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LC−MS Analysis of Carbonyl Compounds and Their Occurrence in Diesel Emissions

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Liquid chromatography coupled with atmospheric pressure chemical ionization (APCI) ion trap mass spectrometry (ITMS) is applied to atmospheric aerosol relevant carbonyls. Characterization of positive and negative ion detection mass spectra are presented for 24 model compounds analyzed in their underivatized and *O*-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine (PFBHA) oxime forms. The addition of PFBHA derivatization enhanced the detection and sensitivity for many of the carbonyls investigated. For all but five of the carbonyls examined, a pseudomolecular $(M + H)^+$ ion is the base peak in the APCI positive ion mass spectra of PFBHA oxime derivatives and is observed in four of the five exceptions. Application of the evaluated analysis methodology to heavy-duty diesel source emissions facilitated the quantification of 10 aliphatic carbonyls (5 C_5−C_9 ketones, 4 C_6 unsaturated ketones, 1 C_6 dicarbonyl) and 14 aromatic carbonyls (1 C_9 aldehyde, 5 C_8−C_{13} ketones, 8 C_6−C_{14} quinones). Diesel truck engine emission factors spanning 0.55−540 μg km^{-1} were measured for gas- and particle-phase carbonyls. Good agreement was observed for gas-phase emission factors with results obtained by gas chromatography with ITMS.

There are now over 150 published epidemiological studies considering the health effects of inhaled airborne particles.[1] The exact mechanism by which aerosols cause injury is still under investigation, but findings suggest that the size and chemical composition of particles influence their health effects (see for example refs 2−5). One hypothesis about aerosol health effects focuses on the oxidative potential of organic compounds contained in airborne particles.[6−8] Atmospheric aerosols typically contain numerous organic compounds with a wide range of chemical properties. Gas chromatography coupled to mass spectrometry (GC/MS) analysis of the organic fraction of aerosols has yielded useful molecular markers for source apportionment studies (see for example refs 9−12), but this method is not well suited to directly quantify the concentration of oxygenated organic species that may be responsible for oxidative stress. The identification and quantification of oxygenated organic species contained in airborne particles may be a key to the understanding the mechanistic health effects of aerosols.

Carbonyls are one example of oxygenated compounds that are commonly present in atmospheric particles but are difficult to analyze. Significant concentrations of carbonyls have been measured in diesel engine exhaust,[13,14] a major aerosol source in the United States and abroad with well recognized health risks.[15−17] Quantitative chemical analysis of carbonyls has been attempted by a variety of techniques, which try to overcome the polar, reactive, and semivolatile nature of these compounds. Derivatization methods to enhance carbonyl analysis typically utilize either dinitrophenylhydrazone (DNPH) or *O*-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine (PFBHA). Several chemical analysis techniques have been applied to DNPH carbonyl hydrazones including high-performance liquid chromatography (HPLC) with diode array detection (DAD),[18−20] HPLC with MS detection,[21−24] and GC/MS

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(1) Pope, C. A. *Aerosol Sci. Technol.***2000**, *32*, 4−14.

(2) Salonen, R. O.; Halinen, A. I.; Pennanen, A. S.; Hirvonen, M. R.; Sillanpaa, M.; Hillamo, R.; Shi, T. M.; Borm, P.; Sandell, E.; Koskentalo, T.; Aarnio, P. *Scand. J. Work Environ. Health* **2004**, *30*, 80−90.

(3) Grahame, T.; Hidy, G. *Inhalation Toxicol.* **2004**, *16*, 143−152.

(4) Claiborn, C. S.; Larson, T.; Sheppard, L. *Environ. Health Perspect.* **2002**, *110*, 547−552.

(5) Hannigan, M. P.; Busby, W. F.; Cass, G. R. *J. Air Waste Manage.* **2005**, *55*, 399−410.

(6) Risom, L.; Moller, P.; Loft, S. *Mutat. Res. Fundam. Mol. Mech. Mutat.* **2005**, *592*, 119−137.

(7) Xia, T.; Korge, P.; Weiss, J. N.; Li, N.; Venkatesen, M. I.; Sioutas, C.; Nel, A. *Environ. Health Perspect.* **2004**, *112*, 1347−1358.

(8) Li, N.; Venkatesan, M. I.; Miguel, A.; Kaplan, R.; Gujuluva, C.; Alam, J.; Nel, A. *J. Immunol.* **2000**, *165*, 3393−3401.

(9) Schauer, J. J.; Fraser, M. P.; Cass, G. R.; Simoneit, B. R. T. *Environ. Sci. Technol.* **2002**, *36*, 3806−3814.

(10) Schauer, J. J.; Cass, G. R. *Environ. Sci. Technol.***2000**, *34*, 1821−1832.

(11) Zheng, M.; Salmon, L. G.; Schauer, J. J.; Zeng, L. M.; Kiang, C. S.; Zhang, Y. H.; Cass, G. R. *Atmos. Environ.* **2005**, *39*, 3967−3976.

(12) Zheng, M.; Cass, G. R.; Schauer, J. J.; Edgerton, E. S. *Environ. Sci. Technol.* **2002**, *36*, 2361−2371.

(13) Schauer, J. J.; Kleeman, M. J.; Cass, G. R.; Simoneit, B. R. T. *Environ. Sci. Technol.* **1999**, *33*, 1578−1587.

(14) HEI. *Research directions to improve estimates of human exposure and risk from diesel exhaust*; Health Effects Institute, 2002.

(15) CalEPA. *Proposed Identification of Diesel Exhaust as a Toxic Air Contaminant*; Prepared by the Air Resources Board and Office of Environmental Health Hazard Assessment for California Environmental Protection Agency,1998.

(16) EPA *Characterization of potential human health effects of diesel exhaust: hazard dose−response assessments*; United States Environmental Protection Agency, 2000.

(17) Madden, M. C.; Dailey, L. A.; Stonehuerner, J. G.; Harris, D. B. *J. Toxicol. Environ. Health, A* **2003**, *66*, 2281−2297.

(18) Druzik, C. M.; Grosjean, D.; Vanneste, A.; Parmar, S. S. *Int. J. Environ. Anal. Chem.* **1990**, *38*, 495−512.

(19) Kiss, G.; Varga, B.; Puchony, Z. V.; Gelencser, A.; Krivacsy, Z.; Hlavay, J. *Talanta* **1999**, *48*, 755−762.

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with selected ion monitoring detection.[25] In contrast, PFBHA carbonyl oximes are typically analyzed using GC/MS.[26−28] While these are the predominant methodologies employed for carbonyl analysis, others have performed direct analysis of select underivatized compounds, such as oxygenated polycyclic aromatic hydrocarbons, using GC/MS [29−32] and HPLC−MS.[33−35]

Although a variety of analytical techniques exist, their application to the characterization of diesel vehicle source emissions suffers from certain limitations. The application of DNPH derivatization with HPLC−MS and HPLC−DAD detection has previously been applied to diesel emissions;[13,36,37] however, this approach cannot distinguish between gas- and particle-phase emissions due to the cartridge collection method utilized without a second sampling configuration containing an upstream filter. Methods employing PFBHA derivatization with GC/MS for carbonyl characterization of motor vehicles were conducted by Rao et al.,[38] but limitations of the analytical mass range of the MS and inability to adequately volatilize PFBHA oximes of compounds with multiple carbonyl moieties warranted further investigation.

We describe and evaluate a new HPLC technique with atmospheric pressure chemical ionization (APCI) MS for direct analysis of carbonyls and as their PFBHA oximes. The utility of HPLC-APCI-MS for carbonyl characterization to diesel source emissions is examined for phase-separated source emissions from a heavy-duty diesel truck.

EXPERIMENTAL SECTION

Chemicals. Carbonyl species examined (butanal, decanal, tetradecanal, 2-butanone, 2-heptanone, 2-undecanone, α-ketobutyric acid, acetylbutyric acid, 7-oxooctanoic acid, 1-hydroxy-2-butanone, benzaldehyde, biphenyl-4-carboxaldehyde, 1-pyrenecarboxaldehyde, 2-indanone, 9-fluorenone, benzanthrone, dicinnamalacetone, 1,4-naphthoquinone, anthraquinone, 1,4-chrysenequinone, 4-hydroxybenzaldehyde, 2-hydroxy-9-fluorenone, 2-hydroxy-1,4-naphthoquinone, α-naphtholbenzein) were purchased from Sigma-Aldrich Chemical Co. (Milwaukee, WI). The derivatization reagent PFBHA was also obtained from Sigma-Aldrich. Water (HPLC grade) was purchased from Fisher Scientific International (New Hampton, NH). Prior to its use in any phase of the chemical analysis, the water was treated with potassium permanganate and glass distilled. Burdick and Jackson acetonitrile (carbonyl-free) and dichloromethane (DCM, trace analysis grade) were obtained from VWR International (West Chester, PA).

Mobile-phase solvents consisted of water and methanol. Analytical grade water was produced from a MilliQ Gradient A10 (18.2 MΩ cm, UV-irradiated, TOC 4−6 ppb) purchased from Millipore (Billerica, MA). J. T. Baker methanol (HPLC grade) was purchased from VWR. The nitrogen (liquid dewar headspace) and helium (99.999%) gases used by the mass spectrometer were passed through VICI mat/sen gas purifiers obtained from Restek (State College, PA).

Sample Collection. Heavy-duty diesel vehicle emissions were collected in Riverside, CA, during June 2003. The emissions sampling system used in this study was based on a design described by Schauer et al.[39] Briefly, heavy-duty diesel vehicles (HDVs) were driven through a five-mode cycle on a mobile chassis dynamometer operated by West Virginia University (WVU). Vehicle inertial weight of 56 000 lbs was simulated using flywheels and electrical motor resistance. Each five-mode cycle (HHDDT, heavy heavy-duty diesel truck) consisting of a 30-min idle, 17-min creep, 11-min transient stage, and two cruise stages of 34 and 31 min, with a top speed of 65 mph for the second cruise. The entire test required 3 h for completion; for further details, see Gautam et al.[40] In the current study, measurements of carbonyls contained in the emissions from a 1999 Freightliner tractor will be used to illustrate the new analysis technique. A 1998 Detroit Diesel Series 60 engine powers the vehicle, with 138 553 miles driven at the time of sample collection. The engine has six cylinders with a displacement of 12.7 L and 500 base horsepower.

Emissions were captured at the end of the vehicle exhaust system and transferred through heated 3-in. stainless steel tubing to a mixing box where they diluted with HEPA-filtered air before passing through a dilution tunnel operated at constant flow. After primary dilution, a portion of the exhaust was drawn through a 0.5-in. stainless steel tube into a secondary dilution system consisting of an upstream cyclone, venturi flow meter, stack dilution tunnel (SDT), and residence time chamber (RTC). Emissions drawn into the SDT underwent a second turbulent dilution with air passed through a HEPA filter and activated charcoal to remove background particles and organic gases (see Hildemann et al.[41] for a complete description).

(20) Liggio, J.; McLaren, R. *Int. J. Environ. Anal. Chem.* **2003**, *83*, 819−835.
(21) Grosjean, E.; Green, P. G.; Grosjean, D. *Anal. Chem.* **1999**, *71*, 1851−1861.
(22) Van den Bergh, V.; Coeckelberghs, H.; Vankerckhoven, H.; Compernolle, F.; Vinckier, C. *Anal. Bioanal. Chem.* **2004**, *379*, 484−494.
(23) Brombacher, S.; Oehme, M.; Dye, C. *Anal. Bioanal. Chem.* **2002**, *372*, 622−629.
(24) Brombacher, S.; Oehme, M.; Beukes, J. A. *J. Environ. Monit.* **2001**, *3*, 311−316.
(25) Zhu, J. P.; Aikawa, B.; Cao, X. L. *Can. J. Anal. Sci. Spectrosc.* **2002**, *47*, 171−176.
(26) Lelacheur, R. M.; Sonnenberg, L. B.; Singer, P. C.; Christman, R. F.; Charles, M. J. *Environ. Sci. Technol.* **1993**, *27*, 2745−2753.
(27) Yu, J. Z.; Flagan, R. C.; Seinfeld, J. H. *Environ. Sci. Technol.* **1998**, *32*, 2357−2370.
(28) Jaoui, M.; Kleindienst, T. E.; Lewandowski, M.; Edney, E. O. *Anal. Chem.* **2004**, *76*, 4765−4778.
(29) Gogou, A. I.; Apostolaki, M.; Stephanou, E. G. *J. Chromatogr., A* **1998**, *799*, 215−231.
(30) Rogge, W. F.; Hildemann, L. M.; Mazurek, M. A.; Cass, G. R.; Simoneit, B. R. T. *Environ. Sci. Technol.* **1993**, *27*, 636−651.
(31) Fraser, M. P.; Cass, G. R.; Simoneit, B. R. T.; Rasmussen, R. A. *Environ. Sci. Technol.* **1998**, *32*, 1760−1770.
(32) Allen, J. O.; Dookeran, N. M.; Taghizadeh, K.; Lafleur, A. L.; Smith, K. A.; Sarofim, A. F. *Environ. Sci. Technol.* **1997**, *31*, 2064−2070.
(33) Koeber, R.; Niessner, R.; Bayona, J. M. *Fresenius J. Anal. Chem.* **1997**, *359*, 267−273.
(34) Letzel, T.; Poschl, U.; Rosenberg, E.; Grasserbauer, M.; Niessner, R. *Rapid Commun. Mass Spectrom.* **1999**, *13*, 2456−2468.
(35) Letzel, T.; Poschl, U.; Wissiack, R.; Rosenberg, E.; Grasserbauer, M.; Niessner, R. *Anal. Chem.* **2001**, *73*, 1634−1645.
(36) Grosjean, D.; Grosjean, E.; Gertler, A. W. *Environ. Sci. Technol.* **2001**, *35*, 45−53.
(37) Kristensson, A.; Johansson, C.; Westerholm, R.; Swietlicki, E.; Gidhagen, L.; Wideqvist, U.; Vesely, V. *Atmos. Environ.* **2004**, *38*, 657−673.
(38) Rao, X.; Kobayashi, R.; White-Morris, R.; Spaulding, R.; Frazey, P.; Charles, M. J. *J. AOAC Int.* **2001**, *84*, 699−705.
(39) Schauer, J. J.; Kleeman, M. J.; Cass, G. R.; Simoneit, B. R. T. *Environ. Sci. Technol.* **2002**, *36*, 1169−1180.
(40) Gautam, M.; Clark, N.; Riddle, W.; Nine, R.; Wayne, W. S.; Maldonado, H.; Agrawal, A.; Carlock, M. *SAE Technol. Pap. Ser.* **2002**, *SP-1715*.
(41) Hildemann, L. M.; Cass, G. R.; Markowski, G. R. *Aerosol Sci. Technol.* **1989**, *10*, 193−204.

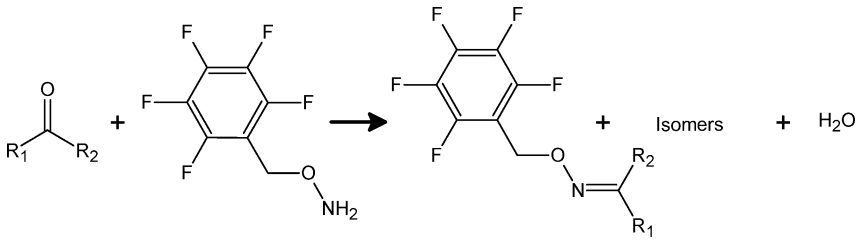

Figure 1. Chemical reaction of carbonyls with PFBHA to form their corresponding oxime isomers.

The diluted emissions sample was drawn from the bottom of the RTC through a 0.5-in. stainless steel tube connected to a $PM_{2.5}$ cyclone (URG, Chapel Hill, NC) leading to a sampling train designed to collect semivolatile organic compounds.[39] Gas-phase organics were collected on two annular denuders (URG 8-channel) in series, coated with XAD-4 polystyrene resin (Sigma-Aldrich) as described elsewhere.[42,43] Particles remaining in the exhaust stream were then collected on 47-mm quartz fiber filters (Pall Gelman, Ann Arbor, MI), contained in Teflon filter packs (URG). Semivolatile organics that were "blown off" the filters were collected on two polyurethane foam (PUF) plugs (URG) in series. Two sampling trains were operated in parallel at a flow rate of 16.7 L min^{-1} using electronic mass flow controllers (Hastings, Hampton, VA).

The samples collected using denuders were stored on dry ice until extraction, typically within 24 h of sample collection. Denuder extracts were stored within silanized amber vials at −20 °C until their chemical analysis was performed. The filter samples were stored in glass Petri dishes that were covered with aluminum foil (baked at 550 °C for 12 h) and wrapped with PTFE tape prior to placement in a desiccator, under 99.999% nitrogen. Each PUF plug was stored individually within a silanized amber glass jar with a PTFE-lined cap. Both the filter and PUF samples were stored at −20 °C until solvent extraction was completed.

Sample Extraction/Derivatization. A detailed diagram of the procedures for solvent extraction of the filter and denuder substrates is provided in the Supporting Information (see Figures S1 and S2). To minimize potential sorption of the carbonyls, all glassware was surface-deactivated via a silanization procedure.[44] Where possible low-actinic glassware was employed to minimize any photodegradation of the carbonyls. Sample extracts for carbonyl derivatization are first reduced in volume to <50 μL under organic-free nitrogen blow down. Once the extract volume has been reduced, a 9:1 (v/v) mixture of carbonyl-free acetonitrile/DCM is added to bring each sample to a volume of 200 μL. To each sample for derivatization is added a 50 mg mL^{-1} solution of PFBHA in methanol to a target PFBHA concentration of 10 mM. Each sample is capped, wrapped with Teflon tape, covered with baked foil, and left at room temperature for a period of 24 h. This procedure is a variation of methods previously utilized for carbonyl analysis in our laboratory. The balanced chemical reaction for the conversion of carbonyls into their pentafluorobenzyl (PFB) oximes is provided in Figure 1.

(42) Gundel, L. A.; Lee, V. C.; Mahanama, K. R. R.; Stevens, R. K.; Daisey, J. M. *Atmos. Environ.* **1995**, *29*, 1719−1733.
(43) Gundel, L. A.; Lane, D. A. *Adv. Environ. Ind. Process Cont. Technol.* **1999**, *2*, 287−332.
(44) Jakober, C. A.; Riddle, S. G.; Robert, M. A.; Cahill, T. M.; Kleeman, M. J.; Charles, M. J. Oxygenated organics in fine particle emissions from gasoline and diesel vehicles for source apportionment. Final report prepared for the California Air Resources Board, Contract 00-318 00-318, 2005.

HPLC−ITMS. An Agilent 1100 HPLC, with a temperature-controlled autosampler interfaced with DAD and an ion trap (IT) MS was employed for the chemical analyses (Agilent Technologies, Palo Alto, CA and Bruker Daltronics, Billerica, MA). Separation of the derivatives was achieved using a Prodigy C_{18} chromatographic column (2-mm i.d., 100-mm length, 5-μm particle size; Phenomenex, Torrance, CA). The sample compartment was at 20 °C for the analyses, with 35 °C for the column compartment. An injection volume of 10 μL was employed. The separation used a linear two-phase gradient at 400 μL min^{-1}. The initial eluent was 60:40 water/methanol for 5 min. Methanol was then increased to 95% over 45 min. The final mobile phase was held for 14 min. Following the analysis, a 6-min postrun equilibration preceded injection of the next sample.

For ITMS detection, APCI interface conditions were nebulizer pressure of 60 psi with 4 L min^{-1} of 300 °C N_2 and 350 °C vaporizer temperature. The corona discharge was set to 10 μA for positive ion generation or 20 μA for negative. The capillary entrance was 3500 V opposite in polarity to the ions generated. Mass spectra were collected using an electron multiplier setting of 1700 V, an abundance target of 30 000, and a maximum accumulation time of 250 ms. The mass/charge scan range examined was 100−1000 Da. Additionally, ultraviolet−visible absorption spectra (200−600 nm) were also collected using the in-line DAD, for secondary confirmation purposes.

Quantification. Multiple point calibration curves, typically six or seven points plus a calibration blank, were analyzed preceding and following the set of sample extracts. These calibration solutions range in concentration from 25 to 2100 pg μL^{-1} depending upon the analysis being performed. The calibration solutions were subjected to the same derivatization procedure simultaneously with the sample extracts. Calibration solutions were analyzed in order from the least to most concentrated solution to minimize any potential carryover between analyses. Following the last calibration point, a solvent blank was injected to ensure no analyte carryover occurred.

Calibration curves for the purpose of sample quantification were generated for analytes observed in the sample extracts using the instrument response for both the pre- and postsample calibration curve. The formula utilized to generate the response curves is provided in eq 1:

$$(\text{peak area})_{\text{analyte}}/(\text{peak area})_{\text{IS}} = \text{response factor} \times [\text{conc}]_{\text{analyte}}/[\text{conc}]_{\text{IS}} \quad (1)$$

Multiple quantification internal standards were added to the sample extracts to provide several options with regard to derivatization efficiency, instrument response, or coelution with other components. Select calibration curves for 1,4-naphthoquinone and

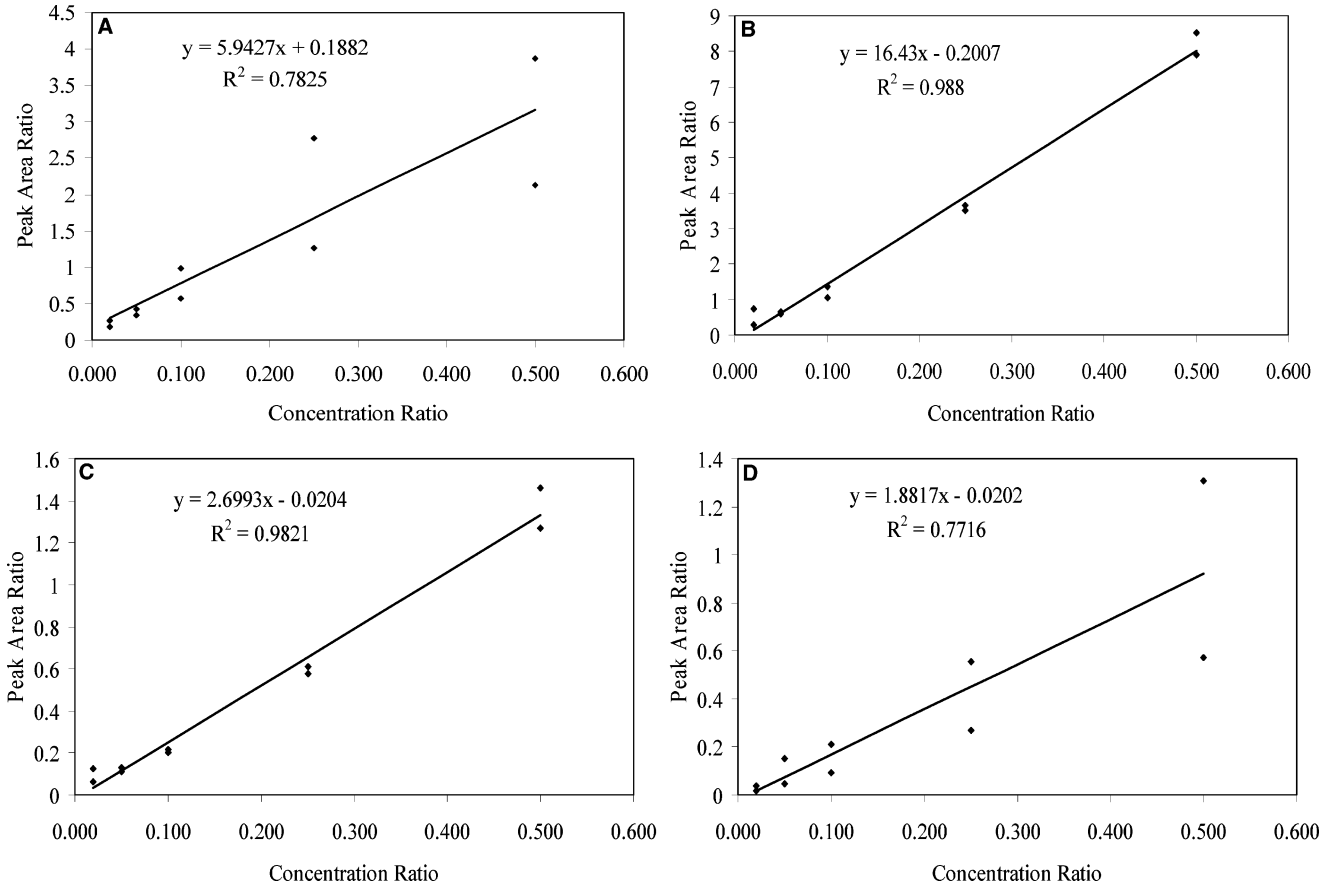

Figure 2. Example calibration curves for 1,4-naphthoquinone using four different compounds as the quantification internal standard: (A) $^{13}C_6$ 4-hydroxybenzaldehyde, (B) 6-fluoro-4-chromanone, (C) 2-fluoro-9-fluorenone, and (D) d_4 1,4-benzoquinone.

perinaphthenone are provided in Figures 2 and 3, showing that when possible the quantification internal standard utilized was 2-fluoro-9-fluorenone and that $^{13}C_6$ 4-hydroxybenzaldehyde and d_4 1,4-benzoquinone were not used for quantification.

Researchers are alerted to the possible hazard from exposure to soot, solvents, and reagents as well as the mechanical hazards of flywheels (providing load to an engine) and cryogenic dewars (which must properly vent excess pressure).

RESULTS AND DISCUSSION

The aim of this work is to devise a means to identify elemental formulas of unknown carbonyl species present in field samples and extend the analytical range of the PFBHA derivatization methodology beyond the mass range limitations of GC/MS.

Characterization of the APCI Mass Spectra of Carbonyls. *Positive Ion Detection*. A summary of the ions and their relative intensities for positive ion detection of the carbonyls is presented in Table S1 (Supporting Information). The mass spectra are characterized by ions arising from charge exchange $(M)^+$, proton transfer $(M + H)^+$, the loss of water from the $(M + H)^+$ ion, and the reaction of the $(M + H)^+$ ion with methanol (from HPLC eluent), followed by the loss of water (e.g., $(M + H + CH_3OH - H_2O)^+$). In general, the base peak in the mass spectra of the aliphatic carbonyls is either the $(M + H + CH_3OH - H_2O)^+$ ion, the $(M + H)^+$ ion, or the $(M + H - H_2O)^+$ ion. The $(M + H)^+$ ion is present at varying abundances in the mass spectra of the aliphatic carbonyls. The $(M + H + CH_3OH - H_2O)^+$ ion is present in the mass spectra of 2-undecanone, acetonylacetone, acetylbutyric acid, and 7-oxooctanoic acid, but not in the mass spectra of the straight-chain aldehydes. Each of these ions, the $(M + H + CH_3OH - H_2O)^+$, $(M + H)^+$, and $(M + H - H_2O)^+$ ions, is only present in the mass spectra of the aliphatic oxo acids, where the $(M + H - H_2O)^+$ ion is the base peak for each respective mass spectrum.

Similarly, the mass spectra of the aromatic carbonyls also contain the $(M)^+$, $(M + H)^+$, and $(M + H + CH_3OH - H_2O)^+$ ions. For all the aromatic aldehydes and ketones, with the exception of biphenyl-1-carboxyaldehyde and 2-indanone, the base peak is the $(M + H)^+$ ion. However, the $(M + H)^+$ ion in the mass spectra of biphenyl-1-carboxyaldehyde (73% relative intensity) and 2-indanone (46% intensity) is sufficiently abundant for molecular weight determinations. The mass spectra of the quinone species are characterized by adduct ions with methanol as well as ions due to the loss of water from the molecule with and without the addition of methanol. Interestingly, the mass spectra of the quinone analytes were the only mass spectra composed of high relative abundance $(M + 2H)^+$ ions, which is the base peak of the 1,4-naphthoquinone mass spectrum. The occurrence of the $(M + 2H)^+$ ion in APCI mass spectra of quinones (presumably due to reduction to dihydroxy forms) has also been previously observed by Letzel et al. for 1,4-benzoquinone.[34]

Although the number of molecules investigated within each class limits the data, we can suggest trends that may be useful in identification of unknown compounds by interpreting the APCI

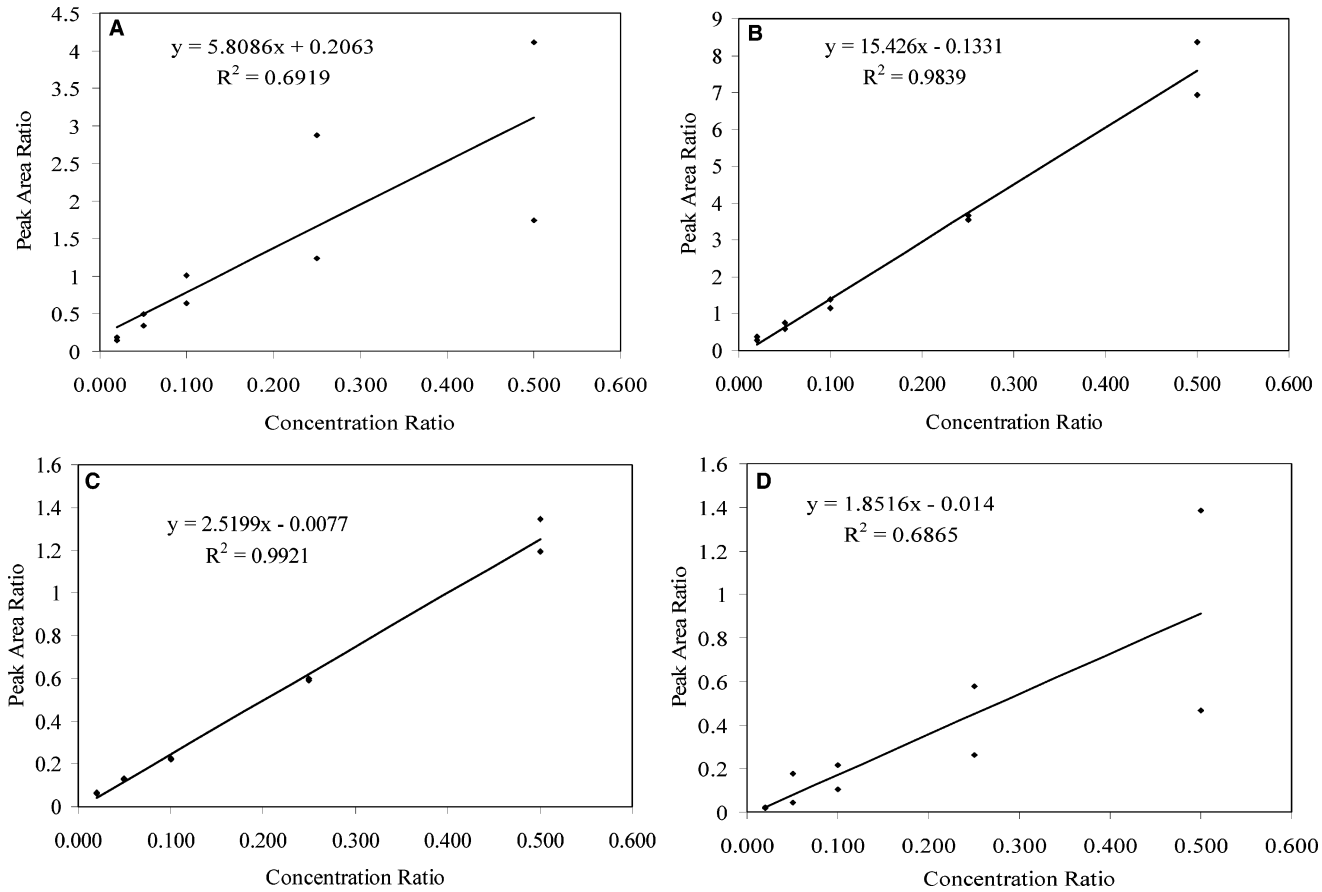

Figure 3. Example calibration curves for perinaphthenone using four different compounds as the quantification internal standard: (A) $^{13}C_6$ 4-hydroxybenzaldehyde, (B) 6-fluoro-4-chromanone, (C) 2-fluoro-9-fluorenone, and (D) d_4 1,4-benzoquinone.

mass spectra of carbonyls using positive ion detection. Foremost, a relationship between the observed ions can be used to identify the $(M + H)^+$ or $(M)^+$ ion. The following relationships may exist if a carbonyl is present: (1) the presence of two ions at high intensity that differ by 14 mass units indicates the presence of $(M + H)^+$ and $(M + H + CH_3OH - H_2O)^+$ ions; (2) the presence of two ions at high intensity that differ by 17 mass units indicates the presence of $(M + H)^+$ and $(M + H - H_2O)^+$ ions; (3) the presence of three high-intensity ions that differ by 1 and 14 mass units indicates the presence of a $(M + 2H)^+$, $(M + H)^+$, and $(M + H + CH_3OH - H_2O)^+$ ion. Any of these occurrences indicates that the compound may be a carbonyl. The first scenario indicates the presence of an aliphatic or aromatic carbonyl, the second may represent the presence of an aliphatic oxo acid, and the third suggests the presence of a quinone species.

An additional observation made through the analysis of other aliphatic carbonyls—it is difficult to obtain APCI mass spectra of aliphatic carbonyls with molecular weights of <120 amu. This may be due to either the inability to stably ionize these compounds or difficulties due to solvent cluster background.

Negative Ion Detection. A summary of the ions and their relative intensities for negative ion detection of the carbonyls is presented in Table S2 (Supporting Information). We attempted to analyze other aliphatic carbonyls (e.g., aldehydes, ketones, diones), including those listed in Table 1. However, the oxo acids, acetylbutyric and 7-oxooctanoic, were the only aliphatic species for which mass spectra were acquired easily. The mass spectra of these compounds is characterized by a base peak corresponding to the $(M - H)^-$ ion. APCI mass spectra of the targeted aromatic species are dominated by either an $(M)^-$ or $(M - H)^-$ ion. Mass spectra of the aromatic aldehyde, ketones, and quinones exhibit $(M)^-$ ions, while the mass spectra of the aromatic hydroxyl carbonyls were characterized by $(M - H)^-$ ions. This result is similar to that of Letzel et al. for aromatic carbonyls.[34] Of note is the mass spectrum for 2-indanone showing a fragmentation pattern different from that of the other aromatic ketones examined by both polarities of detection. One cannot generally explain why certain compounds form $(M)^-$ ions and others form $(M - H)^-$ ions. While the negative ion mass spectra do not provide information to indicate a carbonyl, the data can be used to verify the molecular ion in the positive ion APCI mass spectra.

Characterization of the APCI Mass Spectra of Carbonyl Pentafluorobenzyl Oximes. The results of analyses of PFB oxime derivatives of the targeted carbonyls using APCI/positive ion detection are presented in Table S3 (Supporting Information) and APCI/negative ion detection are presented in Tables S4 and S5 (Supporting Information). It is evident from these tables that the formation about the PFB oximes facilitated the sensitive detection of a larger number of compounds. Moreover, the selectivity of the analysis is enhanced, compared to the analysis of nonderivatized compounds, since PFBHA solely reacts with C=O moieties on the molecule.

Positive Ion Detection. The mass spectra of the PFB oxime derivatives is dominated by the presence of $(M + H)^+$ and $(M - 195)^+$ ions and an ion at m/z 181, corresponding to the PFB cation $(C_7H_2F_5)^+$. The $(M + H)^+$ ion is observed for all the targeted

Table 1. HPLC-APCI-ITMS Method Detection Limits for Model Carbonyls

	limit of detection[a,b] (pg)			
	native		PFBHA oxime	
	(+)	(−)	(+)	(−)
Aliphatics				
aldehyde				
pentanal			2600	
decanal			580	3400
tetradecanal	2300		27000	28000
ketone				
2-butanone			36	470
2-heptanone			18	380
2-undecanone			18	78000
dione				
2,3-butanedione			590	73
acetonylacetone			11	49
oxo acid				
acetylbutyric acid		400	250	210
7-oxooctanoic acid	4300	480	60	360
hydroxycarbonyl				
1-hydroxy-2-butanone			150	55
Aromatics				
aldehyde				
benzaldehyde			3000	33
biphenylcarboxaldehyde	39000		450	110
pyrenecarboxaldehyde	48	320	26	11000
ketone				
2-indanone	31000	1400	62	50
fluorenone	1000		88	450
benz[*de*]anthracenone	25	4100	250	
dicinnamalacetone	50	18000	18	3800
quinone				
1,4-naphthoquinone	27000	6100	26	240
9,10-anthraquinone	23000	4800	180	11000
1,4-chrysenequinone	3600	1100	41	4200
hydroxycarbonyl				
4-hydroxybenzaldehyde			170	20
2-hydroxyfluorenone	6800	3300	33	100
2-hydroxy-1,4-naphthoquinone	3300	240	4500	16000
α-naphtholbenzein	28	250	350	4800

[a] Limit of detection determined at signal/noise ratio of 3:1. [b] Blank cells indicate the analyte was not detected.

species, with the exception of acetylbutyric acid. PFB cation was present in the spectra of the lower molecular weight PFB oxime derivatives within most of the classes of compounds evaluated. Certain compounds' mass spectra contain the $(M - 195)^+$ fragment ion (e.g., decanal, tetradecanal, 2-undecanone, biphenylcarboxyaldehyde, 2-indanone, 9-fluorenone, 7-benz[*de*]anthracenone, and the aromatic hydroxy carbonyls). Fewer compounds exhibit a $(M + H - H_2O)^+$ ion (acetylbutyric acid, 1-hydroxybutanone) and a $(M - 180)^+$ fragment ion (pyrenecarboxyaldehyde, fluorenone, 4-hydroxybenzaldehyde, 2-hydroxyfluorenone).

Again, we can suggest trends that may be useful to identify the presence of a carbonyl and to identify the $(M + H)^+$ ion for molecular weight determinations. In the APCI/positive ion mass spectra of the pentafluorobenzyl oxime derivatives, it is likely that the highest mass ion is the $(M + H)^+$ ion. Similar to the approach used to identify pentafluorobenzyl derivatives by using GC/MS, the analyst can monitor m/z 181. The presence of this ion indicates the presence of a PFB oxime species. There are no absolute relationships among the ions that can uniquely differentiate between the classes of carbonyl species.

Negative Ion Detection. The APCI/negative ion mass spectra of the PFB oxime derivatives are characterized by losses of fluorine and hydrogen from the molecule, as well as fragment ions at m/z 167 $(C_6F_5)^-$, 178 $(C_7H_2F_4)^-$, 197 $(C_7H_2F_5O)^-$, and 218 $(C_9H_4F_4NO)^-$. Additionally, many of the aromatic mass spectra exhibit a fragment ion arising from a loss of the PFB portion of the oxime, i.e., $(M - 181)^-$. Based on the observed mass spectra for the evaluated compounds, it appears that the presence of a m/z 167 or 178 negative ion is a likely indicator of the presence of a PFB oxime. Interestingly, the presence of an ion at m/z 218 appears to be selective to aliphatic ketones, diones, or oxo acids.

Since a high-mass ion is generally absent in the mass spectra of the APCI/negative ion detection mass spectra of the native aliphatic species, it would be difficult to derive the elemental formula of the molecule. In contrast, the mass spectra of the pentafluorobenzyl oximes of the aliphatic may be composed of $(M - H)^-$ ions or $(M - H - HF)^-$ ions that can facilitate elemental formulas. These ions would be the highest mass ions in the mass spectra of aromatic carbonyls.

The application of APCI/negative ion detection mass spectrometry for the detection of carbonyls as DNPH derivatives has been evaluated elsewhere.[21,23,24] The predominant base peak in the DNPH negative ion mass spectra corresponded to the $(M - H)^-$ ion. However, the absence of characteristic fragment ions limits the identification of unknown carbonyl species, unless additional fragmentation is performed using MS(n) techniques.[23,24]

In summary, interpretation of the APCI/positive and negative ion mass spectra of carbonyls and their PFB derivatives provides complementary information, which may facilitate molecular weight determinations of unknowns. While interpretation of the APCI/positive ion detection of pentafluorobenzyl oxime derivatives of carbonyls appears to be the most useful for obtaining molecular weight information, it may also be helpful in suggesting the nature of the carbonyl (aliphatic vs aromatic, and class of the molecule) for high molecular weight species (e.g., $m/z > 200$).

Assessment of Analytical Method Sensitivity. Method sensitivity for the model carbonyl species was determined for all four methods of analysis examined. The instrumental limits of detection, determined at a signal/noise ratio of 3:1, are presented in Table 1. Analysis of the native carbonyl species yielded a detectable signal for 15 of the model carbonyls. For the compounds observed without derivatization, the application of negative ion detection resulted in a lower detection limit for seven compounds, with the exceptions being pyrenecarboxaldehyde, benz[*de*]anthracenone, dicinnamalacetone, and α-naphtholbenzein.

Application of PFBHA derivatization in conjunction with APCI mass spectrometry facilitated the detection of 10 additional carbonyl species. Of the compounds observed by positive ion detection the detection limits of the PFB oximes were lower for 9 of the 14 carbonyls. Compounds that showed significant reductions in the detection limit, more than 1 order of magnitude, were 7-oxooctanoic acid, biphenylcarboxaldehyde, 2-indanone, fluorenone, 1,4-naphthoquinone, 9,10-anthraquinone, 1,4-chrysenequinone, and 2-hydroxyfluorenone. Examining negative and posi-

Table 2. HDV Emission Factors for Carbonyls Determined by HPLC-APCI−ITMS

compound	emission rate[a,b] (μg km^{-1}) gas phase	particle phase
aliphatic ketones		
3-pentanone	23 ± 10	
2-hexanone	260 ± 110	18 ± 7
2-heptanone	63 ± 4	
2-octanone	100 ± 6	
2-nonanone c	440 ± 27	
unsaturated aliphatics		
3-methyl-2-cyclopentenone	40 ± 5	0.80 ± 0.10
4-hexen-3-one		0.55 ± 0.07
5-hexen-2-one	190 ± 24	
2-cyclohexen-1-one	12 ± 2	
aliphatic dicarbonyls		
2,5-hexanedione	110 ± 5	1.6 ± 0.1
aromatic carbonyls		
4-ethylbenzaldehyde	140 ± 34	
acetophenone	110 ± 24	
1-indanone	29 ± 6	
9-fluorenone	120 ± 27	12 ± 3
perinaphthenone	18 ± 4	30 ± 7
benzophenone	47 ± 11	0.72 ± 0.16
quinones		
1,4-benzoquinone	150 ± 7	
methyl-1,4-benzoquinone	16 ± 1	
1,2-naphthoquinone		4.4 ± 0.2
1,4-naphthoquinone	70 ± 3	2.1 ± 0.1
2-methyl-1,4-naphthoquinone	540 ± 26	
acenaphthenequinone		4.3 ± 0.2
anthraquinone		58 ± 3
phenanthrenequinone		3.0 ± 0.1

[a] Empty cells indicate either the species was not observed or the sampled concentration was insignificant in relation to the background concentration. [b] Gas phase corrected for recovery of 5-fluoro-1-indanone and particle phase corrected for recovery of 8-fluoro-1-benzosuberone. [c] Compound identity is tentative due to lack of an authentic standard; quantification is estimated using the response factor of the 3-nonanone isomer.

tive ion detection for the PFB oximes reveals that seven compounds have lower detection limits using negative ion detection. Of these compounds, only benzaldehyde exhibited a detection limit reduction of greater than 1 order of magnitude. Based on the results obtained for the model carbonyls investigated, the application of PFBHA derivatization in conjunction with APCI-MS enhanced the detection or sensitivity for 20 of the 25 compounds examined. Compounds whose HPLC-APCI-MS analysis was not improved by PFBHA derivatization were tetradecanal, benz[*de*]-anthracenone, 2-hydroxy-1,4-naphthoquinone, and α-naphtholbenzein.

Identification of Carbonyls in Heavy-Duty Diesel Vehicle Emissions. The emission factors for a 1999 Freightliner HDV are presented in Table 2. Additional information on the approach utilized to generate the emission factors is available elsewhere.[44] Twenty-four compounds, analyzed as PFB oximes, were identified and quantified in the HDV emissions including aliphatic and aromatic ketones, aldehydes, dicarbonyls, and unsaturated species. Underivatized analyses of the sample extracts were not performed due to the enhanced sensitivity provided by PFBHA derivatization.

Table 3. Method Comparison for HDV Gas-Phase Emission Factors of Carbonyls

compound	emission rate (μg km^{-1}) LC−MS	GC/MS
aliphatic ketones		
3-pentanone	23 ± 10	4.4 ± 1.8
2-hexanone	260 ± 110	150 ± 63
unsaturated aliphatics		
3-methyl-2-cyclopentenone	40 ± 5	60 ± 7
2-cyclohexen-1-one	12 ± 2	23 ± 3
aliphatic dicarbonyls		
2,5-hexanedione	110 ± 5	190 ± 9
aromatic carbonyls		
4-ethylbenzaldehyde	140 ± 34	360 ± 90
acetophenone	110 ± 24	120 ± 27
1-indanone	29 ± 6	41 ± 9
9-fluorenone	120 ± 27	130 ± 30
benzophenone	47 ± 11	66 ± 15
quinones		
1,4-benzoquinone	150 ± 7	420 ± 20

One compound whose identification and quantification are tentative due to the lack of an authentic standard is 2-nonanone. Sample extracted ion chromatograms for the separation of several authentic aliphatic ketone PFB oxime isomers is provided in Figure S3 (Supporting Information), along with the extracted ion for the diesel gas-phase emission extract. The emission factors for the carbonyls identified ranged from 540 to 0.55 μg km^{-1}. The reported values included error estimates based on the relative error assessed during an analyte recovery experiment of model carbonyls determined in our laboratory (data not presented).

In general, the emission factors for carbonyls observed in the gas phase exceed those of the particulate phase. For compounds observed in both phases, the gas-phase emissions are at least a factor of 10 greater than those for the particulate phase for all compounds, except perinaphthenone. To validate the gas-phase emission factors obtained by HPLC-APCI-MS, a comparison is made to results obtained by GC/MS; see Jakober et al. for analysis methodology description.[44] These results are presented in Table 3, with 8 of 11 compounds agreeing with the GC/MS analysis within a factor of 2.

Certain species identified using HPLC-APCI-MS in the HDV emission samples are of particular interest. Eight different quinone compounds were observed in the HDV emissions. Of these compounds, 1,4-benzoquinone, methyl-1,4-benzoquinone, 2-methyl-1,4-naphthoquinone, and acenaphthenequinone are identified here for the first time as components of HDV emissions. Excellent agreement was found for several compounds, on a PM mass basis, with the previous results of Cho et al.[45] The quinone emissions were not isolated to the particulate phase, with the monoaromatic ring species observed solely in the gas phase and the multiaromatic ring quinones in both phases.

CONCLUSIONS

The utility of HPLC-APCI-MS for the analysis of carbonyls in motor vehicle source emissions was verified. Application of

(45) Cho, A. K.; Di Stefano, E.; You, Y.; Rodriguez, C. E.; Schmitz, D. A.; Kumagai, Y.; Miguel, A. H.; Eiguren-Fernandez, A.; Kobayashi, T.; Avol, E.; Froines, J. R. *Aerosol Sci. Technol.* **2004**, *38*, 68−81.

PFBHA derivatization in conjunction with HPLC-APCI-MS enhanced the analysis of targeted carbonyl compounds leading to increased detection and improved detection limits. The developed methodologies lead to the measurement of several new carbonyls as components of HDV emissions. Thus, based on the obtained results, the application of HPLC-APCI-MS in conjunction with traditional GC/MS methods for PFBHA oximes of carbonyls has the ability to enhance the chemical analysis power of the PFBHA derivatization methodologies beyond the chemical speciation of carbonyls previously observed.

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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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