increase in response on the order of 250% going from the first of the triplicate injections to the last. We would expect the response for each injection to be equal in the absence of a matrix effect. Increasing the TE hold time by a factor of 2 (from 5 to 10 min) only partially alleviated the problem reducing the observed increase in response to 80%. Further increases in hold time did not improve these recoveries. The DE matrix appears to have a much greater affinity for coronene—a seven-member-ring PAH. A response increase of

**Table 2. Analytes with Means Displaying Statistical Differences with Respect to the Empty Thermal Desorption Tube<sup>a</sup>**

	DE	JE	WTC	AF	QF
		LVL 1 (1:1 Dilution)			
PAH	benzo[ghi]perylene coronene	benzo[a]pyrene benzo[k]fluoranthene fluoranthene	benzo[a]pyrene benzo[k]fluoranthene benzo[b]fluoranthene methylchrysene retene methylfluoranthene fluoranthene pyrene anthraquinone	octacosane	
oxy-PAH	naphthalic anhydride				
<i>n</i> -alkanes	octacosane	decane	octacosane squalene		
alkenes					
phthalates	butylbenzyl phthalate bis-2-ethylhexyl phthalate				
cholestanes	ethylcholestane				
		LVL 2 (1:2 Dilution)			
PAH	benzo[ghi]perylene coronene	methylchrysene	naphthalene		
	dibenzo[ah]anthracene				
oxy-PAH	indeno[1,2,3- <i>cd</i> ]pyrene				
<i>n</i> -alkanes	naphthalic anhydride				octacosane
phthalates	octacosane butylbenzyl phthalate				
		LVL 3 (1:5 Dilution)			
PAH	benzo[ghi]perylene coronene	benzo[b]fluoranthene fluoranthene	naphthalene methylfluoranthene		
	dibenzo[ah]anthracene	methylchrysene			
	indeno[1,2,3- <i>cd</i> ]pyrene	retene			
	fluorene				
	methylfluoranthene				
	phenanthrene				
	anthracene				
oxy-PAH	9-methylanthracene			naphthalic anhydride	
	naphthalic anhydride				
	9 <i>H</i> -fluoren-9-one				
<i>n</i> -alkanes	octacosane		octadecane tridecane		octacosane
alkenes	tetradecane		squalene		squalene
phthalates	squalene				
	butylbenzyl phthalate	dioctyl phthalate			
	bis-2-ethylhexyl phthalate	dibutyl phthalate			
	diethyl phthalate				
	dimethyl phthalate				
cholestanes		ethylcholestane			

<sup>a</sup> As described in the text, an additional constraint that the difference between the compared means must be greater than 20% has also been imposed.

over 400% for coronene across the triplicate runs was observed for the DE matrix, but paradoxically, the compound is never fully recovered at the highest injection concentration. The increase in TE hold time (10 min) did lower the analytical response for coronene to 160% of what was expected. On a relative scale, the remedial power of increasing the hold time appears to have been more effective for coronene than for the six-ring PAH, though the recovery values obtained for the six-ring PAH are more accurate by comparison. Regardless of why these trends emerged, they are likely to have important implications for the analytical characterization of source and atmospheric aerosols alike.

The spiked WTC aerosol followed the DE sample in terms of displaying relevant differences with the empty tube. The majority of these differences materialized at the highest examined concentration level again for the PAH (see Tables 2 and S4). Heavy-duty diesel engine exhaust due to debris removal operations was known to have contributed to the WTC aerosol.<sup>36</sup> Perhaps this

helps to explain why benzo[*k*]anthracene, benzo[*b*]fluoranthene, and benzo[*a*]pyrene spiked onto the WTC matrix are never fully recovered.

Of the 66 compounds recovered from the QF matrix, only *n*-C<sub>28</sub> and squalene meet the criteria established for inclusion in Table 2. For these compounds, it is therefore not possible to confirm a matrix effect due to nonvolatile aerosol exclusively.

## CONCLUSIONS

Little, if any, effort has been expended to fully verify the off-line extraction and chromatographic methodologies used to quantify the wide range of trace organic compounds in aerosols. Here, a novel validation approach is developed to study the potential effect that the nonvolatile PM matrix has on the TE-GC/MS quantification of semivolatile organic markers. Thermally clearing the PM matrix of its semivolatile organic matter yields a durable analytical platform for studying such bias. Due to its

stability and representativeness, the use of a thermally cleared PM matrix for validation purposes is likely expandable to additional sample pretreatment and instrumental techniques also being applied to quantify organic markers in aerosols. We view the matrix effects due to the EC in the DE sample as considerable. For all the PM matrixes and concentration levels, recovery of the PAHs bearing five or more rings could be challenged when using TE-GC/MS. Therefore, caution is warranted when using TE-GC/MS results to estimate inhalation exposures to PAH (with 5 rings or more) in aerosols replete with diesel engine exhaust (e.g., near roadways or in polluted urban air). Important molecular markers for petroleum and coal source emissions, hopanes and steranes, seem mostly impervious to any nonvolatile matrix bias. Though

the injection standard compounds and levels used to refortify the PM matrixes do not always perfectly mimic the actual matrixes, it is quite plausible in an externally mixed atmospheric particle collection that such chemical combinations do exist.

#### **SUPPORTING INFORMATION AVAILABLE**

Additional information as noted in text. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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