

GC/ITMS Measurement of Carbonyls and Multifunctional Carbonyls in PM_{2.5} Particles Emitted from Motor Vehicles

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A method was developed and tested to identify and quantitate carbonyls and multifunctional carbonyls in fine particulate matter (PM_{2.5}; <2.5 μm aerodynamic diameter). The method relies on ultrasonic extraction of particulate matter on filters at -8°C; derivatization with *O*-(2,3,4,5,6-pentafluorobenzyl) hydroxylamine (PFBHA), and PFBHA along with *bis* (trimethylsilyl) trifluoroacetamide (BSTFA); and detection of the derivatives by gas chromatography/ion trap mass spectrometry. Ultrasonic extraction of model compounds from enriched particles was affected by solvent polarity (water > methylene chloride > toluene-isopropanol (2 + 1, v/v)). Water provided the highest recovery for dihydroxy acetone, pyruvic acid, and hydroxy acetone, compared to methylene chloride, and toluene-isopropanol. Lowering the ultrasonication bath temperature from 0° to -8°C improved the recoveries of the less water soluble and more volatile species—methacrolein, methyl vinyl ketone, 2,3-butanedione, and tolualdehyde. The power of the method was demonstrated by identification and quantitation of carbonyls and multifunctional carbonyls in sample extracts of fine particulate matter (PM_{2.5}) collected in the Caldecott tunnel, CA. The identities of crotonaldehyde, 2,3-butanedione, glyoxal, 9H-fluoren-9-one, glycolaldehyde, glyoxylic acid, levulinic acid, and 3-hydroxybenzaldehyde were confirmed by comparing the relative retention time and mass spectra of the analyte in the sample extract with an authentic standard. Quantitation of crotonaldehyde, glyoxal, 2,3-butanedione, glyoxylic acid, and levulinic acid was accomplished. This is the first report of glyoxylic acid, levulinic acid, and 3-hydroxybenzaldehyde in PM_{2.5} particles sampled in a roadway tunnel. It is also the first report of a C₁₀ carbonyl with the molecular formula of C₁₀H₁₆O₂, a hydroxy carbonyl with the molecular formula of C₁₇H₂₁NO₂, and a hydroxy or dihydroxy carbonyl with the molecular formula of C₁₆H₁₄O₂ or C₉H₁₀O₃. The high-molecular weight

hydroxy carbonyls, which were found only in the heavy-duty (diesel) bore, may be tracers of diesel emissions in air.

Motor vehicle emissions are primary sources of particulate matter, volatile organic compounds (VOCs), and NO_x. There is a growing interest and need for molecular speciation of motor vehicle emissions (1–5) due to their impact on air quality and human health. Insight into the complex mixture of organic compounds emitted from mobile sources has been gained chiefly from roadway tunnel studies. In the eastern United States, approximately 50% of the total nonmethane hydrocarbon (NMHC) emissions from heavy-duty diesel engines in the Fort McHenry Tunnel, MD, and the Tuscarora Mountain Tunnel, PA, were comprised of high molecular weight C₁₀–C₂₀ hydrocarbons (4, 5). These high molecular weight compounds accounted for only 10–25% of the total NMHC diesel emission rates (4). Aromatic compounds, including naphthalene and substituted naphthalenes, were identified as the reactive constituents with respect to ozone-forming potential. Carbonyls were reported to represent a minor contribution to the ozone forming potential, although formaldehyde was the only carbonyl quantitated (4–6). In contrast, other studies conducted in the Caldecott Tunnel, CA, the Van Nuys Tunnel, CA, and the Gubrist Tunnel, Switzerland, demonstrate that carbonyls are important reactive components of diesel and gasoline vehicle exhaust (7–9). Most notably, increased use of oxygenated and reformulated gasoline in the San Francisco Bay Area, CA, led to an increase in aliphatic aldehyde and a decrease in aromatic hydrocarbon and aromatic aldehyde emissions in the Caldecott Tunnel, a traffic tunnel between Oakland and Orinda, CA (9). The presence of several aliphatic carbonyls, including methyl glyoxal, in motor vehicle exhaust in the Van Nuys Tunnel demonstrates that the low-molecular weight oxygenated organics known to arise from photooxidation reactions can be generated in the combustion process (7).

Limitations of previous studies are the lack of data on high-molecular weight (>C₁₀) species, and particle-phase carbonyls. A recent study addressed this limitation by measuring C₁–C₃₀ organic compounds emitted from medium duty diesel trucks (10). The results indicated the importance of C₁–C₁₃ carbonyls as gas phase constituents and the significance of C₁₄–C₂₀ alkanolic and C₈–C₉ alkanedioic acids in the particle

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Table 1. Recovery of model carbonyls and multifunctional carbonyls in enriched particles

Compound	Vapor pressure, mm Hg ^a	Water solubility, mg/L ^a	Solvent		
			Water	Methylene chloride	Toluene-isopropanol
% Mean recovery (SD of <i>n</i> = 2)					
Methacrolein	1.55×10^2 (at 25°C)	5.00×10^4 (at 20°C)	14 (± 4)	64 (±3)	2 (±1)
2,3-Butanedione	5.68×10^1 (at 15°C)	2.00×10^5 (at 25°C)	27 (± 6)	39 (±3)	2 (±1)
Dihydroxy acetone	2.08×10^{-2} (at 25°C)	5.03×10^5 (at 25°C)	144 (±34)	89 (±8)	28 (±8)
Tolualdehyde	2.5×10^{-1} (at 25°C)	2.27×10^3 (at 25°C)	55 (±46)	63 (±13)	39 (±5)
Pyruvic acid	1.29 (at 20°C)	1.00×10^6 (at 25°C)	129 (±36)	70 (±11)	7 (±1)
Hydroxy acetone	2.95 (at 20°C)	1.00×10^6 (at 25°C)	110 (±30)	64 (±11)	2 (±1)

^a Howard, P.H., & Meylan, W.M. (1997) *Handbook of Physical Properties of Organic Chemicals*, Lewis Publishers, New York, NY.

phase. Although hypothesized to exist in the water-soluble fraction of particles, the significance of particle-phase carbonyls and multifunctional carbonyls (e.g., hydroxy carbonyls and oxo-acids) is unknown (11–13).

In this study, we developed and tested a method that relies on *O*-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine (PFBHA) derivatization of carbonyls, and PFBHA in combination with *bis* (trimethylsilyl) trifluoroacetamide derivatization of multifunctional carbonyls to measure carbonyls and multifunctional carbonyls in fine particulate matter (PM_{2.5}). The method is an improvement over the typical method used to measure carbonyls that rely on 2,4-dinitrophenylhydrazine derivatization (DNPH) of the carbonyl moiety. In contrast to the DNPH method, the use of PFBHA and PFBHA/BSTFA provides excellent chromatographic separation and detection of multifunctional carbonyls, including hydroxy carbonyls (14–16). In addition, (M+H)⁺ and (M+181)⁺ ions generated by using methane and pentafluorobenzyl alcohol chemical ionization ion trap mass spectrometry facilitate molecular weight, and hence elemental formula determinations of non-targeted compounds (14, 17).

Experimental

Materials

Methyl *tert*-butyl ether (MTBE; HPLC grade) and water (HPLC grade) were purchased from Fisher Scientific, Inc. (Fairlawn, NJ). The MTBE was further purified by in-glass distillation. The water was further purified by in-glass distillation and oxidation of organics in the water with potassium permanganate. *O*-(2,3,4,5,6-pentafluorobenzyl)-hydroxylamine hydrochloride, *bis* (trimethylsilyl) trifluoroacetamide, and all authentic standards were obtained from Aldrich Chemical Company, Inc. (Milwaukee, WI). The glassware was soaked in dichlorodimethylsilane in toluene (15%, v/v) overnight to silylate active sites.

Sample Collection

Fine particulate matter (PM_{2.5}) was sampled inside the Caldecott Tunnel, a traffic tunnel on U.S. Highway 24 be-

tween Oakland and Orinda, CA. Samples were collected with a single IMPROVE (Interagency Monitoring of Protected Visual Environments) Module Aerosol during a 4-day period from November 17 to November 21, 1997. The sampler inlet was located 5 cm below the tunnel ceiling on the exit end of the tunnel. A cyclone separator was operated at 22.8 L/min to remove particles larger than 2.5 μm in diameter. Particles were collected using 2 samplers in parallel. One sampler was equipped with 47 mm Teflon filters with a pore size of 2 μm. A total aerosol mass measurement was obtained by weighing these filters before and after sample collection. The other sampler was equipped with 47 mm quartz fiber filter. These filters were baked at 500°C for 4 h to remove organic contaminants prior to their use.

Motor vehicle emissions were sampled in the heavy-duty and light-duty bores of the Caldecott tunnel. The heavy-duty bore is characterized by diesel emissions from trucks and the light-duty bore is characterized by gasoline emissions from automobiles. The heavy-duty bore was sampled on November 17th from 12:15 p.m. to 1:45 p.m. (Sample No. 1) and from 12:00 p.m. to 3:00 p.m. on November 18th (Sample No. 3). On November 19th, motor vehicle emissions were sampled from the light-duty bore from 3:30 p.m. to 6:30 p.m. (Sample No. 5), and from 6:45 p.m. on the 19th to 3:30 p.m. on November 20th (Sample No. 6). On November 20th, the light-duty bore was also sampled from 3:30 p.m. to 6:30 p.m. (Sample No. 7) and from 6:45 p.m. on November 20th to 3:30 p.m. on November 21st (Sample No. 8).

Recovery Studies

Studies were conducted to compare the effect of solvent and temperature on the recovery of model compounds enriched on particles. For these experiments, particulate samples were obtained by sampling air in Davis, CA. The particulates on the quartz fiber filters were enriched with tolualdehyde, methacrolein, methyl vinyl ketone, 2,3-butanedione, hydroxy acetone, and pyruvic acid (1 μg of each compound). The concentration of these compounds in the particulates did not affect the recovery because the filters were enriched with μg

Table 2. The effect of temperature on the recovery of model carbonyls and multifunctional carbonyls on enriched particles

Compound	% Recovery (SD of <i>n</i> = 2)		% Difference
	0°C	-8°C	
Methacrolein	12 (±25)	50 (±25)	+ 38
Methyl vinyl ketone	14 (±14)	42 (±28)	+ 28
2,3-Butanedione	27 (±15)	94 (±5)	+ 67
4-Fluorobenzaldehyde	63 (±22)	96 (±3)	+ 33
Tolualdehyde	55 (±46)	109 (±5)	+ 54
2,3-Dihydroxybenzaldehyde	66 (±1)	69 (±5)	+ 3
5-Nitro-2-furaldehyde	114 (±2)	124 (±8)	+ 10
Hydroxyacetone	110 (±30)	118 (±30)	+ 8
1-Hydroxy-2-butanone	111 (±19)	99 (±2)	- 12
Pyruvic acid	129 (±20)	106 (±21)	- 23
1,3-Dihydroxyacetone	144 (±17)	103 (±19)	- 41

quantities, at least 100× background levels observed in the laboratory. The recoveries were calculated as a ratio of the concentration of the analyte extracted from the appropriate solvent divided by the concentration of the same analyte in the appropriate solvent (e.g., water, methylene chloride, or toluene-isopropanol).

For the experiments in which the extraction efficiency of different solvents was investigated, the filters were placed in a beaker in an ice water bath at 0°C, and 60 mL water, methy-

lene chloride, or toluene-isopropanol were added. The compounds on the filter were then ultrasonically extracted for 2 min (550 Sonic Dismembrator, Fisher Scientific). The carbonyls and multifunctional carbonyls were derivatized with PFBHA, and PFBHA/BSTFA, respectively, as described in previous research (14, 17). The methylene chloride and toluene-isopropanol extracts were exchanged to water prior to derivatization, and the particles were removed by filtration after ultrasonication. For the experiments exploring the effect of

Table 3. Tentatively identified and confirmed carbonyls in PFBHA-derivatized extracts of fine particulate matter (PM_{2.5})

Molecular formula (molecular weight of the derivative)	Molecule ^a	Sample					
		Heavy-duty bore			Light-duty bore		
		1	3	5	6	7	8
C ₄ H ₆ O (265)	Crotonaldehyde	X	X	X	X	X	X
C ₄ H ₆ O (265)		X	X		X		X
C ₄ H ₆ O ₂ (281)	2,3-Butanedione	X	X	X	X	X	X
C ₅ H ₄ O (275)		X	X	X	X	X	X
C ₆ H ₈ O (291)		X	X	X	X	X	X
C ₉ H ₈ O (327) or C ₇ H ₄ N ₂ O				X			
C ₁₃ H ₈ O (375)	9H-fluoren-9-one	X	X	X	X	X	X
C ₂ H ₂ O ₂ (448) ^b	Glyoxal	X	X	X	X	X	X
C ₁₇ H ₁₉ NO (448)		X	X		X	X	X
C ₇ H ₁₂ O ₂ (518)		X	X		X	X	
C ₁₀ H ₁₆ O ₂ (558)		X	X	X	X	X	X

^a Compounds were confirmed by comparing the retention time and the mass spectra of the PFBHA derivative of the analyte with the PFBHA derivative of an authentic standard.

^b The compound at *m/z* 448 is the molecule formed by the derivatization of both carbonyl moieties.

temperature on the % recovery, the enriched filters were treated in the same manner except the temperature of the ice bath was lowered to -8°C by adding potassium chloride.

The recoveries were calculated as a ratio of the concentration of the analyte extracted from the appropriate solvent divided by the concentration of the same analyte in the appropriate solvent (e.g., water, methylene chloride, or toluene-isopropanol). The overall recoveries were not affected by background levels of carbonyls because the filters were enriched with microgram quantities, at least $100\times$ background levels observed in the laboratory.

Gas Chromatography/Ion Trap Mass Spectrometry

A Varian Star 3400 CX gas chromatograph/Varian Saturn 2000 ion trap mass spectrometer (GC/ITMS; Varian, Walnut Creek, CA) was used in this study. The injector liner was silanized to reduce sorption of the compounds, and an RTX-5MS chromatographic column (30 m, 0.32 mm id, 0.25 μm film thickness; Restek Corp., Bellefonte, PA) was used for GC separation of the derivatives. The injector temperature was increased from 280° to 320°C at $180^{\circ}\text{C}/\text{min}$ and held at 320°C for 33 min. The GC oven temperature was initially held at 69°C for 1 min ramped from 69° to 100°C at $5^{\circ}\text{C}/\text{min}$, then from 100° to 320°C at $10^{\circ}\text{C}/\text{min}$, and held at 320°C for 4 min.

The extracts were analyzed by using electron, ionization (EI), methane chemical ionization (methane-CI), and pentafluorobenzyl alcohol chemical ionization (PFBOH-CI). The complementary nature of these modes of ionization has been described in previous publications (14, 17). A mass range of 50 to 650 amu was scanned in the performance of EI and methane CI experiments, and a mass range of 230 to 650 amu was scanned when conducting the PFBOH-CI experiment.

Identification and Quantitation

Identification of the compounds was accomplished by interpreting the EI, methane-CI, and PFBOH-CI mass spectra as described by Spaulding et al. and Frazey et al. (14, 17). The identities of the compounds were confirmed by comparing the retention time and ion trap (low resolution) mass spectra of the derivative of the analyte with the derivative of an authentic standard. Quantitation was accomplished by using 4-fluorobenzaldehyde as an internal standard. The particles on filters were enriched with the internal standard prior to extraction. Five-point calibration curves were constructed from the analysis of standard solutions ranging from 20 to 500 $\mu\text{g}/\mu\text{L}$ prior to and after the analysis of sample extracts. The peak area (m/z 181_{analyte})/peak area (m/z 181 ion_{internal standard}) vs concentration of the analyte was plotted and the linear regression equation was obtained. The concentration of the analyte in the sample extract was calculated using the linear regression equation.

Results and Discussion

Recovery Studies

The mean ($n = 2$) recoveries from water, methylene chloride, and toluene-isopropanol of particles enriched with tolualdehyde, methacrolein, 2,3-butanedione, pyruvic acid and hydroxy acetone, and the vapor pressure and water solubility of the compounds are presented in Table 1. The polarity index (P'), which is a measure of the relative polarity of the solvents, is 10.2 for water, 3.1 for methylene chloride, 2.4 for toluene, and 3.9 for isopropanol (18). The P' for the mixture of toluene and isopropanol was calculated to be 2.08 according to protocol outlined by Snyder, 1974 (19). Overall, as expected, the recovery is affected by the solvent polarity and water solubility of the compound. Methylene chloride, which is

Table 4. Tentatively identified and confirmed^a multifunctional carbonyls in PFBHA/BSTFA derivatized extracts of fine particulate matter ($\text{PM}_{2.5}$)

Molecular formula (molecular weight of derivative)	Molecule	Sample					
		Heavy-duty bore			Light-duty bore		
		1	3	5	6	7	8
$\text{C}_2\text{H}_4\text{O}_2$ (327)	Glycolaldehyde		X		X		X
$\text{C}_2\text{H}_2\text{O}_3$ (341)	Glyoxylic acid	X	X	X	X	X	X
$\text{C}_4\text{H}_9\text{NO}$ (354) or $\text{C}_3\text{H}_5\text{NO}_2$						X	
$\text{C}_5\text{H}_8\text{O}_3$ (383)	Levulinic acid	X	X	X	X	X	X
$\text{C}_7\text{H}_6\text{O}_2$ (389)	Hydroxybenzaldehyde		X	X			
$\text{C}_{16}\text{H}_{14}\text{O}_2$ (505) or $\text{C}_9\text{H}_{10}\text{O}_3$		X	X				
$\text{C}_{17}\text{H}_{21}\text{NO}_2$ (538)			X				

^a Compounds were confirmed by comparing the retention time and mass spectra of the PFBHA/BSTFA derivative of the analyte with the PFBHA/BSTFA derivative of an authentic standard.

less polar than water and more polar than toluene–isopropanol (2 + 1, v/v), is a better solvent for the less water soluble compounds (e.g., tolualdehyde, methacrolein, and 2,3-butanedione). Water, which is more polar than methylene chloride or toluene–isopropanol (2 + 1, v/v), is a better extraction solvent for dihydroxy acetone, pyruvic acid, and hydroxy acetone, the more water soluble and less volatile compounds. For each solvent, the lowest recoveries (2–28%) were obtained for the more volatile compounds, suggesting evaporative losses. Since PFBHA derivatization is conducted in water, and water appears to be a better solvent for the more highly water soluble species, we chose to use water as an extraction solvent.

To determine if the recovery for the less water soluble species could be improved by decreasing any evaporative losses during ultrasonication, an experiment was performed at an ice bath temperature of -8°C . The results are presented in Table 2. Improvements of 3–67% in the recovery were observed for the first 6 compounds listed in Table 2. The recovery for the remaining compounds was virtually complete at both temperatures. Relative differences $<20\%$ are likely insignificant due to error inherent in the analyses. Based on the results of these experiments, we chose to extract the compounds by ultrasonication in water bath at a temperature of -8°C .

Identification of Carbonyls and Multifunctional Carbonyls in Motor Vehicle Exhaust

We tentatively identified 11 carbonyls and 7 multifunctional carbonyls by interpreting the methane–C1 and PFBOH–C1 mass spectra. The molecular formulas of the tentatively identified and confirmed compound are presented in Tables 3 and 4. We confirmed the identities of crotonaldehyde, 2,3-butanedione, glyoxal, 9H-fluoren-9-one, and the oxo-acids, glyoxylic acid and levulinic acid by comparing the retention time and mass spectra of the analyte derivative with the derivative of an authentic standard of the analyte. Crotonaldehyde, 2,3-butanedione, glyoxal, and levulinic acid were identified in particulate extracts from both the heavy- and light-duty vehicle bores of the Caldecott tunnel. Crotonaldehyde and glyoxal have previously been identi-

fied as gas phase emissions from gasoline- and diesel-vehicles (7, 9, 10, 20), and 2,3-butanedione was identified in the gas phase in emissions from a diesel vehicle (10). 9H-fluoren-9-one was also previously identified in gasoline- and diesel-particulate emissions, and also as a product of combustion reactions (20–22).

Although oxo acids, such as glyoxylic acid, have been reported in arctic aerosol samples (23), characterization of acids emitted from motor vehicles has mostly been limited to carboxylic and dicarboxylic acids (24, 25). The identification of glyoxylic and levulinic acid in motor vehicle fine particulate matter in this study is unique. Glyoxylic acid was only detected in fine particulate matter collected in the light-duty bore (Sample 6), while levulinic acid was detected in all the samples. We also tentatively identified $>\text{C}_{10}$ compounds which have not been identified previously—a carbonyl with a molecular formula of $\text{C}_{10}\text{H}_{16}\text{O}_2$, and hydroxy carbonyls with a molecular formula of $\text{C}_{17}\text{H}_{21}\text{NO}_2$, and a molecular formula of either $\text{C}_{16}\text{H}_{14}\text{O}_2$ or $\text{C}_9\text{H}_{10}\text{O}_3$. The $\text{C}_{16}\text{H}_{14}\text{O}_2$ molecule would have one $-\text{OH}$ group and the $\text{C}_9\text{H}_{10}\text{O}_3$ compound would have 2 $-\text{OH}$ groups. Possible identities of these molecules are hydroxy trimethylfluorenone and dihydroxy ethyl benzaldehyde. The carbonyls were present in emissions from both the heavy-duty and light-duty bore, thus, indicating that they are combustion products of diesel- and gasoline-emissions. The $>\text{C}_{10}$ hydroxy carbonyls were only present in samples collected in the heavy-duty bore. These data suggest that $>\text{C}_{10}$ hydroxy carbonyls may serve as tracers for diesel emissions in air.

The carbonyls and dicarbonyls (e.g., crotonaldehyde, glycolaldehyde, glyoxal, and 2,3-butanedione) are thought to be too volatile to exist in the particulate phase. The association of these compounds with fine particulate matter, in this study, may, therefore, be a sampling artifact. Turpin and Huntzicker (26) demonstrated that quartz fiber filters adsorb organic matter and that the particulate loading does not impact the extent of adsorption because the surface area of the particles is small compared to the surface area of the filter. In contrast, Saxena and Hildemann (13) predicted that multifunctional compounds, including glyoxal, glyoxylic acid, and C_3 – C_5 oxocarboxylic acids may be present in the water soluble organic fraction of atmospheric fine particles. Measurements of polar compounds, including hydroxy carbonyls (e.g., hydroxy benzaldehyde, hydroxy benzoic acids) in diesel particulate matter substantiates this prediction (27). To shed further light on this controversy, further work is needed which uses the sample preparation and analysis protocol described herein in concert with another sampling technique, which is capable of separating gas- and particulate-phase species.

Quantitation of Carbonyls and Multifunctional Carbonyls in Motor Vehicle Exhaust

The levels of crotonaldehyde, 2,3-butanedione, glyoxal, glyoxylic acid, and levulinic acid were quantitated (Table 5). In fine particulate matter sampled from the heavy-duty bore, the concentration of crotonaldehyde ranged from ND

Table 5. Concentration of select carbonyls and multifunctional carbonyls in fine particulate matter ($\text{PM}_{2.5}$) sample extracts

Compound	Concentration, ng/mg			
	Heavy-duty bore		Light-duty bore	
	1	3	5	6
Crotonaldehyde	67	ND ^a	ND	48
Glyoxal	93	216	231	48
2,3 Butanedione	90	ND	128	49
Glyoxylic acid	ND	ND	ND	568
Levulinic acid	192	320	286	114

^a ND = nondetectable

(nondetectable) to 67 ng/mg; the concentration of glyoxal ranged from 93 to 216 ng/mg; the concentration of 2,3-butanedione ranged from ND to 90 ng/mg; and the concentration of levulinic acid ranged from 192 to 220 ng/mg. Glyoxylic acid was not detected in these samples. In fine particulate matter sampled from the light-duty bore, the concentration of crotonaldehyde ranged from ND to 48 ng/mg; the concentration of glyoxal ranged from 49 to 128 ng/mg; the concentration of glyoxylic acid ranged from ND to 568 ng/mg; and the concentration of levulinic acid ranged from 114 to 286 ng/mg. Emission factors for glyoxal calculated in one roadway tunnel study suggest that gasoline emissions are a greater source of glyoxal than diesel vehicle emissions (8). Data in our study indicate similar levels of glyoxal in extracts obtained from sampling from 3:30 p.m. to 6:30 p.m. in the heavy-duty bore and light-duty bore (26 versus 24 ng/m³ in the heavy-duty bore and light-duty bore, respectively).

Reduction of Contaminants

A limitation to the identification of carbonyls in fine particulate matter was the presence of contaminants in the field blank. Likely sources were contamination in the reagents—MTBE, PFBHA, and the LC grade water, and the laboratory air. We investigated the effect of redistillation of MTBE, recrystallization of PFBHA, sample preparation in a N₂ atmosphere, and permanganate oxidation of the organics in the water on the levels of acetaldehyde, acetone, propionaldehyde, and 2-butanone and 4 unidentified compounds recovered from a filter that was processed through the analytical protocol. The results are presented in Table 6.

Removal of 80–100% of the compound was evident after redistillation of MTBE, recrystallization of PFBHA, sample preparation under N₂, and oxidation of the organics in the wa-

ter with potassium permanganate. Oxidation of the water with potassium permanganate appears to be the most effective removal step. Sample preparation under nitrogen was also effective for reducing impurities of acetaldehyde, acetone, propionaldehyde, and 2-butanone, as was recrystallization of the PFBHA 2× for all the compounds. From these data, it is difficult to suggest which of the treatments might be eliminated because we did not quantitate the reduction of each step by itself and any contamination, even at a low level, can reduce the method detection limit. Accordingly, we have initiated all the procedures to minimize contamination of our samples and to increase sensitivity of the method.

Conclusions

Carbonyls and multifunctional carbonyls can be identified in fine particulate matter (PM_{2.5}) collected on filters by ultrasonication extraction, followed by derivatization with PFBHA, and a combination of PFBHA/BSTFA. The derivatives were identified and quantitated using GC/CI-ITMS. The recovery of model carbonyls (tolualdehyde, methacrolein, and 2,3-butanedione) and multifunctional carbonyls (dihydroxy acetone, pyruvic acid, and hydroxy acetone) using water, methylene chloride, and toluene-isopropanol (2 + 1, v/v) as extraction solvents were compared. The recovery of the multifunctional carbonyls followed the solvent polarity (water > methylene chloride > toluene-isopropanol (2 + 1, v/v), with water providing the highest (100%) recoveries. Lowering the ultrasonication bath temperature from 0° to -8°C proved critical to improving the more volatile and less water soluble carbonyls and dicarbonyls. Improvements of 33 to 54% were obtained for methacrolein, methyl vinyl ketone, 2,3-butanedione, and 4-fluorobenzaldehyde. The power of the method was demonstrated by the identification and

Table 6. The effect of purification procedures on removal of contaminants

Compound	Treatment				
	Redistillation of MTBE	Redistillation of MTBE; recrystallization of PFBHA	Redistillation of MTBE; recrystallization of PFBHA (2×)	Redistillation of MTBE; recrystallization of PFBHA (2×); sample preparation under N ₂	Redistillation of MTBE; recrystallization of PFBHA (2×); sample preparation under N ₂ ; treatment of water with KMnO ₄
Normalized area (× 10 ² ; % change relative to redistillation of MTBE)					
Acetaldehyde	1284	1227 (-4%)	938 (-27%)	682 (-47%)	113 (-91%)
Acetone	962	1045 (+9%)	842 (-12%)	470 (-50%)	153 (-84%)
Propionaldehyde	730	719 (-2%)	802 (+11%)	610 (-16%)	131 (-81%)
2-Butanone	598	706 (+18%)	330 (-45%)	191 (68%)	75 (-87%)
Unknown #1	15	12 (-20%)	7.4 (-51%)	6.7 (-55%)	0.2 (-99%)
Unknown #2	16	8 (-50%)	3 (-81%)	3 (-81%)	0 (-100%)
Unknown #3	11	5 (-55%)	4 (-63%)	3 (-90%)	0 (-100%)
Unknown #4	87	9 (-90%)	5 (-94%)	3 (-96%)	0.9 (-99%)

quantitation of carbonyls and multifunctional carbonyls. The identities of crotonaldehyde, 2,3-butanedione, glyoxal, 9H-fluoren-9-one, glyoxylic acid, and levulinic acid were confirmed. The identification of glyoxylic acid and levulinic acid in motor vehicle exhaust is unique in this study. Most noteworthy is the first report of high-molecular weight carbonyls with molecular formulas of $C_{10}H_{16}O_2$, and hydroxy carbonyls with molecular formulas of $C_{17}H_{21}NO_2$, and either $C_{16}H_{14}O_2$ or $C_9H_{10}O_3$. The high-molecular weight hydroxy carbonyls may be markers of diesel emissions. Crotonaldehyde, glyoxal, 2,3-butanedione, glyoxylic acid, and levulinic acid were quantitated. Concentrations of these compounds ranged from ND to 568 ng/mg. A limitation to the identification of the analytes was the presence of contaminants in the field blank. Protocol involving the recrystallization of the solvent, recrystallization of PFBHA, sample preparation under N_2 , and treatment of the water with potassium permanganate removed 80–100% of the contaminants. This work is significant because a method capable of identifying high-molecular weight ($>C_{10}$) carbonyls and multifunctional carbonyls for which no data exist, and which may be significant combustion products in fine particulate matter, was developed and tested.

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References

- (1) Siegl, W.O., Hammerle, R.H., Herrmann, H.M., Wenclawiak, B.W., & Luers-Jongen, B. (1999) *Atmos. Environ.* **33**, 797–805
- (2) Miguel, A.H., Kirchstetter, T.W., Harley, R.A., & Hering, S.V. (1998) *Environ. Sci. Technol.* **32**, 450–455
- (3) Weingartner, E., Keller, C., Stahel, W.A., Burtscher, H., & Baltensperger, U. (1977) *Atmos. Environ.* **31**, 451–462
- (4) Zielinska, B., Sagebiel, J.C., Harshfield, G., Gertler, A.W., & Pierson, W.R. (1966) *Atmos. Environ.* **30**, 2269–2286
- (5) Pierson, W.R., Gertler, A.W., Robinson, N.F., Sagebiel, J.C., Zielinska, B., Bishop, G.A., Stedman, D.H., Zweidinger, R.B., & Ray, W.D. (1996) *Atmos. Environ.* **30**, 2233–2256
- (6) Sagebiel, J.C., Zielinska, B., Pierson, W.R., & Gertler, A.W. (1996) *Atmos. Environ.* **30**, 2287–2296
- (7) Fraser, M.P., Cass, G.R., & Simoneit, B.R.T. (1998) *Environ. Sci. Technol.* **32**, 2051–2060
- (8) Staehelin, J., Keller, C., Staehl, W., Schlapfer, K., & Wunderlis, S. (1998) *Atmos. Environ.* **32**, 999–1009
- (9) Kirchstetter, T.W., Singer, B.C., Harley, R.A., Kendall, G.R., & Chan, W. (1996) *Environ. Sci. Technol.* **30**, 661–670
- (10) Schauer, J.J., Kleeman, M.J., Cass, G.R., & Simoneit, B.R.T. (1999) *Environ. Sci. Technol.* **33**, 1578–1587
- (11) Aumont, B., Madronich, S., Bey, I., & Tyndall, G.S. (2000) *J. Atmos. Chem.* **35**, 59–75
- (12) Pun, B.K., Seigneur, C., Grosjean, D., & Saxena, P. (2000) *J. Atmos. Chem.* **35**, 199–223
- (13) Saxena, P., & Hildemann, L.M. (1996) *J. Atmos. Chem.* **24**, 57–109
- (14) Spaulding, R.S., Frazey, P., Rao, X., & Charles, M.J. (1999) *Anal. Chem.* **71**, 3420–3427
- (15) Yu, J., Jeffries, H.E., & Le Lacheur, R.M. (1995) *Environ. Sci. Technol.* **29**, 1923–1932
- (16) Le Lacheur, R.M., Sonnenberg, L.B., Singer, P.C., Christman, R.F., & Charles, M.J. (1993) *Environ. Sci. Technol.* **27**, 2745–2753
- (17) Frazey, P., Rao, X., Spaulding, R., Beld, B., & Charles, M.J. (1999) *International Journal of Mass Spectrometry* **190/191**, 343–357
- (18) Snyder, L.R. (1978) *J. Chromatogr. Sci.* **16**, 223–234
- (19) Snyder, L.R. (1974) *J. Chromatogr.* **92**, 223–230
- (20) Graedel, T.E., Hawkins, D.T., & Claxton, L.D. (1986) *Atmospheric Chemical Compounds—Sources, Occurrence, and Bioassay*; Academic Press, Orlando, FL
- (21) Rogge, W.F., Hildemann, L.M., Mazurek, M., & Cass, G.R. (1993) *Environ. Sci. Technol.* **27**, 636–651
- (22) Behymer, T.D., & Hites, R.A. (1985) *Environ. Sci. Technol.* **19**, 1004–1006
- (23) Kawamura, K., & Gagosian, R.B. (1987) *Nature* **325**, 330–332
- (24) Kawamura, K. (1985) *Environ. Sci. Technol.* **19**, 1082–1086
- (25) Kawamura, K., & Kaplan, I.R. (1987) *Environ. Sci. Technol.* **21**, 105–110
- (26) Turpin, B.J., & Huntzicker, J.J. (1995) *Atmos. Environ.* **29**, 3527–3544
- (27) Wenclawiak, B.W., Jensen, T.E., & Richert, J.F.O. (1993) *Fresenius J. Anal. Chem.* **346**, 808–812