Final Report

Linkages Between Measurements of Multifunctional and Polar Organics in Chamber Studies and the Ambient Environment

Prepared For:

State of California Air Resources Board
Research Division
PO Box 2815
Sacramento, CA. 95812

Prepared By:

M. Judith Charles and Reggie S. Spaulding
Department of Environmental Toxicology
University of California, Davis
Davis, CA. 95616

under contract

98-311

May 30, 2002

Disclaimer

The statements and conclusions in this Report are those of the contractor and not necessarily those of the California Air Resources Board. The mention of commercial products, their source, or their use in connection with material reported herein is not to be construed as actual or implied endorsement of such products.

Acknowledgents

This work was possible due to the significant contributions of many outstanding scientists. Foremost, we thank Paul Frazey, Xin Rao, Brian Beld, Reiko Kobayashi and Rochelle White-Morris for performing experiments described herein. We thank Dr. Robert W. Talbot for providing expertise in the design and operation of the mist chamber (Cofer scrubber). We thank Dr. Allen Goldstein and Dr. Gunnar Schade for facilitating sampling of isoprene photooxidation products at the Blodgett Forest Research Station; David Paige for help with construction of the mist chamber and Elsie Ovrahim for help with sample collection. We also thank Dr. Elliott Atlas for suggesting the use of the mist chamber, and Dr. Dan Chang and Dr. Myoseon Jang for helpful discussions. We sincerely thank Matthew Lashley and Dr. Michael H. Nantz for the synthesis of 2-hydroxy-2-methylpropanal. We are deeply grateful to Drs. Roger Atkinson, Janet Arey and Ernesto Tuazon, Air Pollution Research Center, University of California, Riverside for their support and assistance with chamber experiments. Evaluation of the ozone removal devices was performed at the Inhalation Exposure Facility, California Regional Primate Center, University of California Davis, which is supported by NIH/NCRR Grant No. P51RR00169. In addition, we want to acknowledge additional support by the National Science Foundation, Atmospheric Chemistry Program (Grant No. 00137) and an NIEHS Training Grant (Grant No. T32 ES07059).

Table of Contents

List of Tables

Chapter 1.

Chapter 2

List of Figures.

Chapter 1.

Chapter 2

Abstract

This work develops and applies methods to measure oxygenated organics in aerosols and fine particulate matter. Such methods are needed to gain further insight into chemical processes affecting the generation and fate of oxidation products of hydrocarbon emissions, and source apportionment of fine particulate matter. We establish the power of methods that rely on employment of *O*- (2,3,4,5,6-pentalfuorobenzyl)-hydroxylamine (PFBHA) and *bis* (trimethylsilyl) triflouroeacetamide (BSTFA) to derivatize carbonyls and multifunctional carbonyls, and measurement of the derivatives by using gas chromatography/ion trap mass spectrometry (GC/ITMS). By using this approach, we report for the first time in the ambient atmospheric environment, the presence of hydroxy acetone, 3-hydroxy-butanone, and 2-hydroxy-2-methylpropanal, and novel high molecular weight ($>C_{10}$) oxygenated organics in $PM_{2.5}$ that may be tracers of diesel- particulate matter. We also establish the utility of using a mist chamber to sample water-soluble organics, with Henry's law constants greater than 10^3. We applied the method to measurements of pptv levels of isoprene and 2-methyl-3-buten-2-ol (MBO) photooxidation products in the Blodgett Forest, CA. using sampling times of 10 minutes to support the results of chamber studies.

Executive Summary.

Background: Tropospheric ozone (O_3) is an important infrared active ("greenhouse") gas and air pollutant while the OH radical has a key role in removing trace gases from the atmosphere. Fine particles are also significant air pollutants that affect visibility, the production of haze, and the oxidative capacity of the atmosphere. Both ozone and fine particles adversely affect human health. Ozone is a respiratory irritant that is associated with an increase in asthma in children. An increase in mortality, morbidity and hospital admissions on days of poor air quality are associated with high concentrations of fine particles in air. In spite of enormous efforts to control ozone and particulate matter in the environment, millions of people reside in counties that exceed the regulatory standards. Two significant gaps that affect the formulation of effective strategies to reduce levels of these pollutants are: 1) an understanding of chemical processes and reactions that affect the formation of ozone, fine particulate matter and secondary organic aerosols which includes knowledge of the generation and fate of first-, second- and third- generation oxidation products of anthropogenic and biogenic emissions, and 2) a complete understanding of sources of fine particulate matter, and photooxidation reactions occurring on the particles as they are transported from source to receptor. Herein, we address these gaps by developing and applying methods to measure oxygenated organics that arise from biogenic and anthropogenic emissions in aerosols, and developing and applying a method for molecular speciation of diesel- and gasoline- emissions, with the hope of identifying novel organics that enable differentiation of diesel- and gasoline- particles in the ambient environment.

Methods: The methods used in this study rely on either utilization of impingers or a mist chamber filled with an aqueous solution of *O*- (2,3,4,5,6-pentalfuorobenzyl)-hydroxylamine (PFBHA) to sample oxygenated organics in aerosols, or employment of an Interagency Monitor of Protected Visual Environments (IMPROVE) Module Aerosol to sample fine particulate matter with aerodynamic diameters <2.5μm ($PM_{2.5}$). After derivatization, the PFBHA derivatives are extracted into solvent, and the PFBHA derivatives of multifunctional carbonyls are further derivatized with *bis* (trimethylsilyl)

triflouroacetamide (BSTFA) to silyate the -OH and -COOH moieties on the molecules. The derivatives are analyzed by using gas chromatography/ion trap mass spectrometry (GC/ITMS). Identification of the analytes are determined by interpretation of the electron-ionization, methane chemical ionization, and pentaflurobenzyl alcohol (PFBOH) chemical ionization ion trap mass spectra. Quantification was accomplished by using internal standardization. $^{13}C_3$-acetone was chosen as the internal standard for quantification of mono-functional carbonyls because the retention time of the PFBHA derivative of $^{13}C_3$-acetone is similar to the retention time of other mono-functional carbonyls of interest to this project. 4-hydroxybenz-$^{13}C_6$-aldehyde was chosen as the internal standard for quantification of hydroxycarbonyls and keto-acids because for both classes of compounds the carbonyl moiety is derivatized with PFBHA, and the -OH or -COOH moiety is derivatized with BSTFA. 4-fluorobenzaldehyde was used as the internal standard for quantification of the dicarbonyls due to previous success using this internal standard. Semi-quantification of 2-hydroxy-2-methylpropanal in ambient air samples was accomplished by using 3-hydroxy-3-methyl-2-butanone standard as a surrogate and 4-hydroxybenz-$^{13}C_6$-aldehyde as the internal standard.

Results. We first established the power of using PFBHA and PFBHA/BSTFA derivatization in concert with GC/ITMS by sampling and measuring carbonyls and multifunctional carbonyls in air collected in Azusa, CA. In this study, the methods afforded the first report of hydroxy acetone and 3-hydroxy-2-butanone in the ambient atmospheric environment. This initial work was a significant contribution to the measurement of hydroxy carbonyls in air. The research establishes the potential of the method to measure oxygenated organics for which no or little ambient air data exist, and it is the first study that applies pentafluorobenzyl derivatization along with ion trap mass spectrometry to measure carbonyls in the ambient atmospheric environment. A limitation of the sampling method however was the use of impingers, which due to the low flow-rates (0.5-1L/min.) compatible with their use, require long (4-8 hr.) sampling times to measure part-per-trillion levels of the analytes. To improve the method, we optimized and evaluated a mist chamber, which operates at a flow rate about 20 to 25L/minute. The use of this sampler provided sampling times of 10 minutes. The results establish a

relationship between the Henry's law constant (K_H) and the collection efficiency, and establishes the suitability of the method to measure analytes with $K_H \geq 10^3$ M atm^{-1}. Adjusting the pH, adding quaternary ammonium salts, or decreasing the temperature of the collecting solution in the mist chamber did not significantly affect the collection efficiency. We tested the method by sampling photooxidation products of isoprene (glyoxal, methyl glyoxal, hydroxyacetone, and glycolaldehyde) and 2-methyl-3-buten-2-ol (2-hydroxy-2-methylpropanal) near the Blodgett Forest, CA. This first report of a study the employs the mist chamber to sample hydroxy carbonyls establishes that by using a mist chamber in concert with the derivatization methods and GC/ITMS, pptv levels of photooxidation products of isoprene, a biogenic hydrocarbon can be obtained by using sampling times of 10 minutes. The use of short sampling times is significant advancement over existing methods. It enables further studies on the generation and fate of carbonyls and multifunctional carbonyls to be conducted with a time resolution sufficient to gain insight into photoxidation reactions in the ambient environment. Support of research conducted in chambers was obtained by collaborating with Drs. Atkinson, Arey and Tuazon at the Air Pollution Research Center, University of California, Riverside. In this study, chamber and ambient air experiments to provide further evidence that 2-hydroxy-2-methylpropanal is generated by ·OH reaction of 2-methyl-3-buten-2-ol (MBO), and to support chemical mechanisms elucidated from chamber studies. Tentative identification of 2-hydroxy-2-methylpropanal was possible by using knowledge gained in this study regarding the mass spectrometry of PFBHA-BSTFA derivatives of carbonyls with primary, secondary, and tertiary -OH groups, and aldo- and keto-acids. The identification was confirmed by comparing the methane CI mass spectra and relative gas chromatographic retention time obtained by analyzing 2-hydroxy-2-methylpropanal in a sample extract and a synthesized authentic standard. Since the standard became available at the end of this study (after all samples were analyzed), we also developed a method for semi-quantification of 2-hydroxy-2-methylpropanal, with a detection limit of 27 pptv in air. Investigators who have not synthesized an authentic standard can use this method.

The power of the method to identify novel oxygenated organics was further established in the previous studies and in a study conducted that measured these compounds ($PM_{2.5}$) collected in the Caldecott tunnel. 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 to an authentic standard. Quantification 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-hydroxybenzaldheyde in $PM_{2.5}$ particles sampled in a roadway tunnel. It is also the first report of a C_{10} carbonyl with the molecular formula of $C_{10}H_{16}O_2$, a hydroxy carbonyl with the molecular formula of $C_{17}H_{21}NO_2$, and a hydroxy or di-hydroxy carbonyl with the molecular formula of $C_{16}H_{14}O_2$ or $C_9H_{10}O_3$. The high-molecular weight hydroxy carbonyls, which were found only in the heavy- duty (diesel) bore, may be tracers of diesel emissions in air.

Conclusions: We established the power of using PFBHA and PFBHA/BSTFA derivatization in conjuction with interpretation of the elelctron-ionization, methane chemical ionization and PFBH chemical ionization ion trap mass spectra to identify pptv levels of carbonyls in complex mixtures. By using the method, we identified novel carbonyls in aerosols and particulate matter, for which authentic standards and a paucity of ambient air data exist. In addition, the method provides accurate and precise quantification of the analytes. Sampling aerosols can be conducted by using impingers that utilize long sampling times (e.g., 4-8 hours) or by a mist chamber that employ short sampling times (e.g., 10 minutes). The method provides detection limits that are an order of magnitude more sensitive than other methods for the measurement of glyoxal and hydroxyacetone, and similar detection limits for glycolaldehyde and glyoxal. A limitation of the current mist chamber method is that it affords the measurement of compounds with Henry's law constants greater than 10^3. Further work is needed to improve the method to broaden the range of compounds that can be investigated, including the less polar carbonyls and carboxylic acids. The methods as they exist however, can be employed to gain insight into the formation and fate of first-, second-,

and third- photooxidation products, and to investigate oxygenated molecules that may be unique to diesel- or gasoline- emissions.

Overview

Tropospheric ozone (O_3) is an important infrared active ("greenhouse") gas and air pollutant while the OH radical has a key role in removing trace gases from the atmosphere. Fine particles are also significant air pollutants that affect visibility, the production of haze, and the oxidative capacity of the atmosphere. Both ozone and fine particles adversely affect human health. Ozone is a respiratory irritant that is associated with an increase in asthma in children. An increase in mortality, morbidity and hospital admissions on days of poor air quality are associated with high concentrations of fine particles in air. Two significant gaps that affect the formulation of effective strategies to reduce levels of ozone, fine particulate matter and secondary organic aerosols in the ambient environment are: 1) a complete understanding of chemical processes and reactions that affect the formation of ozone, fine particulate matter and organic aerosols in the ambient environment which considers the generation and fate of first-, second- and third- generation oxidation products of anthropogenic and biogenic emissions, and 2) a complete understanding of sources of fine particulate matter, and photooxidation reactions occurring on the particles as they are transported from source to receptor. Herein, we address these gaps by: 1) developing and applying methods to measure oxygenated organics that arise from biogenic and anthropogenic emissions in aerosols, and 2) developing and applying a method for molecular speciation of diesel- and gasoline- emissions, with the hope of identifying novel organics that enable differentiation of diesel- and gasoline- particles in the ambient environment.

The specific objectives of the project were to:

1) Complete characterization of multifunctional carbonyls in samples collected in Azusa on September 23rd and 24th as part of the 1997 Southern California Study.

2) Improve, evaluate and validate methodology to measure multifunctional carbonyls by conducting collaborative research with Drs. Atkinson and Arey, University of California, Riverside, and sampling the ambient environment.

3) Complete the characterization of polar organics in fine particulate matter collected from the Caldecott Tunnel on November 17-20, 1997.

4) Collaborate with Air Resources Board to investigate oxygenated multifunctional compounds as markers for stationary sources.

In Chapter 1, entitled " The Measurement of Hydroxy Carbonyls and other Carbonyls in Ambient Air Using Pentafluorobenzyl Alcohol as a Chemical Ionization Reagent", we describe research that fulfills the first objective. In Chapter 2, entitled "Optimization of a Mist Chamber (Cofer Scrubber) for Sampling Water-Soluble Organics in Aerosols", and Chapter 3, entitled "Advances in the Analytical and Atmospheric Chemistry of 2-hydroxy-2-methylpropanal, a Proposed Photooxidation Product of 2-methyl-3-buten-2-ol, we desecribe research that fulfills the second objective. Research that completes the fourth and fifth objectives is dessribed in Chapter 4 entitled " Measurement of Carobnyls and Multifunctional Carbonyls in $PM_{2.5}$ Particles Emitted from Motor Vehicles". Although we discuss the method in relationship to the investigation of compounds in mobile sources, the method is also applicable to the identification of compounds in stationary sources. ARB provided us with a list of compounds that may be specific to stationary sources. It is possible to use the methods developed herein, or modifications of the methods developed to investigate tracers of stationary sources. For example, we can use pentafluorobenzyl bromide to derivatize carboxylic acids. We will work with ARB to identify approaches applicable for source apportionment of stationary sources. We anticipate ensuing discussions in the near future. Each chapter is written so that the chapters stand independently of each other, and thus have their own Abstract, Table of Contents, List of Tables, List of Figures and References. Chapters 1, 3 and 4 were published as the following journal articles:

Spaulding, R. S., Frazey, P., Rao, X., Charles, M. J. **1999**. The Measurement of Hydroxy Carbonyls and other Carbonyls in Ambient Air Using Pentafluorobenzyl Alcohol as a Chemical Ionization reagent. *Anal. Chem.,* 16:3420-3427. (Chapter 1).

Spaulding, R. S., Talbot, R. W., Charles, M. J., **2002**. Optimization of a Mist Chamber (Cofer Scrubber) for Sampling Water Soluble Organics in Air. *Environ. Sci. & Technol.* 36:1798-1808. (Chapter 2).

Spaulding, R. S., Tuazon, E. C., Lashley, M., Charles, M. J. **2002.** Ion Trap Mass Spectrometry Affords Advances in the Analytical and Atmospheric Chemistry of 2-hydroxy-2-methylpropanal, a Proposed Photooxidation Product of 2-methyl-3-buten-2-ol. *JASMS*, 13:530-542. (Chapter 3).

Rao, X., Kobayshi, R., White, R., Spaulding, R., Frazey, P., Charles, M. J. **2001**. GC/ITMS Measurement of Carbonyls and Multifunctional Carbonyls in $PM_{2.5}$ Particles Emitted from Motor Vehicles. *JAOAC International,* 84:699-705. (Chapter 4).

Chapter 1.

The Measurement of Hydroxy Carbonyls and other Carbonyls in Ambient Air Using Pentafluorobenzyl Alcohol as a Chemical Ionization Reagent.

Table of Contents

List of Tables

List of Figures.

Figure 1.6. Ion trap mass spectra of an unknown PFBHA/BSTFA derivative in an extract of air collected in Davis, CA.

Figure 1.7. Ion trap mass spectra of a PFBHA derivative in an extract of air Collected in Davis, CA.

Abstract

Hydroxy carbonyls and other carbonyls were measured in air by sampling with impingers filled with an aqueous solution of *O*-(2,3,4,5,6-pentafluorobenzyl)-hydroxylamine hydrochloride (PFBHA), further reacting the PFBHA derivatives of hydroxy carbonyls with *bis* (trimethylsilyl) trifluoroacetamide (BSTFA), and detecting the derivatives with gas chromatography/ion trap mass spectrometry. Molecular weight determinations of ultratrace (pptv) levels of the derivatives in the presence of co-eluting interferences was made possible by using pentafluorobenzyl alcohol (PFBOH) as a chemical ionization reagent. Methyl vinyl ketone, methacrolein, methyl glyoxal, glycolaldehyde and hydroxy acetone were identified in air collected in Azusa, CA. Methyl vinyl ketone, methacrolein, methyl glyoxal, hydroxy acetone, glyoxal and 3-hydroxy-2-butanone were identified in samples collected in Davis, CA. To our knowledge, this is the first report of hydroxy acetone and 3-hydroxy-2-butanone in the ambient atmosphere. This work is a significant contribution to the measurement of hydroxy carbonyls in air. It demonstrates the potential of the method to measure water-soluble carbonyls for which no or little ambient air data exist. It is also the first study that applies pentafluorobenzyl derivatization along with ion trap mass spectrometry to measure carbonyls in the ambient atmospheric environment.

I. Introduction.

Photochemical reaction studies conducted in chambers rely on the identification of reaction products to elucidate chemical mechanisms. Such studies demonstrate that the photooxidation of anthropogenic and biogenic hydrocarbons yields multi-functional carbonyls, including hydroxy carbonyls. The production and subsequent atmospheric reactions of these water-soluble organics influences the population of radical species (*e.g.*, OH radicals) and NO_x that play a critical role in tropospheric ozone formation. Water-soluble organics also act as cloud condensation nuclei, and alter characteristics of aerosols that affect the impact of fine particulate matter on human health and the environment (Saxena et al., 1995, Lee et al., 1995, Li et al., 1996, Lee et al., 1998). The generation and fate of hydroxy carbonyls and other multi-functional carbonyls in the ambient environment, and their impact on air quality however is not well understood. This is primarily due to the absence of methods suitable to measure ultratrace (pptv) levels of these compounds in air.

Both atmospheric pressure chemical ionization mass spectrometry (APCI/MS) and *O*-(2,3,4,5,6-pentafluorobenzyl)- hydroxyl amine (PFBHA) derivatization/chemical ionization ion trap mass spectrometry (CI/ITMS) were employed to identify hydroxy carbonyls and other carbonyls in chamber studies (Kwok et al., 1996a, Kwok et al., 1996b, Shu et al., 1997, Kwok et al., 1995, Yu et al., 1997, Yu et al., 1995, Chien et al., 1998, Tuazon and Atkinson, 1990). In the ambient environment, hydroxy carbonyls were measured by using dansylhydrazine (DNSH) impregnated cartridges and HPLC/fluorescence detection (Nondek et al., 1992), and a pyrex coil gas-liquid scrubber with 2,4-dinitrophenylhydrazine (DNPH) derivatization/high-performance liquid chromatography (Lee and Zhou, 1993). The DNPH method has been widely used to measure carbonyls, and other more polar carbonyls, including glyoxal, methyl glyoxal and glycolaldehyde in air and aerosols (Lee et al., 1995, Li et al., 1996, Lee et al., 1998, Kleinman et al., 1994, Lee et al. 1996). Neither of these methods has however afforded the measurement of hydroxy acetone or other hydroxylated carbonyls identified as photooxidation products in chamber studies (*e.g.*, hydroxy methyl vinyl ketone, 1-hydroxy-3-methyl-3-buten-2-one,

hydroxy methyl glyoxal, C_5 hydroxy carbonyls and C_4 hydroxy dicarbonyls). Other limitations of the DNPH method are that it suffers from poor chromatographic resolution of similar carbonyls, difficulties differentiating α-hydroxycarbonyls from dicarbonyls, the inability to identify carbonyls for which authentic standards do not exist, the formation of artifacts, and retention of glycolaldehyde and hydroxyacetone on DNPH cartridges (Yu et al., 1995, Grosjean et al., 1994, Martin et al., 1991, Tanner and Meng, 1984, Lipari and Swarin, 1982). In contrast, the PFBHA/ion trap method provides excellent chromatographic separation of carbonyl derivatives, unambiguous molecular weight determinations of carbonyls for which authentic standards do not exist, and measurement of the various types of carbonyls identified as products of photooxidation reactions (*i.e.*, carbonyls, dicarbonyls, hydroxy carbonyls, epoxy carbonyls and oxo acids). A unique feature of the measurement of pentafluorobenzyl derivatives in the ion trap is the generation of $(M+H)^+$ and $(M+181)^+$ ions in the methane chemical ionization mass spectra that facilitate molecular weight determinations of the derivatives (Yu et al., 1995).

By using pentafluorobenzyl alcohol (PFBOH) as a chemical ionization reagent, the intensity of the $(M+H)^+$ and $(M+181)^+$ ions can be increased to simplify molecular weight determinations (Chien et al., 1998, Frazey et al., 1999). In combination with methane, PFBOH chemical ionization (CI) was utilized to identify novel phenolic and carboxylic acid products of photooxidation reactions in chamber studies (Chien et al., 1998). PFBOH, itself effects the generation of $(M-H)^+$, $(M)^{+\cdot}$, $(M+H)^+$ and $(M+181)^+$ ions. This knowledge along with isolation of a reagent ion prior to reaction with the neutral analyte derivative was employed to identify a component of filter extract in fine particulate diesel exhaust (Frazey et al., 1999). Herein, we present a modification of the method to sample ultratrace (pptv) levels of hydroxy carbonyls and other carbonyls in air. To our knowledge, this is the first report of hydroxy acetone and 3-hydroxy-2-butanone in the ambient atmosphere. Thus, this work is a significant contribution to the measurement of hydroxy carbonyls in air. It demonstrates the ability of the method to measure multi-functional carbonyls for which no or little ambient air data exist. It is also the first study that applies pentaflurobenzyl derivatization along with ion trap mass spectrometry to measure carbonyls in ambient air.

II. Experimental

A. Experimental Chemicals.

Carbonyl moieties were derivatized with *O*-2,3,4,5,6-pentafluorobenzyl)-hydroxylamine hydrochloride (PFBHA). *Bis* (trimethylsilyl) trifluoroacetamide (BSTFA), and N-*tert*-butyldimethylsilyl)-N-methyltrifluoroacetamide (MTBSTFA) were employed as silylation reagents. Derivatization reagents, pentafluorobenzyl alcohol and authentic standards were purchased from Aldrich Chemical Co., Inc., Milwaukee, WI. HPLC- grade water, methyl- *tert*-butylether (MTBE) and concentrated sulfuric acid were purchased from Fisher Scientific, Fairlawn, NJ. Prior to sampling air in Azusa, CA., the HPLC water was purified by passing the water through a Norganic cartridge (Millipore Corporation, Bedford, MA) to remove organic contaminants. Prior to sampling air in Davis, CA. , the MTBE and the HPLC water were purified by distillation, and organic compounds in the HPLC water were oxidized with potassium permanganate before distillation.

B. Sample Collection.

Samples were collected in Azusa, CA as part of the 1997 Southern California Oxidant Study (SCOS). Air was sampled at a flow rate of 0.5L/minute into four 400 mL. impingers in series. Samples were collected on September 23 and 24, 1997. On September 23, air was sampled from 1:00-4:00 p.m., and from 5:00-8:00 p.m. On September 24, air was sampled from 1:00 p.m. to 5:00 p.m. In Davis, air was sampled by using four 20 mL impingers in series. Davis air was sampled on the roof of Meyer Hall on May 15, 1998 from 12:35-6:15 p.m. Each impinger contained 0.10 mM of an aqueous solution of PFBHA prepared in purified HPLC grade water. Potassium iodide (KI) scrubbers were employed to remove ozone. In Davis, air was also sampled in the absence of KI traps. In this case, the sampler inlet was identical except the tubing was not coated with KI. The volume of air sampled in Azusa, CA. was measured with a dry gas meter and corrected to ambient pressure and temperature conditions. The system was tested for leaks to ensure that losses of air did not contribute to greater than 10% of the flow. The

impingers were immersed in an ice bath to minimize volatilization of the analytes and covered with aluminum foil to prevent photolysis reactions from occurring in solution.

C. Potassium Iodide (KI) Scrubbers.

Potassium iodide traps were prepared by passing a saturated KI solution through 1-m lengths of stainless steel tubing (3/8" o.d., 1/4" i.d.). The tubes were dried with a stream of nitrogen and the traps were sealed until used. Prior to sampling in the field, we established that the traps were capable of removing 99.5% of the ozone from a 1 ppm ozone standard sampled at a flow rate of 2L/min.

D. Preparation of Samples, Field Blank and Matrix Spike.

The field blank was a 0.10 mM aqueous solution of PFBHA kept in an ice bath aside the impingers during sampling. The matrix spike for the samples collected in Azusa, CA. was an aqueous solution of PFBHA enriched to contain 2.5 ng/mL each of methyl vinyl ketone, methacrolein, 2,3-butanedione and hydroxy acetone. The internal standard (1 μg of 4-fluorobenzaldehyde) was added to each sample and the PFBHA was allowed to react with the analytes for 24 hours at room temperature. For the 400-mL samples, the solution was acidified with 5 mL of 18N H_2SO_4 before extracting the derivatives from solution by using C_8 solid phase cartridges (6 mL, 500 mg; Varian Associates, Sugarland, TX), and eluting the derivatives from the cartridges with 12 mL of methyl *tert*-butyl ether (MTBE). The 10-mL samples were acidified with four drops of 18N H_2SO_4 before liquid-liquid extraction of the derivatives into 4 mL MTBE. In both cases, the extract was passed through a glass column (6 mm i.d. x 6.5 cm) filled with Na_2SO_4 to remove water, and the volume was reduced to 475 μL by evaporating the solvent under a gentle stream of nitrogen. An aliquot was transferred to another vial. The solvent was evaporated with nitrogen and redissolved in 200 μL of BSTFA. The air was displaced from the vial with nitrogen. The vials were sealed and heated to 42°C. The BSTFA was allowed to react with the PFBHA derivative at this temperature for 12 hours.

E. Gas Chromatography/Ion Trap Mass Spectrometry (GC/ITMS).

A Varian Star 3400 CX gas chromatograph, with a temperature programmable injector port interfaced to a Saturn 2000 ion trap mass spectrometer (Varian Associates, Sugarland, TX) was employed. Chromatographic separation of the derivatives was accomplished on a RTX-5MS chromatographic column (60 m, 0.32 mm i.d., 0.25-μm film thickness; Restek Corp., Bellefonte, PA). The oven of the gas chromatograph was held at 69°C for one minute. The temperature was then increased to 100°C at a rate of 5°C/minute, and then to 320°C at a rate of 10°C/minute, and held at 320°C for four minutes. The injection port was programmed to increase from 280°C to 320°C at 180°C/minute.

Electron-impact ionization experiments were conducted at an ion trap temperature of 200°C and an emission current of 10 μamps. The auto-tune program was used to optimize the automatic gain control (AGC) target and multiplier voltage. The axial modulation voltage was 4.0 V. The mass spectra were acquired over a mass range of 50 to 650 amu. For methane chemical ionization (CI), the methane pressure was adjusted so that the ratio of m/z 17:29 was about 1:1. A filament current of 10 μamps and an ion trap temperature of 150°C were employed. The automatic reaction control (ARC) target was 50% of the optimum AGC setting, as recommended by the manufacturer. For pentafluorobenzyl alcohol (PFBOH) chemical ionization, PFBOH was introduced into the mass spectrometer by a method similar to that of Chien *et al.*, 1998. An ARC ionization time of 100 μs; a maximum ionization time of 2000 μs; a maximum reaction time of 40 ms; and CI ionization storage level of m/z 25 were employed. The reagent ions were ejected prior to mass analysis by using a background mass of m/z 235 in the software.

F. Quantification.

Calibration curves were constructed on three different days over a six month period (1/20/98; 5/5/98; 6/28/98) by measuring 50, 75, 100, 250, 500 and 1000 pg/μL standard solutions of PFBHA or PFBHA/BSTFA derivatives prepared in the same fashion as the samples. On the first and third day of analysis, the six-point calibration curve was constructed from the analysis of two

replicate standards analyzed before and after the analysis of samples. On the second day of analysis, the six-point calibration curve was constructed from the analysis of one set of standards. The recovery of derivatives was established through the analysis of solutions enriched with 1 ng/μL of hydroxy acetone, 2,3-butanedione, methyl vinyl ketone and methacrolein.

Methyl vinyl ketone (MVK), methacrolein (MACR), methyl glyoxal, glycolaldehyde and hydroxy acetone were quantified because of their relationship to each other. Methyl vinyl ketone and methacrolein are "first" generation products of hydroxyl radical oxidation of isoprene, a biogenic hydrocarbon. Methyl glyoxal, glycolaldehyde and hydroxy acetone are "second" generation products. Oxidation of methyl vinyl ketone yields methyl glyoxal and glycolaldehyde, and methacrolein is transformed to methyl glyoxal and hydroxy acetone (Yu et al., 1995, Grosjean et al., 1993, Tuazon and Atkinson, 1990, Tuazon and Atkinson, 1989). Glyoxal and methyl glyoxal are also generated from the photooxidation of other biogenic hydrocarbons (*e.g.*, α-pinene, Δ^3-carene and linalool) (Yu et al., 1998, Grosjean and Grosjean, 1997). The photooxidation of alkyl benzenes components of gasoline produces glyoxal, methyl glyoxal, glycolaldehyde and hydroxy acetone are photooxidation of alkyl benzenes, components of gasoline (Yu et al., 1997).

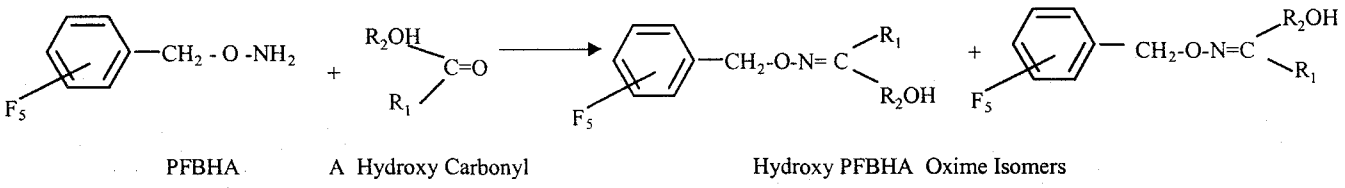
III. Results and Discussion.

A. Comparison of Sensitivity and Chromatography for PFBHA and PFBHA/BSTFA derivatives.

The chemical reactions describing PFBHA derivatization (Scheme 1) and BSTFA derivatization of the resulting hydroxy PFBHA oxime (Scheme 2) are presented in Figure 1.1. PFBHA reacts with the carbonyl moiety (R_1COR_2) to produce two oxime isomers, where R_1 and R_2 are not the same. In general, the two isomers are chromatographically separated, yielding two peaks per compound in the chromatogram. Silylation of the PFBHA derivative places a trimethylsilyl group on the PFBHA derivative. The PFBHA oxime isomers that are silylated, in

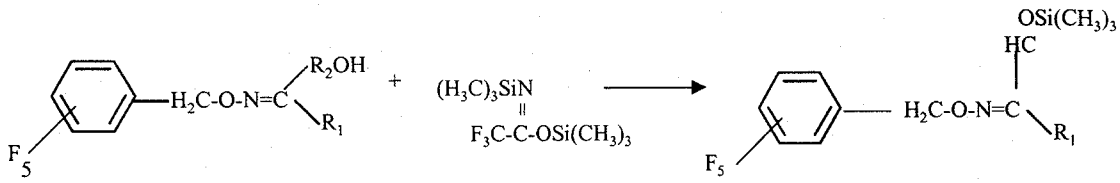
general, are not chromatographically separated. Thus, for most compounds only one peak is observed in the chromatogram.

Scheme 1: Derivatization of a Hydroxy Carbonyl with *O*-(2,3,4,5,6-pentafluorobenzyl) hydroxylamine (PFBHA)



PFBHA A Hydroxy Carbonyl Hydroxy PFBHA Oxime Isomers

Scheme 2: Derivatization of a Hydroxy PFBHA Oxime with *bis* (trimethylsilyl) trifluoroacetamide (BSTFA)



Hydroxy-PFBHA Oxime BSTFA PFBHA Oxime TMS Ether

Figure 1.1. Schematic diagrams of the derivatization of a hydroxy carbonyl with *O*-(2,3,4,5,6-pentafluorobenzyl) hydroxylamine (PFBHA) and *bis* (trimethylsilyl) trifluoroacetamide (BSTFA).

Poor chromatography and hence sensitivity was observed in measuring PFBHA derivatives of hydroxy carbonyls. Subsequent efforts to address this problem by silylating the hydroxyl group on the PFBHA derivatives with N-(*tert*-butyldimethylsilyl)-N-methyltrifluoroacetamide (MTBSTFA) as described in previous research (Le Lacheur et al., 1993) proved unsatisfactory due to poor yields. We began utilizing N,O-*Bis* (trimethylsilyl)trifluoroacetamide (BSTFA) as a silylating reagent after learning that Yu *et al.*, 1998 were developing a similar approach to identify multi-functional carbonyls. We demonstrate the improvements in chromatography and sensitivity that are achieved by silylating PFBHA derivatives of hydroxy carbonyls and oxo acids with BSTFA in Figure 1.2. The top (A) chromatogram was obtained from the analysis of a 500 pg standard of PFBHA derivatives of model hydroxylated carbonyls. The bottom (B)

chromatogram was obtained from analysis of the same standard after the PFBHA derivatives reacted with BSTFA. The PFBHA derivatives of the hydroxy carbonyls and oxo acids were not detected, whereas excellent chromatography and a signal:noise of 5:1 to 34:1 was accomplished after the hydroxyl groups were derivatized with BSTFA. We favor PFHA/BSTFA derivatization of oxo acids compared to pentafluorobenzyl bromide (PFB) derivatization, as conducted in previous work (Chien et al., 1998) due to higher intensity molecular and *pseudo* molecular ions. To exemplify this point, the PFBOH CI mass spectra of the pentafluorobenzyl derivative of pyruvic acid, and the PFBHA/BSTFA derivative of pyruvic acid are presented in Figure 3. The $(M+H)^+$ and $(M+181)^+$ ions are not evident in the PFBOH CI ion trap mass spectra of the pentafluorobenzyl derivative, whereas these ions are >80% relative intensity in the PFBOH mass spectra of the PFBHA/BSTFA derivative. (See Figure 1.3). Utilization of PFBHA and BSTFA may be the reagents of choice due to the excellent chromatography, improved sensitivity, as well as the presence of high intensity molecular ions in the methane and PFBOH CI mass spectra that the combination of these reagents affords.

B. Effect of Ionization Mode on Generation of Molecular and *Pseudo* Molecular Ions.

The intensities of the molecular and *pseudo* molecular ions in the EI, methane CI and PFBOH CI mass spectra of model compounds are presented in Table 1.1. Although as expected from previous work, the EI mass spectra of PFBHA derivatives do not yield intense molecular ions that facilitate molecular weight determinations (Yu et al., 1995, Le Lacheur, 1993, Glaze et al., 1989). Functional group information, however can be gleaned from the presence of the m/z 181 $(C_6F_5CH_2)^+$, $(M-CH_3)^+$ and m/z 73 $[Si(CH_3)_3]^+$ fragment ions. The base peak in the EI mass spectra of the PFBHA/BSTFA derivatives can be either a $(M-CH_3)^+$ fragment ion, the m/z 181 pentafluorobenzyl ion or a fragment ion at m/z 73. The $(M-CH_3)^+$ ion or the ion at m/z 73 is typically 40-100% relative intensity. The m/z 181 ion establishes the presence of a carbonyl moiety. The ion at m/z 73 indicates the presence of a hydroxyl or carboxyl group, and the $(M-CH_3)^+$ ion can indicate the molecular weight of the derivative.

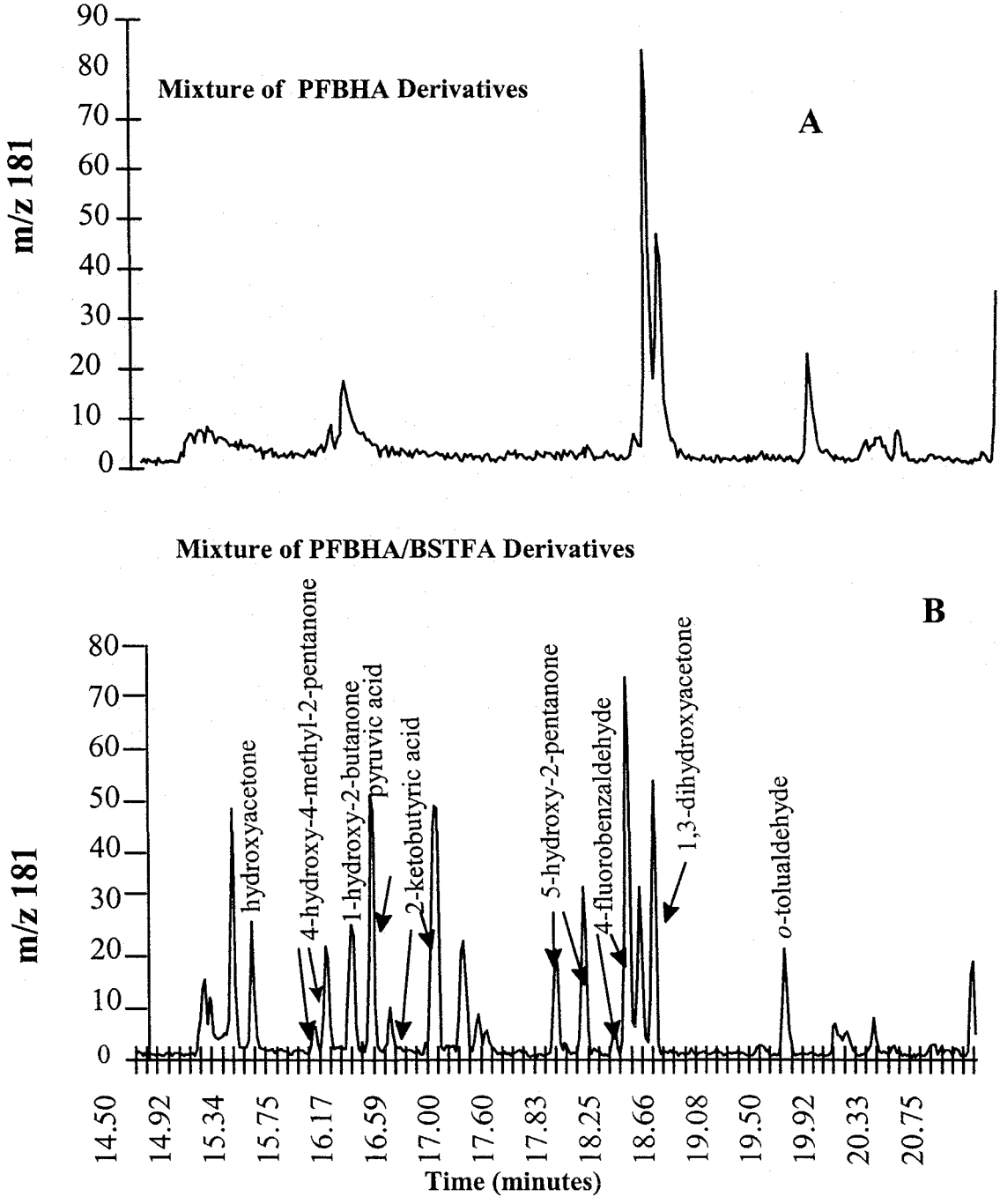


Figure 1.2. Chromatographic comparison of mixtures of PFBHA and PFBHA/BSTFA derivatives.

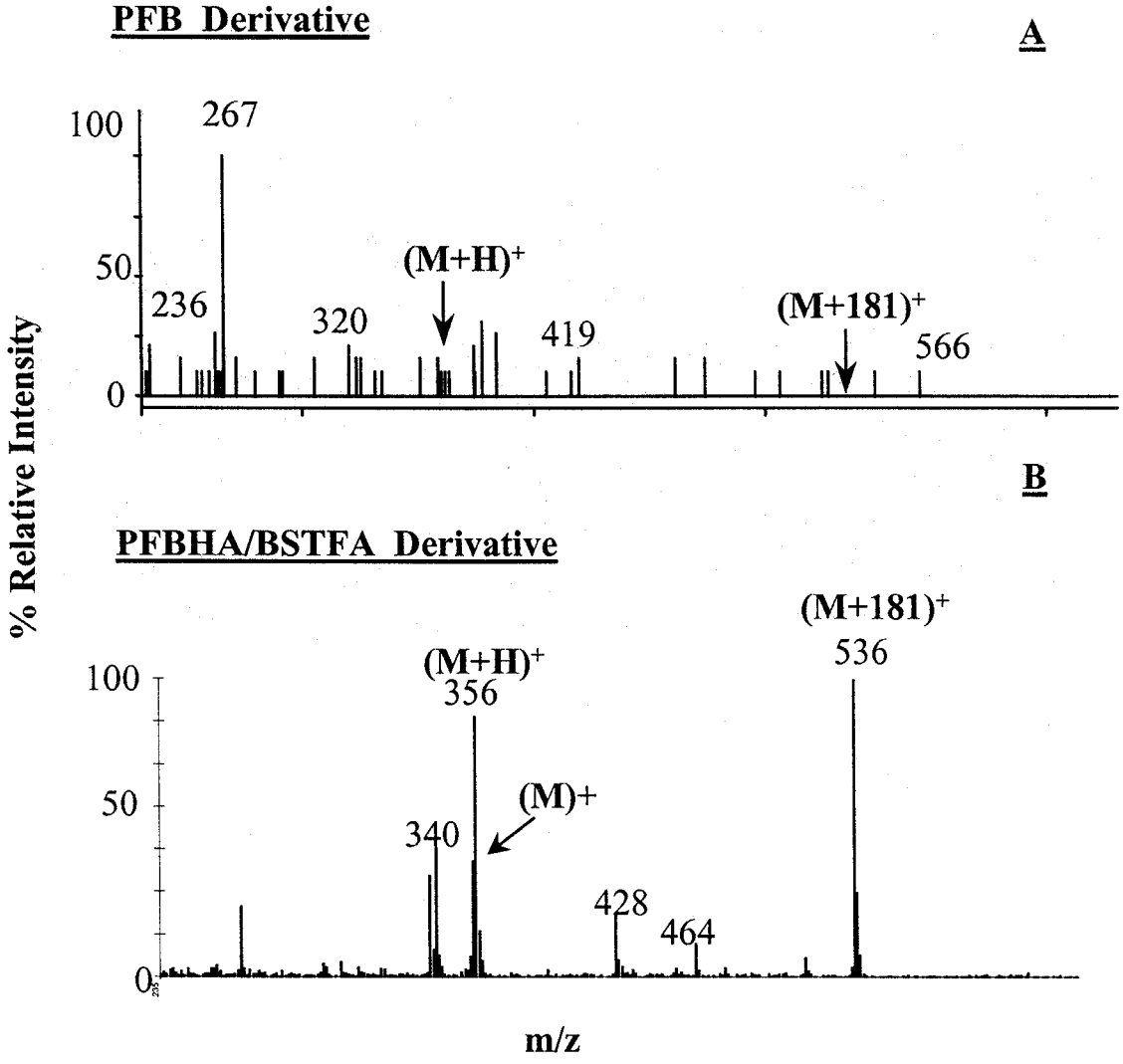


Figure 1.3. Comparison of the PFBOH chemical ionization mass spectra of PFB (A) and PFBHA/BSTFA (B) derivatives of pyruvic acid.

Also as expected from previous work, $(M+H)^+$ ions are often present in the methane CI mass spectra at high relative intensities, and are often the base peak. Low intensity (<10%) $(M-H)^+$, $(M)^+$ and $(M+181)^+$ ions are evident in the methane chemical ionization mass spectra. Molecular weight determinations of PFBHA and PFBHA/BSTFA derivatives can be made by observing the relationship between the $(M+H)^+$ and $(M+181)^+$ ions. PFBOH, used as a chemical ionization reagent enhances the relative intensities of the $(M-H)^+$, $(M)^+$, and $(M+181)^+$ ions for all the compounds evaluated, and the $(M+H)^+$ ions for oxo acids.

The EI, methane CI and PFBOH CI ion trap mass spectra of the pentafluorobenzyl derivatives thus provide complementary information. For PFBHA derivatives of aldehydes and ketones, the m/z 181 ion in the EI mass spectra establishes the presence of a carbonyl moiety. Molecular weight determinations are accomplished by interpreting the methane CI mass spectra and the PFBOH CI mass spectra. For PFBHA/BSTFA derivatives of hydroxy carbonyls and oxo acids, the m/z 181 ion in the EI mass spectra demonstrates the presence of a carbonyl moiety, and the ion at m/z 73 indicates a hydroxy or carboxy moiety on the molecule. The $(M-CH_3)^+$ ion, which is generally the most abundant and highest mass ion indicates the molecular weight of the derivative.

Molecular and *pseudo* molecular ions are present in the methane chemical ionization mass spectra and are enhanced when PFBOH is employed as a chemical ionization reagent. In certain cases, such as for glyoxylic acid, in which the increase in the intensity of the $(M-H)^+$, $(M)^+$, $(M+H)^+$ and $(M+181)^+$ ions are substantial, PFBOH chemical ionization may be preferred to methane chemical ionization.

C. Identification of Carbonyls.

Methyl vinyl ketone, methacrolein, methyl glyoxal, glycolaldehyde, and hydroxy acetone were identified in sample extracts collected in Azusa, CA. A chromatogram of a sample extract derivatized with PFBHA and BSTFA is presented in Figure 4.1 to demonstrate that in contrast to the DNPH method, this method provides good chromatographic separation between

Table 1.1. Effect of Ionization Mode on Production of Molecular and *Pseudo* Molecular Ions for PFBHA and PFBHA/BSTFA Derivatives of Carbonyls.

Compound (molecular weight of the derivative)	**Mode of Ionization**	**% Relative Intensity of Ions**				
		$(M-H)^+$	**$(M)^+$**	**$(M+H)^+$**	**$(M+181)^+$**	**Other**
PFBHA Derivatives						
Acetaldehyde (239)	Electron-Impact	-	0.9	-	0.3	m/z 181 (100)
	Methane CI	1.0	5.0	100.0	4.0	
	PFBOH CI	1.0	19.0	76.0	100	
Acetone (253)	Electron-Impact	-	7.0	-	-	m/z 181 (100)
	Methane CI	3.0	4.0	100.0	-	
	PFBOH CI	15.0	100.0	84.0	-	
Methacrolein (265)	Electron-Impact		14.0	-	4.0	m/z 181 (100)
	Methane CI	3.0	5.0	100.0	0.2	
	PFBOH CI	19.0	100.0	54.0	66	
Methyl vinyl ketone (265)	Electron-impact	-	2.0	-	0.4	m/z 181 (100)
	Methane CI	7.0	7.0	100.0	0.1	
	PFBOH CI	60.0	100.0	49.0	47	
Glyoxal (448)	Electron-Impact	-	17.0	0.1	-	m/z 181 (100)
	Methane CI	-	0.1	16.0	2.0	
	PFBOH CI	7.0	100	73.0	13.0	
Methyl glyoxal (462)	Electron-Impact	-	3.0	-	0.2	m/z 181 (100)
	Methane CI	0.2	-	32.0	0.5	
	PFBOH CI	3.0	32.0	81.0	15.0	

Table 1.1. Effect of Ionization Mode on Production of Molecular and *Pseudo* Molecular Ions for PFBHA and PFBHA/BSTFA Derivatives of Carbonyls (continued).

Compound (molecular weight of the derivative)	**Mode of Ionization**	**% Relative Intensity of Ions**				
PFBHA/BSTFA Derivatives		$(M-H)^+$	$(M)^+$	$(M+H)^+$	$(M+181)^+$	**Other**
Hydroxy acetone (341)	Electron-Impact	-	-	-	-	m/z 181 (100); m/z 73 (83)
	Methane CI	4.0	6.0	92.0	3.0	
	PFBOH CI	13.0	7.0	63.0	62.0	
Pyruvic Acid (355)	Electron-Impact	-	1.0	1.0	-	m/z 181 (100); m/z 73 (50)
	Methane CI	1.0	5.0	100.0	-	
	PFBOH CI	15.0	39.0	88.0	100.0	
2-ketobutyric acid (369)	Electron-Impact	-	1.0	-	-	m/z 181 (100); m/z 73 (70)
	Methane CI	9.0	9.0	100.0	0.4	
	PFBOH CI	20.0	89.0	38.0	96	
Glyoxylic acid (341)	Electron-Impact	-	10.0	1.0	-	m/z 181 (66); m/z 73 (100)
	Methane CI	-	2.0	11.0	0.2	
	PFBOH CI	20.0	38.0	89.0	96.0	

glycolaldehyde and hydroxy acetone. In sample extracts collected in Davis, CA., methacrolein, methyl vinyl ketone, glyoxal, methyl glyoxal, 3-hydroxy-2-butanone, and hydroxy acetone were identified by interpreting the EI, methane CI and PFBOH CI mass spectra. The identities were confirmed by establishing agreement between the EI mass spectra and relative retention time of the analyte in the sample extract to the mass spectra and relative retention time of the analyte in an authentic standard. Here, three cases are presented that establish the power of PFBOH to identify compounds in the ambient environment. In case I, PFBOH CI was critical to the identification of glycolaldehyde. In case II, PFBOH CI was essential to the identification of hydroxy acetone, and in case III, the merits of PFBOH CI to confirm the presence of glyoxal are discussed.

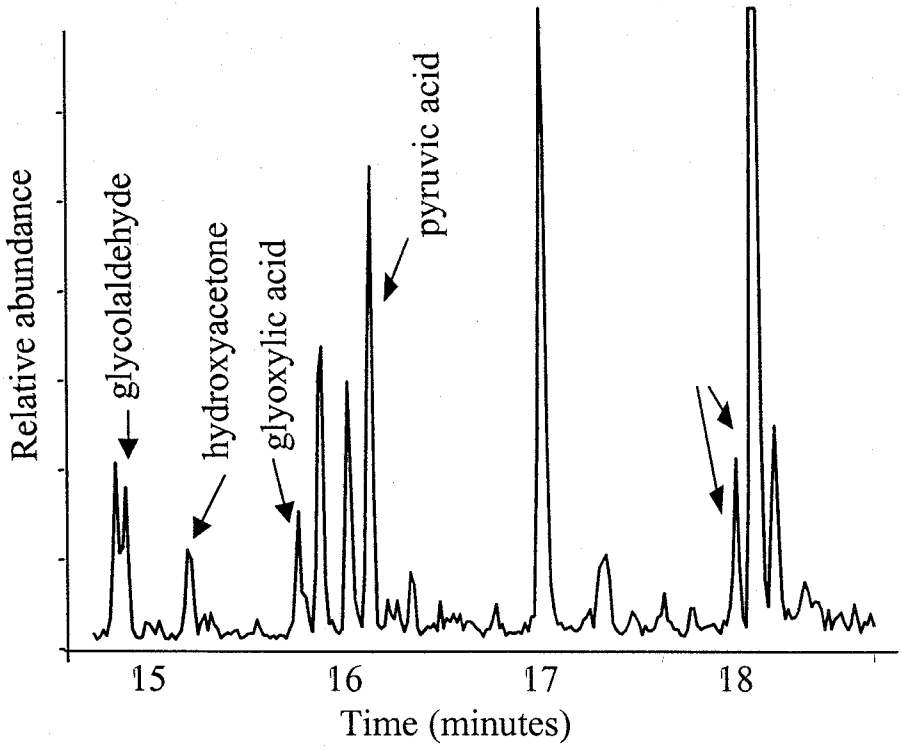


Figure 1.4. Sample chromatogram of PFBHA/BSTFA derivatives in an extract of air collected in Azusa, CA.

1. *Case I: Identification of glycolaldehyde in a sample extract of Azusa, CA. air in the presence of a co-eluting interferant.*

In Figure 1.5, the EI, methane CI and PFBOH CI mass spectra of a PFBHA/BSTFA derivative in a sample extract are presented. In the EI mass spectrum (A), the m/z 181 ion establishes the presence of a carbonyl moiety, and the m/z 73 ion indicates a hydroxyl or carboxyl group on the compound. In this case, the ion at m/z 312 or 387 could be the $(M\text{-}CH_3)^+$ ion. We conducted a methane CI experiment to determine which ion was a fragment ion of the PFBHA/BSTFA. The methane CI mass spectrum is presented in Figure 1.5B. Since the difference between the m/z 328 and m/z 312 is 16 Da, these ions could be the $(M+H)^+$ and $(M\text{-}CH_3)^+$ ions, respectively. However, the presence of an ion at m/z 418 raises some uncertainty regarding this conclusion. The 180 Da difference between the m/z 328 and 508 ions in the PFBOH CI mass spectra suggest that these ions are the $(M+H)^+$ and $(M+181)^+$ ions, respectively, of the same derivative. Similarly, the 180 Da difference between the m/z 418 and 598 ions indicate that they are the $(M+H)^+$ and $(M+181)^+$ ions of a different derivative. The mass spectrum thus represents two co-eluting derivatives. One compound has a molecular weight of 327 and the other has a molecular weight of 417. The derivative with the molecular weight of 327 was tentatively identified as the PFBHA/BSTFA derivative of glycolaldehdye, and later confirmed through the analysis of an authentic standard. The compound with the molecular weight of 417 was determined to be an interferant in the HPLC grade water. In this case, the identification of glycolaldehyde, in the presence of an interferant was only possible through the interpretation of the PFBOH CI mass spectra.

2. *Case II. Identification of hydroxy acetone in a sample extract of Davis, CA. air in the presence of a co-eluting interferant.*

The EI and PFBOH CI mass spectra of a chromatographic peak in an extract of Davis, CA. air is presented in Figure 1.6. By assuming that the ion at m/z 326 in the EI mass spectrum (A) is the $(M\text{-}CH_3)^+$ ion, and by comparing the relative retention time of the derivative in the sample to the relative retention time of the derivative in an authentic standard, the compound was

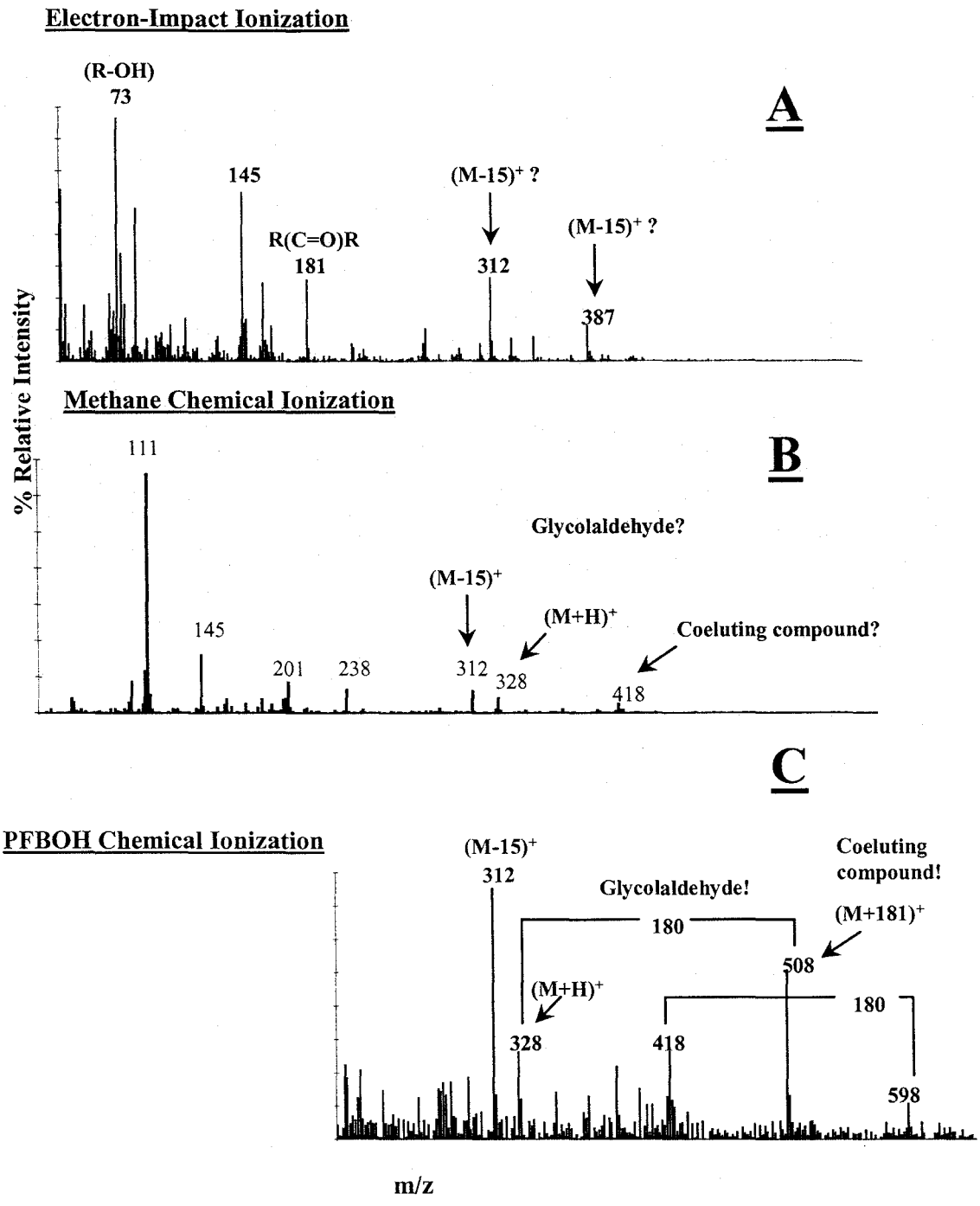


Figure 1.5. Ion trap mass spectra of an unknown PFBHA/BSTFA derivative in an extract of air collected in Azusa, CA.

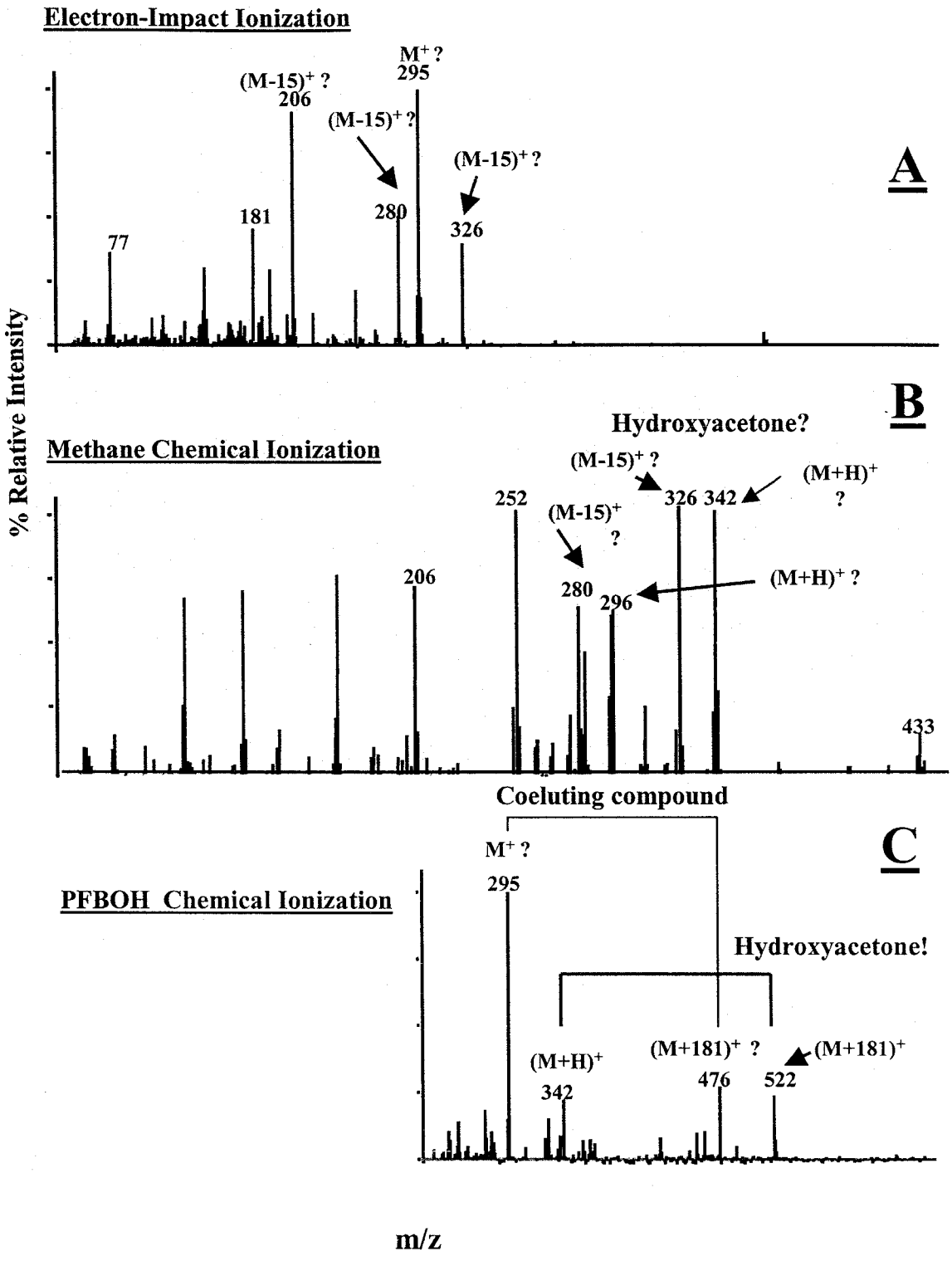


Figure 1.6. Ion trap mass spectra of an unknown PFBHA/BSTFA derivative in an extract of air collected in Davis, CA.

tentatively identified as hydroxy acetone. The high intensity of ions at m/z 206, 280 and 295 in the EI mass spectrum however suggested the presence of a different compound or the presence of co-eluting derivatives. We hypothesized that these ions were generated from two derivatives. One derivative with a molecular weight of 221 (*i.e.*, the m/z 206 ion is an $(M\text{-}CH_3)^+$ ion), and one derivative with a molecular weight of 295.

Support for this hypothesis was derived from the methane CI mass spectrum (B) by the presence of two pairs of ions at m/z 342 and 326 and m/z 296 and 280 that could be the $(M+H)^+$ and $(M\text{-}CH_3)^+$ ions, respectively. No ions were present that indicated a compound with a molecular weight of 221. The identity of hydroxy acetone was confirmed by observing ions at m/z 342 and 522 in the PFBOH CI mass spectrum that correspond to the $(M+H)^+$, and $(M+181)^+$ of the PFBHA/BSTFA derivative of hydroxy acetone, respectively. We also observed ions at m/z 295 ions were present in the mass spectrum to indicate a derivative with a molecular weight of 221. We surmise that the m/z 206 ion arises from another source.

3. *Case III. Confirmation of glyoxal in a sample collected in Davis, CA. by using PFBOH chemical ionization.*

The EI, methane CI, and PFBOH CI mass spectra of glyoxal in an air extract are presented in Figure 1.7. In the EI mass spectrum (A), the appearance of the m/z 181 ion establishes the presence of a carbonyl, and the appearance of the m/z 448 ion suggests the presence of the PFBHA derivative of glyoxal. (The m/z 448 is the $(M)^+$ ion of the PFBHA derivative of glyoxal). We hoped to confirm the identity of the glyoxal derivative by observing the $(M+H)^+$ and $(M+181)^+$ ions evident in the methane CI mass spectra of an authentic standard, but these ions were "in the noise" in the mass spectrum of the sample extract. We could confirm the presence of the PFBHA derivative of glyoxal however by observing $(M)^+$ and $(M+181)^+$ ions in the PFBOH CI mass spectrum (C).

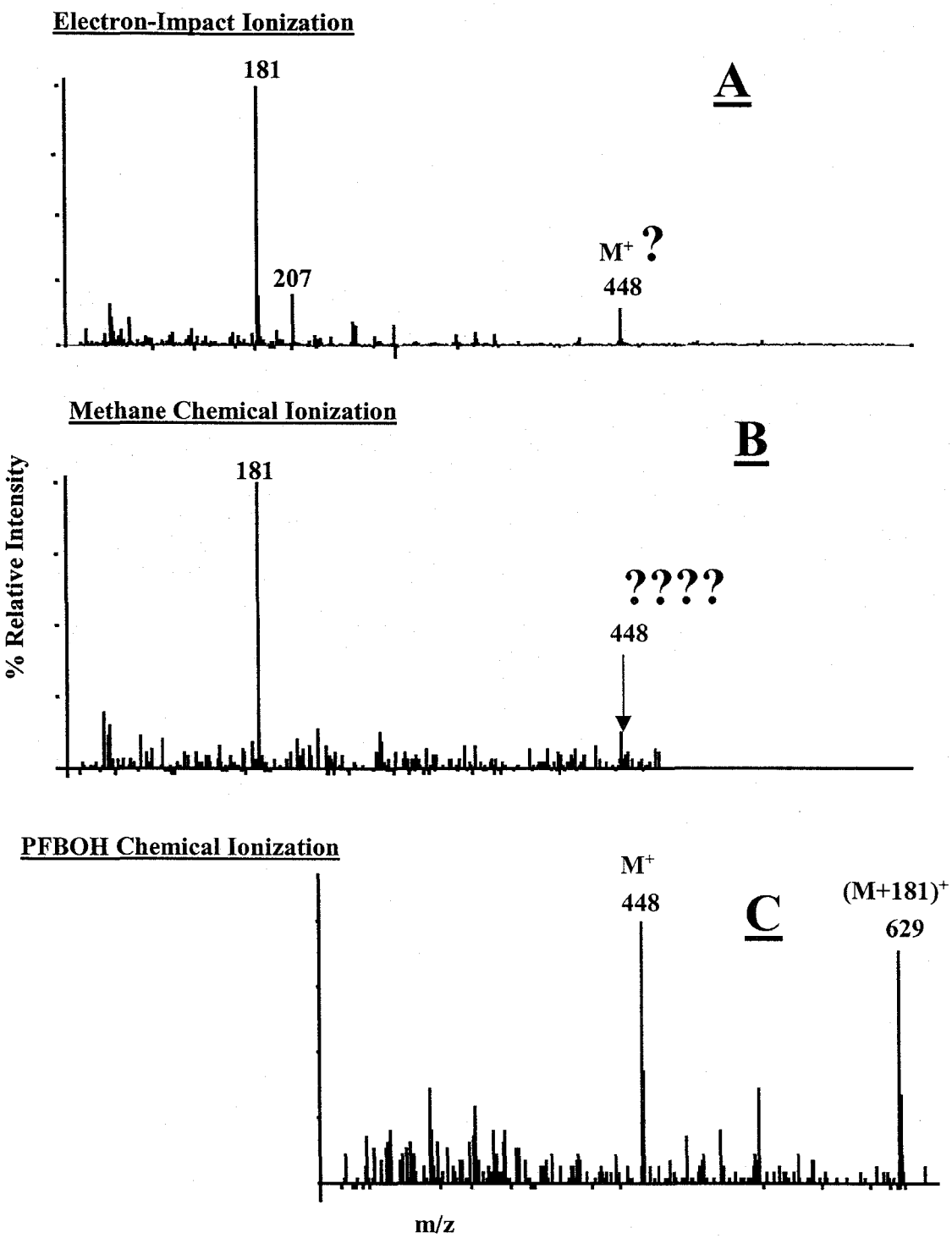


Figure 1.7. Ion trap mass spectra of a PFBHA derivative in an extract of air collected in Davis, CA.

D. Quantification of Methyl vinyl Ketone, Methacrolein, Methyl Glyoxal , Glycolaldehyde and Hydroxy Acetone.

The concentrations of methyl vinyl ketone, methacrolein, methyl glyoxal, glycolaldehyde and hydroxy acetone are reported in Table 1.2. Compounds are reported as non-detectable (ND) if the concentration in the sample extract was not greater than 3 standard deviations above the levels calculated in the field blanks. The concentration of the compounds in air ranged from 67-348 pptv. Such levels are reasonable and expected from chamber studies and the low photochemical activity as indicated by concentrations of ozone in the air. (On September 23, 1997, the average ozone concentration was 53 ppbv from 1:00 to 4:00 p.m. and 34 ppbv from 5:00 to 8:00 p.m. On September 24, 1997 the average ozone concentration was 24 ppbv from 1:00 to 5:00 p.m.).

The method detection limit, (MDL) at 3x the standard deviation above the concentration in the field blank was 42 pptv for methyl vinyl ketone, 40 pptv for methacrolein, 13 pptv for methyl glyoxal, 67 pptv for glycolaldehyde, and 200 pptv for hydroxy acetone. The average recoveries and standard deviations calculated from the analysis of matrix spikes from the three sampling periods (n=3) were 93%±18% for methyl vinyl ketone, 100%±32% for methacrolein, 88±12% for 2,3-butanedione and 76±49% for hydroxy acetone. Future work needs to address the poor precision in the recoveries in the matrix spikes for hydroxy acetone and the poor precision among measurements of replicate samples that was obtained for some of the measurements. For the samples, poor precision could arise due to variations in flow-rate or temperature during sampling and variable and high-levels of contamination in the blank. The samples were maintained in an ice bath during sampling, and the temperature and flow-rate were checked periodically. No differences between replicate samples in temperature or flow-rate were apparent. A major impediment to the analysis of these and other carbonyls, most notably acetone, acetaldehyde and pyruvic acid was contamination of the field blank due to impurities in the reagents (*e.g.*, the derivatization reagent, the water, and the extraction solvent). We have instituted purification measures to decrease this contamination that involve recrystallization of the reagents and oxidation of organic compounds in the water.

Table 1.2. Concentration of Methyl vinyl ketone, Methacrolein, Methyl glyoxal, Glycolaldehyde and Hydroxy Acetone in Air in Azusa, CA.

		Concentration in Air (pptv)	
Date	**Compound**	**Sample 1**	**Sample 2**
9/23/97	Methyl vinyl ketone	318	282
1:00-4:00 p.m.	Methacrolein	113	***
	Methyl Glyoxal	ND	***
	Glycolaldehyde	ND	217
	Hydroxy Acetone	ND	534
9/23/97	Methyl vinyl ketone	348	245
5:00-8:00 p.m.	Methacrolein	218	212
	Methyl Glyoxal	67	ND
	Glycolaldehyde	840	69
	Hydroxy Acetone	ND	ND
9/24/97	Methyl vinyl ketone	259	339
1:00-5:00 p.m.	Methacrolein	***	232
	Methyl Glyoxal	160	182
	Glycolaldehyde	127	***
	Hydroxy Acetone	300	477

***Concentration not reported since analyte was detected in fourth impinger.

E. Interferences from Ozone.

We compare the total concentration of the analytes measured in the four impingers to determine if removal of ozone is necessary (See Table 1.3). The inlets of the two samplers were identical except that a KI trap was fastened to one inlet, and a trap that was not coated with KI was fastened to the other inlet. The concentrations of methacrolein, methyl

vinyl ketone, 3-hydroxy-2-butanone and hydroxy acetone measured were lower in the sample extracts collected without removing ozone than for the extracts of samples in which a KI trap was employed to remove ozone prior to the impinger. These lower values imply oxidation of the carbonyls in solution. Concentrations of 2,3-butanedione and glyoxal were greater in samples collected with a KI trap. These data suggest that compounds were present which upon oxidation produced 2,3-butanedione and glyoxal. Although further investigation of ozone interferences is necessary, we suggest that ozone removal devices be employed with the method.

Table 1.3. Comparison of the Concentration of Analytes Measured in Impingers Employed to Sample Air in Davis, CA.

Analyte	**Total Concentration in Four Impingers (pptv)**	
	KI Trap Present	**KI Trap Absent**
Methacrolein	143	56
Methyl vinyl ketone	235	8
2,3-butanedione	ND	38
Glyoxal	ND	20
3-Hydroxy-2-butanone	20	1
Hydroxy acetone	107	22

IV. Conclusions

Ultratrace (pptv) levels of carbonyls, dicarbonyls and hydroxy carbonyls can be measured in ambient air by sampling with impingers filled with an aqueous solution of *O*- (2,3,4,5,6-pentafluorobenzyl)-hydroxyl amine (PFBHA). Reaction of the PFBHA derivatives of hydroxy carbonyls and oxo acids with BSTFA was necessary to measure these derivatives. The concentration of methyl vinyl ketone, methacrolein, methyl glyoxal, glycolaldehdye and hydroxy acetone in Azusa, CA. air on September 23 and 24, 1997 range from 67 to 840 pptv. Such levels are expected in light of yields obtained in chamber studies and the low photochemical activity on

both days. Most notably, to our knowledge, the first measurements of hydroxy acetone and 3-hydroxy-2-butanone in ambient air are reported.

Identifying glycolaldehyde and hydroxy acetone in the presence of co-eluting interferences, and confirming the identity of glyoxal established the utility of PFBOH CI. Interpretation of the PFBOH CI mass spectra is straight forward. The $(M+H)^+$ and $(M+181)^+$ ions are often present in high relative intensity, and molecular weight determinations are possible by observing the juxtaposition between these ions. Further work is underway to improve the precision of the method and the collection efficiency of the sampling devices.

V. References Cited

Barnett, V.; Lewis, T. *Outliers in Statistical Data*, 2 ed.; John Wiley & Sons: New York, 1984.

Betterton, E. A. In *Gaseous Pollutants: Characterization and Cycling*; Nriagu, J. O., Ed., 1992.

Chien, C. J., Charles, M. Judith, Sexton, K. G., Jeffries, H. E. *Environ. Sci. Technol.* **1998,** *32*, 299-309.

Frazey, P., Rao, X., Spaulding, R., Beld, B. , Charles, M.J. *in press, International Journal of Mass Spectrometry.* **1999.**

Glaze, W. H., Koga, M., Cancilla, D. *Environ. Sci. & Technol.* **1989,** *23*, 838-847.

Grosjean, E.; Grosjean, D. *Journal of Atmospheric Chemistry* **1997,** *27*, 271-289.

Grosjean, D., Grosjean, E., Williams, E. L. II *Environ. Sci. Technol.* **1994,** *28*, 186-196.

Kleinman, L., Lee, Y. N., Springstown, S. R., Nunnermacker, L., Zhou, X., Brown, R., Hallock, K., Klotz, P., Leahy, D., Lee, J. H., Newman, L. *Journal of Geophysical Research* **1994,** *99*, 34693482.

Kwok, E. S. C., Arey, J., Atkinson, R. *J. Phys. Chem.* **1996a,** *100*, 214-219.

Kwok, E. S. C., Atkinson, R., and Arey, J. *Environ. Sci. Technol.* **1996b,** *30*, 1048-1052.

Kwok, E. S. C., Atkinson, R., and Arey, J. *Environ. Sci. Technol.* **1995,** *29*, 2467-2469.

Lee, Y. N., Zhou, X., Kleinman, L.I., Nunnermacker, L. J., Springston, S. R., Daum, P. H., Newman, L., Keigley, W. G., Holdren, M. W., Spicer, C. W., Young, V., Fu, B., Parrish, D. D., Holloway, J., Williams, J., Roberts, J. M., Ryerson, T. B., Fehsenfeld, F. C. *Journal of Geophysical Research* **1998,** *103*, 22,449-22462.

Lee, Y. N., Zhou, X., Leatich, W. R., Baric, C. M. *Journal of Geophysical Research* **1996,** *101*, 29075-29080.

Lee, Y. N., Zhou, X., Hallock, K. *Journal of Geophysical Research* **1995,** *100*, 25,933-25,944.

Lee, Y. N., Zhou, X. *Environ. Sci. Technol.* **1993,** *27*, 749-756.

Le Lacheur, R. M., Sonnenberg, L. B., Singer, P. C., Christman, R. F., and Charles, M. J. *Environ. Sci. Technol.* **1993,** *27*, 2745-2753.

Li, S. M., Banic, C. M., Leatich, W. R., Liu, P. S. K., Isaac, G. A., Zhou, X. L., Lee, Y. N. *Journal of Geophysical Research* **1996,** *101*, 29,111-29,121.

Lipari, F., Swarin, S. J. *J. Chromatogr.* **1982,** *247*, 297.

Martin, R. S., Westberg, H., Allwine, E., Ashman, L., Farmer, J. C., Lamb, B. **1991.,** *13*, 1-32.

Nondek, L., Rodler, D. R., Birks, J. W. *Environ. Sci. Technol.* **1992,** *26*, 1174-1178.

Paulson, S. E., Seinfeld, J. H. *Journal of Geophysical Research* **1992,** *97*, 20,703-20,715.

Saxena, P., Hildemann, L. M., McMurry, P. H., Seinfeld, J. H. *Journal of Geophysical Research* **1995,** *100*, 18755-18770.

Shu, Y., Kwok, E. S.C., Tuazon, E. C., Atkinson, R., and Arey, J. *Environ. Sci. Technol.* **1997,** *31*, 896-904.

Tanner, R. L., Meng, Z. *Environ. Sci. & Technol.* **1984,** *18*, 723-726.

Tuazon, E. C., Atkinson, R. *Inter. Jour. Chem. Kinet.* **1989,** *21*.

Tuazon, E. C., Atkinson, R. *International Journal of Chemical Kinetics* **1990a,** *22*, 1221-1226.

Tuazon, E. C., Atkinson, R. *Inter. Jour. Chem. Kinet.* **1990b,** *22*, 591-602.

Yu, J., Flagan, R. C., Seinfeld, J.H. *Environ. Sci. Technol.* **1998,** *32*, 2357-2370.

Yu, J., Jeffries, H. E., Le Lacheur, R. M. *Environ. Sci. Technol.* **1995,** *29*, 1923-1932.

Yu, J., Jeffries, H.E., Sexton, K.E. *Atmospheric Environment* **1997,** *31*, 2261-2280.

Chapter 2.

Optimization of a Mist Chamber (Cofer Scrubber) for Sampling Water-Soluble Organics in Aerosols

Table of Contents

List of Tables.

List of Figures.

Figure 2.6. Collection efficiencies of analytes for samples collected from a Tedlar™ bag at temperatures of the collecting solution of 16°C and 11°C solution (n=3; error bars = 1σ).

Figure 2.7. Collection efficiencies of analytes sampled from a Tedlar™ bag after addition of salts to the PFBHA aqueous solution (n=2; error bars = 1σ).

Figure 2.8. Collection efficiencies of analytes for sample collected in the Blodgett Forest, CA. with 10 or 20 mL of PFBHA aqueous solution in the mist chamber (n=4; error bars = 1σ).

Figure 2.9. Concentration of the PFBHA derivatives of a model carbonyl (methacrolein), dicarbonyl (methylglyoxal), hydroxycarbonyl (hydroxyacetone), and a keto-acid (pyruvic acid) in CH_2Cl_2 stored under refrigeration (4°C) over 66 days, normalized to the concentration measured on day 0 (n=3; error bars =1σ).

Figure 2.10. Concentration of the PFBHA derivatives of the internal standards employed for quantification in CH_2Cl_2 stored under refrigeration (4°C) over 66 days, normalized to the concentration measured on day 0 (n=3; error bars =1σ).

Figure 2.11. Comparison of analyte concentrations normalized to concentrations obtained in the absence of a KI scrubber for removal of ozone (n-6; error bars =1σ).

Figure 2.12. Mixing ratios of isoprene and its photooxidation products, glycolaldehyde, hydroxyacetone, methyl glyoxal, and glyoxal sampled above a ponderosa pine plantation near the Blodgett Forest, CA. on July 29, 2000.

Abstract

Volatile organic compounds (VOCs) emitted from biogenic and anthropogenic sources play a key role in the generation of tropospheric ozone, atmospheric radical species, and the oxidizing capacity of the atmosphere (Pierce et al., 1998, Trainer et al., 1987 a, b., Chameides et al., 1988, Atkinson, 2000, Jenkin and Clemitshaw, 2000). The formulation of regulatory strategies to control tropospheric ozone requires a thorough understanding of atmospheric transformation reactions, and atmospheric conditions that influence the generation and fate of the reaction products. The lack of such an understanding has contributed to grave uncertainties in photochemical models, and the failure of regulatory actions to control ozone.

While the atmospheric fate and transport of biogenic and anthropogenic hydrocarbons has been extensively studied, little is known about the behavior of first-, second-, and third- generation photooxidation products that arise from OH radical oxidation of the parent species. The results of chamber experiments establish that ·OH oxidation of biogenic and anthropogenic hydrocarbons yields carbonyls, dicarbonyls, hydroxycarbonyls, and keto-acids. A paucity of data exists however on the generation and fate of these products in the ambient atmospheric environment. This is changing due to the advent of methods that rely on *O*- (2,3,4,5,6-pentafluorobenzyl) hydroxylamine (PFBHA) derivatization of carbonyls in concert with gas chromatography/ion trap mass spectrometry (GC/ITMS). Such methods provide the means to identify and quantify water-soluble organics, which historically have been difficult to measure. A limitation of existing sampling methods however is the use of devices that require low flow-rates (0.5-1 L min^{-1}). Accordingly, long sampling times (3-4 hours) are needed to obtain pptv-ppbv detection limits. The mist chamber (Cofer scrubber) is an attractive device due to the high flow-rates (25-70 L min^{-1}) compatible with its use. Herein, we evaluate a mist chamber using a flow-rate of 25-30 L min^{-1} to provide short (10-minute) sampling times and pptv limits of detection. The results establish a relationship between the Henry's law constant (K_H) and the collection efficiency, and demonstrate the suitability of the method to measure analytes with $K_H \geq 10^3$ M

atm^{-1}. Adjusting the pH, adding quaternary ammonium salts, or decreasing the temperature of the collecting solution in the mist chamber did not significantly affect the collection efficiency. We tested the method by sampling photooxidation products of isoprene (glyoxal, methyl glyoxal, hydroxyacetone, and glycolaldehyde) near the Blodgett Forest, CA. This is the first report of a study the employs the mist chamber to sample hydroxy carbonyls. The accuracy and the reproducibility of the method were evaluated by the analysis of duplicate samples and field spikes. The mean recovery of field spikes was $\geq 80\%$, and the relative standard deviation was $\leq 22\%$ between duplicate measurements. The detection limits were 48, 15, 7.7, and 2.7 pptv for glycolaldehyde, hydroxyacetone, methylglyoxal, and glyoxal, respectively.

This work demonstrates the power of the mist chamber in concert with PFBHA derivatization and mass spectrometry to measure pptv concentrations of water-soluble organics with a sampling time of 10 minutes. It is now possible to further characterize isoprene and MBO photochemistry in rural environments by using a mist sampler along with PFBHA and PFBHA/BSTFA derivatization and gas chromatography/ion trap mass spectrometry. The method can also be utilized to gain insight into characterization of polar organics in urban atmospheres, where alkyl benzene photochemistry is important.

I. Introduction.

Volatile organic compounds (VOCs) emitted from biogenic and anthropogenic sources play a key role in the generation of tropospheric ozone, atmospheric radical species, and the oxidizing capacity of the atmosphere (Pierce et al., 1998, Trainer et al., 1987 a,b., Chameides et al., 1988, Atkinson, 2000, Jenkin and Clemitshaw, 2000). The formulation of regulatory strategies to control tropospheric ozone requires a thorough understanding of atmospheric transformation reactions, and atmospheric conditions that influence the generation and fate of the reaction products. The lack of such an understanding has contributed to grave uncertainties in photochemical models, and the failure of regulatory actions to control ozone.

The U.S. Environmental Protection Agency (U.S. EPA) and the State of California recently revised regulatory standards for ozone due to concerns about adverse effects of ozone to public health and the environment. The National Ambient Air Quality Standard (NAAQS) stipulated by the U.S. EPA requires average hourly and eight-hour ozone levels not to exceed 120 and 80 ppbv, respectively. The State of California has imposed stricter standards, requiring the hourly average to not exceed 90 ppbv. In spite of extensive efforts to control VOC emissions that effect ozone formation, millions of people residing in urban and rural areas are exposed to levels of ozone that exceed the NAAQS standard. For example, in 1999, 122.5 million people were exposed to levels of ozone that exceeded the 8-hour ozone standard, and 53.8 million people were exposed to ozone levels exceeding the 1-hour ozone standard in the United States (U.S. Environmental Protection Agency, 1999). In the Sacramento Valley Air Basin and the Mountain Counties Air Basin, over 2 million Californians were exposed to levels of ozone that exceeded the Federal 1-hour, Federal 8-hour, and State 1-hour ozone standards in 1996-1998 (California Environmental Protection Agency, 1998). Clearly, new control strategies must be instituted to reduce tropospheric ozone in air. Accomplishing this goal, requires a better understanding of photooxidation reactions, and conditions that promote tropospheric ozone formation in the ambient environment.

A. Photooxidation Products of Gas-phase Reactions.

Chamber studies establish that OH radical oxidation of biogenic and anthropogenic VOCs yields first-, second-, and third- generation products. Many of these products are carbonyls, hydroxycarbonyls, dicarbonyls, and keto-acids (Atkinson, 2000, Niki et al., 1987). Hydroxy carbonyls are generated from OH radical initiated reactions with C_4-C_8 alkanes (Kwok et al., 1996a), C_4-C_8 alkenes (Kwok et al., 1996b), and 2,4-dimethyl-2-pentanol and 3,5-dimethyl-3-hexanol (Atkinson and Aschmann, 1995). Oxidation of the alkanes yields hydroxy carbonyls with the same number or fewer number of carbon atoms, with the formation yields increasing with increasing carbon numbers (Kwok et al., 1996a). Dihydroxy carbonyls are products of OH radical oxidation of C_4-$_8$ alkenes. OH radical oxidation of 2,4-dimethyl-2-pentanol and 3,5-dimethyl-3-hexanol produces 4-hydroxy-4-methyl-2-pentanone (Atkinson and Aschmann 1995). Hydroxy carbonyls, including glycolaldehyde and hydroxy acetone, and epoxy carbonyls are products of OH radical reactions with isoprene, *cis*-3-hexen-1-ol, and the alkyl benzenes - toluene, *p*-xylene, 1,3,5, -trimethyl benzene, and 1,2,4-trimethyl benzene (Yu et al., 1995, Yu et al., 1997, Yu and Jeffries, 1997). OH radical oxidation of the leaf alcohol *cis*-3-hexen-1-ol yields 1,3-dihydroxy-4-hexanone, 1,4,6-trihydroxy-3-hexanone and 1,4-dihydroxy-3-hexanone (Aschmann et al., 1997).

Several studies document the formation and concentrations of carbonyls in ambient air (Montzka et al., 1993, Yokuchi, 1994, Possanzini and Di Palo, 1996, Biesenthal et al., 1997, Lamanna and Gloldstein, 1999, Grosjean et al., 2001, Stroud et al., 2001). However, few studies measure a broad range of carbonyls, including dicarbonyls, hydroxycarbonyls, and keto-acids in air, and those that do exist often focus on only one class of compound (Munger et al., 1995, Lee et al., 1998, Klotz et al., 199). Measurements of the parents and products are needed to understand chemical reaction mechanisms in the ambient environment, and to evaluate and improve photochemical models formulated to devise strategies to reduce tropospheric ozone.

B. Sampling of Carbonyls and Multifunctional Carbonyls.

Sampling devices previously employed to sample carbonyls include impingers, a coil scrubber, a mist chamber containing an aqueous solution of the derivatization reagent (Monger et al., 1995, Lee et al., 1993, Coffer et al., 1986, Vairavamurthy et al., 1992), cartridges coated with the derivatization reagent (Vairavamurthy et al., 1992), and cooled solid sorbents (Montzka et al., 1993, Yokouchi, 1994, Lamanna and Goldstein). The low-flow rates (0.5-1L min^{-1}) compatible with impingers and coated cartridges necessitates long sampling times (3-4 hours) (Zhou et al., 1990, Spaulding et al., 1999). Full automation and short sampling times (*e.g.*, 10 minutes) are achieved by using cryogenic collection, or cryogenic collection with solid sorbents, along with thermal desorption and gas chromatography with flame-ionization (FID) or mass spectrometric (MS) detection (Montzka et al., 1993, Biesenthal et al., 1997). These methods however do not afford measurement of trace levels of the more polar multifunctional carbonyls. The mist chamber was previously utilized to sample formaldehyde, pyruvic acid, glyoxal, and methylglyoxal, each in a different study (Munger et al., 1995, Cofer et al., 1985, Andreae et al., 1987), but no information exists regarding the collection of hydroxycarbonyls. Because the mist chamber can be operate at flow rates from 25 to 70 L min^{-1}, it is a promising technique for collection of trace levels of water-soluble organics with short sampling times.

Herein, we evaluate a modified mist chamber that operates at flow-rates of 25-30 L min^{-1} and 10-minute sampling periods for collection of water-soluble organics. We explore operational parameters that may affect the collection efficiencies of carbonyls, dicarbonyls, hydroxycarbonyls, and keto-acids, that are first-, second-, and third- generation products from photooxidation reactions of isoprene, 2-methyl-3-buten-2-ol (MBO), and alkylbenzene, parent hydrocarbons that originate from biogenic and anthropogenic sources and are important sources of VOCs (Carter et al., 1996, Yu et al., 1997, Alvarado et al., 1999). The sampling technique was used in conjunction with PFBHA, and PFBHA/BSTFA derivatization of carbonyls and dicarbonyls, and carbonyls containing hydroxy-and carboxy- moieties, respectively, followed by

gas chromatography/ion trap mass spectrometry. We tested and proved the power of the method by measuring isoprene and 2-methyl-3-buten-ol photooxidation products in the Blodgett Forest, CA.

II. Experimental.

A. Reagents.

Water (HPLC grade), methylene chloride (GC Resolv grade; ≥ 99.9% purity), methyl *tert*-butyl ether (MTBE; HPLC grade; ≥ 99.0% purity), methanol (Optima grade; ≥ 99.9% purity), acetonitrile (Optima grade; ≥ 99.9% purity), hexane (Optima grade; ≥ 99.9% purity), and toluene (HPLC grade; 99.8% purity) were purchased from Fisher Scientific, Inc., Fairlawn, N.J. *O*-(2,3,4,5,6-pentafluorobenzyl) hydroxylamine hydrochloride (PFBHA; 98.0% purity), *O*-(2,3,4,5,6-pentafluorobenzyl)alcohol (PFBOH; 98.0% purity), trimethylchlorosilane (TMCS), dichlorodimethyldichlorosilane, 2-propanol (Pesticide residue grade; ≥99.9% purity), formaldehyde (37% wt in H_2O), acetone (HPLC grade; ≥ 99.9% purity), methacrolein (95.0% purity), methyl vinyl ketone (99.0% purity), 3-methyl-2-butenal (97.0% purity), *trans*-2-methyl-2-butenal (95.0% purity), glyoxal (40% wt in H_2O), methylglyoxal (pyurvic aldehyde, 40% wt in H_2O), glycolaldehyde (dimer), hydroxyacetone (acetol; 90.0% purity); 1-hydroxy-2-butanone (95.0% purity), 3-hydroxy-2-butanone, 4-hydroxy-3-methyl-2-butanone (65.0% purity), 3-hydroxy-3-methyl-2-butanone (95.0% purity), 5-hydroxy-2-pentanone (3-acetyl-1-propanol, 95.0% purity), 4-hydroxy-4-methyl-2-pentanone (99.0% purity), pyruvic acid (98.0% purity), 4-fluorobenzaldehyde (98.0% purity), 2,2'-difluorobiphenyl, isoprene (99.0% purity), 2-methyl-3-buten-2-ol (98.0% purity), and tetramethylammonium bromide (98.0% purity), and tetrapropylammonium bromide (98.0% purity) were purchased from Aldrich Chemical Company, Inc., Milwaukee, WI. $^{13}C_3$-acetone (99.0% purity) and 4-hydroxybenz-$^{13}C_6$-aldehyde (99.000% purity) were purchased from Isotec, Inc., Miamisburg, OH. *Bis* (trimethylsilyl) trifluoroacetamide (BSTFA) was purchased from Supelco Chromatography Products, Bellefonte,

P.A. Ultra-high purity zero grade air (< 0.1 ppm hydrocarbons) and N_2(g) (99.995%) were purchased from Puritan-Bennett, San Ramon, CA.

The water was further purified by distillation with $KMnO_4$, and the methylene chloride, MTBE, methanol, acetonitrile, and hexane were further purified by distillation. The PFBHA was re-crystallized two times in re-distilled 2-propanol. The other chemicals were used without further purification.

B. Preparation of Glassware.

All glassware was soaked overnight in 15% (v/v) dichlorodimethylsilane in toluene. The glassware was then rinsed with toluene, methanol, and methylene chloride, three times each, and dried at 150°C.

C. Standard Solutions.

Standard solutions were prepared in a N_2(g) environment when possible by evacuating vials with 99.99% N_2(g) each time they were opened. For the experiments conducted to optimize the collection efficiency of the mist chamber, stock and working standard solutions of formaldehyde, acetone, methacrolein, methyl vinyl ketone, glycolaldehyde, hydroxyacetone, glyoxal, methylglyoxal, and pyruvic acid were prepared in methanol and stored at -80°C. The concentration of the analytes in the stock standard solutions was approximately 10.0 μg/μL, except for acetone which was 99.7 μg/μL. The concentration of the analytes in the working standard solution was approximately 25 ng/μL, except for acetone which was 249 ng/μL. A stock solution containing 5.09 μg/μL of $^{13}C_3$-acetone, 5.54 μg/μL of 4-flurobenzaldehdehyde and 0.936 μg/μL of 4-hydroxybenz-$^{13}C_6$-aldehyde was also prepared. This solution was diluted to produce a working standard solution that contained 20.9 ng/μL of 4-fluorobenzaldehyde,

18.2 ng/μL of $^{13}C_3$-acetone, and 19.7 ng/μL of 4-hydroxybenz-$^{13}C_6$-aldehyde in methanol. For experiments conducted in the ambient environment, a stock solution was prepared containing 4.81 μg/μL of formaldehyde, 4.16 μg/μL of glycolaldehyde, 3.90 μg/μL of hydroxy acetone, 3.69 μg/μL of 3-hydroxy-3-methyl-2-butanone, 1.01 μg/μL of glyoxal, 1.88 μg/μL methylglyoxal and 4.97μg/μL pyruvic acid. This solution was diluted to produce a working standard solution containing 9.62 ng/μL formaldehyde, 4.16 ng/μL glycolaldehyde, 3.90 ng/μL hydroxy acetone, 3.69 ng/μL 3-hydroxy-3-methyl-2-butanone, 1.01 ng/μL glyoxal, 1.88 ng/μL methylglyoxal and 4.97 ng/μL pyruvic acid. A stock solution containing 5.09 μg/μL of $^{13}C_3$-acetone, 4.54 μg/μL of 4-flurobenzaldehdehyde and 2.09 μg/μL of 4-hydroxybenz-$^{13}C_6$-aldehyde was also prepared. This solution was diluted to produce a working standard solution that contained 4.07 ng/μL of 4-fluorobenzaldehyde, 1.8 ng/μL of $^{13}C_3$-acetone, and 4.18 ng/μL of 4-hydroxybenz-$^{13}C_6$-aldehyde in methanol.

D. Extraction of Filters.

The mist chamber contains a housing containing 1-μm diameter pore size Zefluor™ (Pall-Gelman Laboratory, Ann Arbor, MI) Teflon™ filter fitted to the top of the glass chamber to prevent loss of water vapor. In experiments in which the analytes on Teflon™ filters were measured, the filters were cut into small pieces, transferred to 20 mL of a 1 mM PFBHA solution in acetonitrile, and enriched with the internal standards. After 24 hours, the solution containing pieces of filter were placed in a KCl ice bath (-8°C) and the PFBHA derivatives were extracted by sonication for five minutes by using a 550 Sonic Dismembrator (Fisher Scientific, Inc., Fairlawn, NJ), operated at level 8 with a 1-second pulse and a 0.1-second pause. The extract was passed through a 70 mm x 7 mm o.d. glass column filled with silanized glass wool (35 cm) to remove particles, and anhydrous Na_2SO_4 (35 mm) to remove water. The eluate was collected in a round bottom flask, reduced to 3 ml by rotary evaporation, and transferred to a graduated centrifuge tube. The final volume was adjusted to 4.0 mL by either reducing the volume further by N_2(g)-evaporation or increasing the volume by adding acetonitrile.

E. PFBHA Derivatization and Extraction of PFBHA Derivatives.

For laboratory experiments, 10 mL of a 2 mM aqueous PFBHA solution was employed as the collecting solution. For experiments conducted in the ambient environment, the mist chamber was filled with 20 mL of a 1-mM aqueous PFBHA solution. The carbonyls were allowed to react with PFBHA for 24 hours at room temperature. After derivatization, the PFBHA derivatives were extracted two times with 4 mL of methylene chloride. Five ml of H_2O containing 2 drops of concentrated H_2SO_4 was added to each vial to remove any excess PFBHA remaining (Cancilla et al., 1992). The organic fraction was filtered through a 70 mm x 7 mm o.d. column of anhydrous Na_2SO_4 to remove water. The column was conditioned with 0.5 ml CH_2Cl_2 prior to use and any compounds remaining in the column were eluted with an additional 0.5 ml CH_2Cl_2. The eluate was collected and evaporated under a stream of $N_2(g)$ to a final volume of 4.0 mL in laboratory studies, and 200 μL in the ambient atmosphere studies. Each time a vial was opened to add reagent or transfer the extract to another vial, the headspace was evacuated with $N_2(g)$ before it was sealed.

F. BSTFA Derivatization.

A solution of BSTFA:TMCS (90:10) was prepared by adding 100 μL TMCS to a 1-mL ampoule of BSTFA. Unused BSTFA:TMCS solution was discarded and TMCS was stored under nitrogen. A 100 μL aliquot of the PFBHA-derivatives in CH_2Cl_2 was transferred to a 500 μL silanized glass auto-sampler vial insert. Twenty μL of BSTFA:TMCS (90:10) was added to the vial, the headspace in the vial was evacuated with $N_2(g)$, and the vial was sealed with a Teflon™-coated cap. The solution was then allowed to react for 12 hours at 42°C, after which the PFBHA and PFBHA-BSTFA derivatives were analyzed by using gas chromatography/ion trap mass spectrometry.

G. Gas Chromatography/Ion Trap Mass Spectrometry (GC/ITMS).

A Varian Star 3400 CX gas chromatograph, with a temperature-programmable injector port interfaced to a Saturn 2000 ion trap mass spectrometer (Varian Assoc., Walnut Creek, CA) was employed. Gas chromatographic (GC) separation of the derivatives was accomplished by using a DB-XLB capillary GC column. The dimensions of the columns were 30 m x 0.25 mm i.d. and 0.25 mm film thickness (J&W Scientific, Inc., Folsom, CA). A 5 m integrated guard column was used prior to the DB-XLB analytical column. The injector temperature was held at 280°C for 1 min., increased to 310°C at a rate of 50°C/min., and held at 310°C for 25 min. The oven of the gas chromatograph was held at 70°C for 1 min. The temperature was increased to 100°C at a rate of 5°C/min.; then increased to 280°C at 10°C/min. and to 310°C at 30°C/min. The oven temperature was held at 310°C for 10 min. The injection volume was 2 μL.

Electron-ionization, methane chemical ionization and pentafluorobenzyl alcohol chemical ionization (PFBOH) mass spectra were acquired. For all three modes of ionization, a filament current of 10 μA and an ion trap temperature of 150°C were employed. The electron multiplier was set at 10^5 gain. The electron-ionization mass spectra were acquired by scanning from m/z 65 to m/z 650 using automatic gain control (AGC) with the maximum ionization time set at 25,000 μs and a target total ion counts (TIC) of 20,000. For methane chemical ionization the methane pressure was adjusted so that the m/z 17:29 ratio was approximately 1:1. The methane chemical ionization mass spectra were acquired by scanning from m/z 150 to m/z 550. Automatic reaction control (ARC) was used with a target TIC set at 5,000 counts. The maximum ionization time was 500 μs and the maximum reaction time was 80 ms. For PFBOH chemical ionization, the PFBOH was introduced from a vial containing PFBOH into the ion source through a piece of deactivated fused silica tubing (0.25 mm x 1 m). The vial and fused silica tubing was wrapped with heating tape so that the temperature of the PFBOH solution was 40°C, and the fused silica tubing was maintained at a temperature of 100 to 150°C. The CI storage level was set at m/z 25, with an ejection amplitude of m/z 0.0. The PFBOH chemical ionization mass spectra were acquired by scanning from m/z 235 to m/z 650. Automatic reaction control was used with a

target TIC of 5,000 counts, a maximum ionization time of 2,000 μs, and a maximum reaction time of 128 ms.

H. Identification and Quantification.

Identification of the analytes was accomplished by interpreting the mass spectra and by matching the relative retention time and mass spectra of an authentic standard to the analyte in the sample extract. Quantification was accomplished by using internal standardization. In the experiments investigating the efficiency of different solvents for extraction of PFBHA derivatives, the stability of the PFBHA derivatives in methylene chloride, and the efficiency of BSTFA derivatization under different conditions, 2,2'-difluorobiphenyl was employed as the internal standard. This compound was chosen because it is easily protonated in the ion trap under methane chemical ionization conditions. In these experiments, the internal standard was added to the sample extract after PFBHA derivatization and extraction of the derivatives. The final concentration of 2,2'-difluorobiphenyl was 1 ng/μL in these solutions. For all other experiments, $^{13}C_3$ -acteone, 4-hydroxybenz-$^{13}C_6$- aldehyde and 4-fluorobenzaldehyde were employed as the internal standards, and the standard was introduced prior to derivatization and extraction of the analytes. $^{13}C_3$-acetone was chosen as the internal standard for quantification of mono-functional carbonyls because it is a mono-functional carbonyl, and the retention time of the PFBHA derivative of $^{13}C_3$-acetone is similar to the retention time of other mono-functional carbonyls of interest to this project. 4-hydroxybenz-$^{13}C_6$-aldehyde was chosen as the internal standard for quantification of hydroxycarbonyls and keto-acids because for both classes of compounds the carbonyl moiety is derivatized with PFBHA, and the -OH or -COOH moiety is derivatized with BSTFA. 4-fluorobenzaldehyde was used as the internal standard for quantification of the dicarbonyls due to previous success using this internal standard (Spaulding et al., 1999, Frazey et. al., 2000).

The retention times and relative retention times of the analytes and the internal standards on a DB-XLB column are presented in Table 2.1. The gas chromatographic separation of the analytes on the DB-XLB column is demonstrated in Figure 2.1. The mean retention times relative to the internal standard $^{13}C_3$-acetone for the PFBHA derivatives of the carbonyls are 0.667 for formaldehyde, 1.00 for acetone, 1.176 for methacrolein, and 1.187 and 1.193 for methyl vinyl ketone ranged from 0.644 to 1.200. Each of these compounds elute within 5.5-minutes of each other. For hydroxycarbonyls and keto-acids, the mean retention time relative to 4-hydroxybenz-$^{13}C_6$-aldehyde is 0.650 for glycolaldehyde, 0.648 for 2-hydroxy-2-methylpropanal and 3-hydroxy-2-butanone (these compounds co-elute on a DB-XLB high-resolution gas chromatographic column), 0.662 and 0.660 for hydroxy acetone, 0.686 and 0.684 for 3-hydroxy-3-methyl-2-butanone, 0.705 for pyruvic acid, and 0.728 for 4-hydroxy-3-methyl-2-butanone. Each of the hydroxycarbonyls and keto-acids, including the internal standard, elute within 9.0 minutes of each other. The mean retention time for glyoxal and methylglyoxal, relative to 4-fluorobenzaldehyde was 1.157 and 1.167 for glyoxal, and 21.43 and 21.76 for methyl glyoxal. Each of the dicarbonyls, including the internal standard, elute within 3.4 minutes of each other. In the experiments conducted to optimize the method, the PFBHA and PFBHA/BSTFA derivatives were analyzed separately. After optimization of the derivatization conditions, the PFBHA and PFBHA/BSTFA derivatives were analyzed in one gas chromatographic analyses. The relative retention times for PFBHA derivatives were consistent for both types of analyses. A 4- or 5-point calibration curve was constructed by analyzing extracts of solutions comprised of the PFBHA and PFBHA/BSTFA derivatives of authentic standards ranging in concentration of underivatized analyte from 50 pg/μL to 1 ng/μL. For laboratory studies, the standard solutions contained approximately 63, 125, 250, 500, 1,000, and 6,000 pg/μL of the analyte and 250 pg/μL of the internal standard. For experiments investigating the stability of PFBHA derivatives, the effect of solvent on the extraction of the derivatives, and the silylation conditions, 1 ng/μL of 2,2'-difluorobiphenyl, the internal standard, was added to the sample extracts prior to analysis by GC/ITMS. For the experiments conducted in the ambient environment, standard solutions were comprised of approximately 40, 100, 300, 800, 1,600, and 4,000 pg/μL glycolaldehyde,

Table 2.1. Retention time and relative retention time of analytes and internal standards on a DB-XLB capillary gas chromatographic column.

Compound	Internal Standard	Retention Time Mean ± S.D. (%RSD)	Relative Retention Time Mean ± S.D. (%RSD)
Carbonyls			
$^{13}C_3$-acetone		10.26 ± 0.02 (0.20)	
Formaldehyde	$^{13}C_3$-acetone	6.84 ± 0.01 (0.15)	0.667 ± 0.001 (0.15)
Acetone	$^{13}C_3$-acetone	10.26 ± 0.02 (0.19)	1.00± 0.00 (0.00)
Methacrolein	$^{13}C_3$-acetone	12.06 ± 0.03 (0.25)	1.176 ± 0.003 (0.26)
Methyl Vinyl Ketone, Peak 1	$^{13}C_3$-acetone	12.17 ± 0.02 (0.16)	1.187 ± 0.000 (0.00)
Methyl Vinyl Ketone, Peak 2	$^{13}C_3$-acetone	12.23 ± 0.02 (0.16)	1.193 ± 0.001 (0.08)
Dicarbonyls			
4-fluorobenzaldehyde		18.41 ± 0.03 (0.16)	
Glyoxal, Peak 1	4-fluorobenzaldehyde	21.34 ± 0.03 (0.14)	1.157 ± 0.002 (0.17)
Glyoxal, Peak 2	4-fluorobenzaldehyde	21.48 ± 0.03 (0.14)	1.167 ± 0.001 (0.09)
Methylglyoxal, Peak 1	4-fluorobenzaldehyde	21.43 ± 0.04 (0.19)	1.164 ± 0.001 (0.09)
Methylglyoxal, Peak 2	4-fluorobenzaldehyde	21.76 ± 0.03 (0.14)	1.182 ± 0.001 (0.08)

Table 2.1. Retention time and relative retention time of analytes and internal standards on a DB-XLB capillary gas chromatographic column (continued).

Compound	Internal Standard	Retention Time Mean ± S.D. (%RSD)	Relative Retention Time Mean ± S.D. (%RSD)
Hydroxycarbonyls			
4-hydroxybenz-$^{13}C_6$-aldehyde		21.87 ± 0.00 (0.00)	
4-hydroxybenz-$^{13}C_6$-aldehyde		21.65 ± 0.00 (0.00)	
Glycolaldehyde	4-hydroxybenz-$^{13}C_6$-aldehyde	14.20 ± 0.01 (0.07)	0.650 ± 0.000 (0.00)
2-hydroxy-2-methylpropanal/ 3-hydroxy-2-butanone	4-hydroxybenz-$^{13}C_6$-aldehyde	14.18 ± 0.02 (0.14)	0.648 ± 0.001 (0.15)
Hydroxyacetone	4-hydroxybenz-$^{13}C_6$-aldehyde	14.43 ± 0.02 (0.14)	0.662 ± 0.001 (0.15)
Hydroxyacetone	4-hydroxybenz-$^{13}C_6$-aldehyde	14.29 ± 0.03 (0.21)	0.660 ± 0.002 (0.30)
3-hydroxy-3-methyl-2-butanone	4-hydroxybenz-$^{13}C_6$-aldehyde	14.99 ± 0.01 (0.07)	0.686 ± 0.000 (0.00)
3-hydroxy-3-methyl-2-butanone	4-hydroxybenz-$^{13}C_6$-aldehyde	14.80 ± 0.00 (0.00)	0.684 ± 0.000 (0.00)
Pyruvic Acid	4-hydroxybenz-$^{13}C_6$-aldehyde	15.26 ± 0.01 (0.07)	0.705 ± 0.000 (0.00)
4-hydroxy-3-methyl-2-butanone	4-hydroxybenz-$^{13}C_6$-aldehyde	15.77 ± 0.00 (0.00)	0.728 ± 0.00 (0.00)

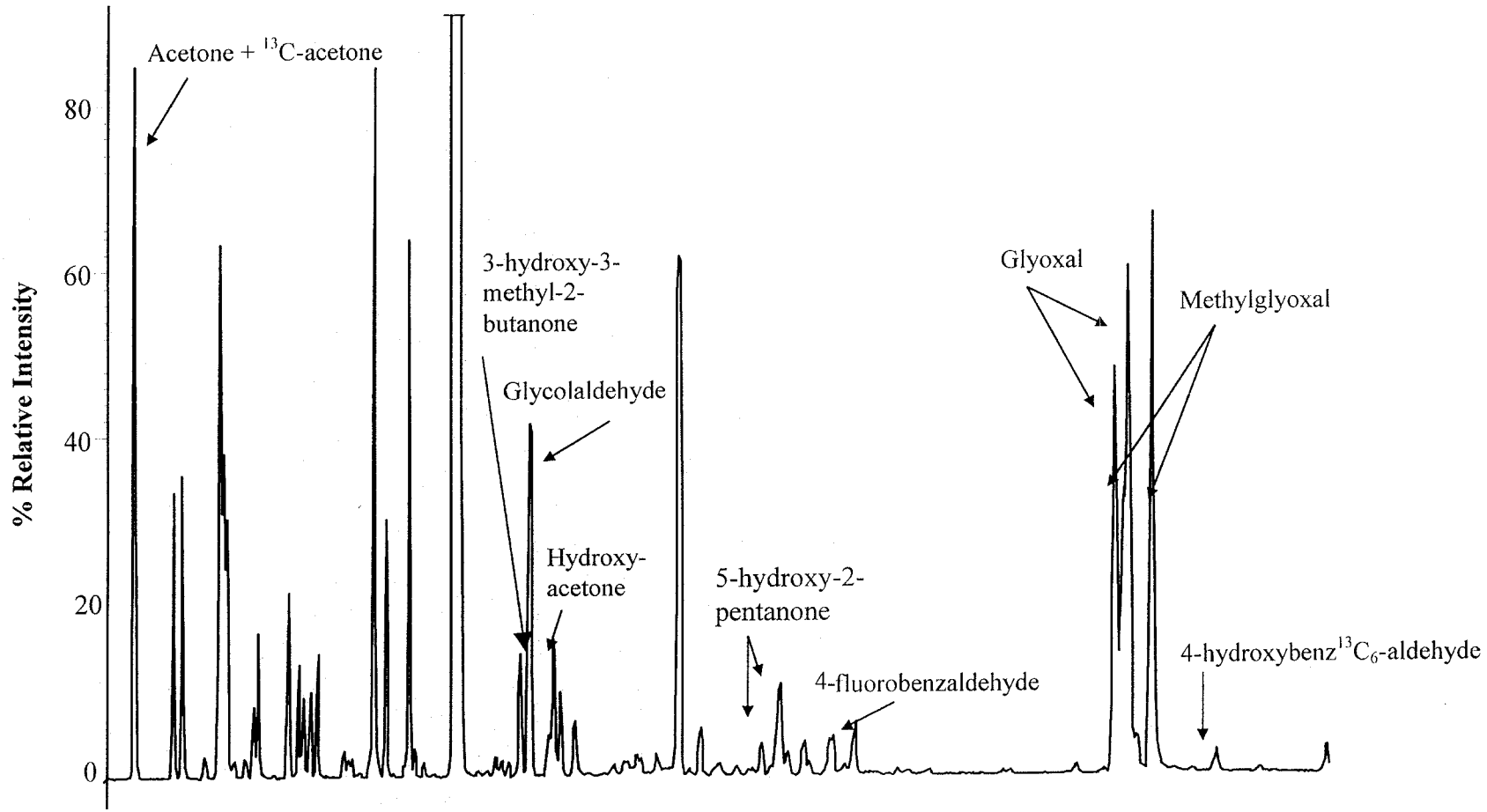


Figure 2. 1. m/z 181 chromatogram generated from an electron ionization mass spectra of a solution containing 1 ng/μL of PFBHA and PFBHA/BSTFA derivatives of authentic standards.

hydroxyacetone, 3-hydroxy-3-methyl-2-butanone, glyoxal, and methylglyoxal, and 120, 300, 900, 2,400, 4,800, and 12,000 pg/μL formaldehyde. The concentration of the internal standards was 1 ng/μL of $^{13}C_3$-acetone, 4-fluorobenzaldehyde, and 4-hydroxybenz-$^{13}C_6$-aldehyde.

The peak area of the $(M+H)^+$ ion of the analyte relative to the $(M+H)^+$ ion of the internal standard, obtained from the methane chemical ionization mass spectrum was plotted versus the concentration of the analyte, and the resulting linear regression equations used to quantify the analytes were calculated from the data. When the response (peak area) of the $(M+H)^+$ ion of the PFBHA or PFBHA/BSTFA derivative relative to the response of the $(M+H)^+$ ion of the PFBHA or PFBHA/BSTFA derivative of the internal standard exceeded the relative response observed for the highest concentration (1 μL) standard extract, a standard curve was generated that encompassed analyte concentrations ranging from 500 pg/μL to 6 ng/μL.

Standard solutions comprised of the derivatives of authentic standards were analyzed before and after the analysis of sample extracts. A "mid-point" standard solution containing either 250, 300, or 500 pg/μL of the PFBHA and PFBHA/BSTFA derivatives was analyzed after every 5 samples to evaluate the stability of the calibration curve. Typically, during the analytical period, 15 samples and 2 mid-point standard solutions were analyzed. A calibration curve was generated from the analysis of two standard extracts to produce a composite calibration curve comprised of 8 or 10 points (2 points for each concentration).

The stability of the calibration curves was evaluated by analyzing a standard solution containing the PFBHA derivative of methyl glyoxal and the PFBHA/BSTFA derivative of hydroxy acetone and pyruvic acid over a period of 18 hours. (See Table 2.2). The % relative standard deviation, and the % relative difference between Time 0 and a specific time was calculated. At each time, good agreement overall (< 28% RSD) was obtained among the relative response factors over a concentration range of about 50 to 1000 pg/μL for the model compounds investigated. The greatest variability was observed for the PFBHA derivative of methylglyoxal.

For methylglyoxal, the relative standard deviation among the relative response factors varied from 21-27%, with an overall relative standard deviation of 28%. A relative standard deviation of <5% and <20% was observed for the PFBHA/BSTFA derivatives of hydroxyacetone and pyruvic acid, respectively. The data demonstrate that the response of the analyte derivatives relative to the internal standard derivative was stable over a period of 18 hours.

The linearity of the calibration curves was evaluated by: 1) examining the correlation coefficient of the linear regression equations, and 2) comparing the relative response factors of the analyte over the range of concentrations. In previous work, we observed that upon visual inspection, calibration curves exhibiting R^2 values greater than 0.85 may be non-linear at the low end of the calibration curve, and thus a better measure of linearity was the % relative standard deviation among the relative response factors (RRF; $[(\text{Peak area})_{\text{analyte}} / (\text{Peak area})_{\text{internal standard}} \times (\text{Concentration})_{\text{internal standard}}] / (\text{Concentration})_{\text{analyte}}]$). Ninety-nine per cent of the correlation coefficients were ≥ 0.85; 94% were ≥ 0.90; and 78% were ≥ 0.95. Linear calibration curves for hydroxyacetone, 3-hydroxy-3-methyl-2-butanone, glyoxal, and methylglyoxal are indicated by good agreement among the relative response factors (*i.e.*, a % relative standard deviation among the relative response ≤ 25%). The concentration of these compounds in the reagent blank was typically < 50 pg/μL, the lowest point on the calibration curve. For formaldehyde, glycolaldehyde, and pyruvic acid, contamination of the reagent blank with concentrations of the PFBHA and PFBHA/BSTFA derivatives typically ranged from 50 to 100 pg/μL. This level of contamination affected the linearity of the calibration curve, as indicated by the % RSD among the RRF. In these cases, the % RSD was significantly reduced from values > 25% RSD to values < 25% by accounting for contamination of the analyte in the reagent blank. This was accomplished by subtracting the response factor of the analyte relative to the internal standard ($(\text{Peak area})_{\text{analyte}} / (\text{Peak area})_{\text{internal standard}}$) in the reagent blank from the response factor of the analyte relative to the internal standard ($(\text{Peak area})_{\text{analyte}} / (\text{Peak area})_{\text{internal standard}}$) in the solution comprised of the authentic standards.

Table 2.2. Reproducibility of response of peak area of an analyte to the internal standard over a 18-hour period.

Analyte	Time (hrs.)	Concentration (pg/μL)	Response Factor	Relative Response Factor (RRF)	Mean RRF ± S.D. (%RSD)	Overall Mean ± S.D. (%RSD)
Methylglyoxal	0	51.8	0.260	1.14	1.36 ± 0.29	1.30 ± 0.37
		259	1.406	1.24	(21)	(28)
		1036	7.671	1.69		
	5.4	51.8	0.290	1.28	1.49 ± 0.27	
		259	1.581	1.39	(18)	
		1036	8.157	1.80		
	9.5	51.8	0.281	1.23	1.53 ± 0.37	
		259	1.608	1.42	(24)	
		1036	8.826	1.94		
	13.6	51.8	0.305	1.34	1.58 ± 0.43	
		259	1.506	1.33	(27)	
		1036	9.444	2.08		
	17.7	51.8	0.316	1.39	1.50 ± 0.34	
		259	1.401	1.23	(23)	
		1036	8.533	1.88		
Hydroxyacetone	0	244	0.646	0.622	0.629 ± 0.009	0.624 ± 0.014
		976	2.639	0.635	(1)	(2)
	5.4	244	0.657	0.633	0.623 ± 0.014	
		976	2.547	0.613	(2)	
	9.5	244	0.648	0.624	0.624 ± 0.001	
		976	2.595	0.625	(0)	
	13.6	244	0.660	0.636	0.632 ± 0.005	
		976	2.610	0.628	(1)	
	17.7	244	0.658	0.633	0.611 ± 0.031	
		976	2.448	0.589	(5)	

Table 2.2. Reproducibility of response of peak area of analyte to internal standard over a 18-hour period. (continued).

Analyte	Time (hrs.)	Concentration (pg/μL)	Response Factor	Relative Response Factor (RRF)	Mean RRF ± S.D. (%RSD)	Overall Mean ± S.D. (%RSD)
Pyruvic Acid	0	248	1.150	1.09	1.09 ± 0.00	1.00 ± 0.06
		992	4.607	1.09	(0)	(6)
	5.4	248	1.098	1.04	1.01 ± 0.04	
		992	4.150	0.983	(4)	
	9.5	248	1.010	0.957	0.944 ± 0.018	
		992	3.933	0.932	(2)	
	13.6	248	1.014	0.961	0.955 ± 0.008	
		992	4.005	0.949	(1)	
	17.7	248	0.933	0.884	0.884 ± 0.000	
		992	3.730	0.884	(0)	

1. Semi-Quantification.

Since an authentic standard of 2-hydroxy-2-methylpropanal was not commercially available, quantification was accomplished by using the response (peak area) of the analyte relative to the internal standard and comparing this to a standard curve generated from 3-hydroxy-3-methyl-2-butanone, which has a similar structure.

2. Limit of Detection (LOD).

The limit of detection was calculated by the following equation: $LOD = 3\sigma_{blnk} + ave_{blnk}$, where ave_{blnk} and σ_{blnk} are the mean and standard deviation of the response factor for the analyte in three or more reagent blanks.

3. Quality Assurance.

For laboratory experiments, solutions for standard curves were derivatized and extracted at the same time as samples. The accuracy of the method was determined by the analysis of matrix spikes (samples enriched with the analytes), and determining the % recovery of the analytes. The precision of the method was determined by the analysis of duplicate samples. The analysis of reagent blanks was performed to determine the contamination of the reagents with the analytes. For the experiments conducted in the ambient environment, zero-grade air was passed through two mist chambers in series to determine the concentration of the analytes in the reagents.

Typically, the matrix spike was 10mL or 20mL of a 1 or 2 mM aqueous PFBHA solution enriched with 750 to 1000 pg/μL of each analyte. The analytes in the matrix spike were derivatized, extracted and analyzed along with the samples. In certain experiments, the composition of the collection solution in the mist chamber was altered by changing the pH or

adding salts. For these experiments, the matrix spike was a solution of identical composition to the sample enriched with analytes. In experiments in which the analytes were extracted from filters or a stainless steel annular denuder, the matrix spike was prepared by enriching the filter or stainless steel denuder with a solution of the analytes.

I. Mist chamber.

The mist chamber ("Cofer") scrubber is a nebulization-reflux concentrator (Cofer et al, 1985; Klemm and Talbot, 1991). All parts were made from polytetrafluoroethylene (PTFE, commonly known as Teflon™ or silanized glass. We present a schematic diagram of the mist chamber in Figure 2. The scrubber consists of a glass mist chamber with an air inlet, a nebulizing nozzle, and a port for addition and removal of solution. A PTFE filter housing containing 1-μm diameter pore size Zefluor™ (Pall-Gelman Laboratory, Ann Arbor, MI) Teflon™ filter was fitted to the top of the glass chamber to prevent loss of water vapor. The air outlet tube was connected to a GAST 1023, 50 Hz, ¾ horse power vacuum pump, TECO Pneumatic, Inc., Pleasanton, CA. During sampling, air was drawn in through the inlet at 25 to 30 L/min. The reservoir was filled with a collecting solution. For laboratory experiments, 10 ml of a 2 mM aqueous PFBHA solution was employed as the collecting solution. For experiments conducted in the ambient environment, the scrubber was filled with 20 mL of a 1 mM aqueous PFBHA solution.

The collecting solution was drawn from the reservoir into the nozzle by the Bernouli effect. Impaction of the solution with the incoming air forms a fine aqueous mist. The fine aqueous drops provide a large surface area for efficient extraction of water-soluble compounds from air. The mist is drawn upward through the chamber until it reaches the hydrophobic membrane, where aqueous droplets containing scrubbed atmospheric gases coalesce and are recycled into the reservoir (Cofer et al, 1985; Klemm and Talbot, 1991).

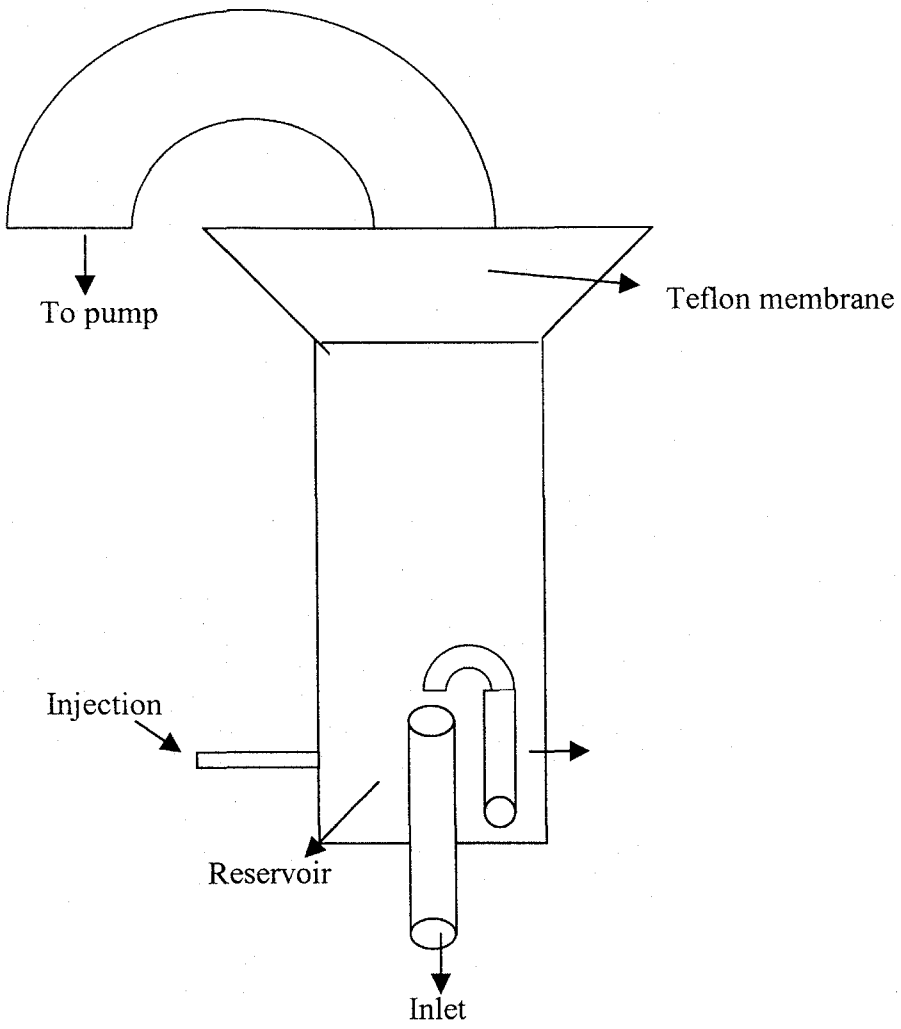


Figure 2.2. Schematic diagram of a mist chamber (Cofer scrubber).

J. Tedlar™ Bag Experiments.

For laboratory experiments conducted to investigate the relationship between the collection efficiency and Henry's law constant (K_H), optimization of conditions in the mist chamber, and sorption of analytes to the stainless steel annular denuder, the analytes were introduced into a Tedlar™ bag, and air was sampled from the bag. In these experiments, a 200-L Tedlar™ bag was partially filled with ultra-high purity (UHP), zero grade air that was passed through an activated charcoal filter (Dasibi Environmental Corp., Glendale, CA) and a rotameter. The

analytes were introduced into the Tedlar™ bag by preparing a mixture of the analytes (10 μg/μL of each compound) in methanol. A 25 μL aliquot of the solution was placed in a silanized ¼" o.d. glass U-tube. The U-tube was connected to the zero air tank with ¼" stainless steel tubing at one end, and to the Tedlar™ bag with ¼" PTFE tubing at the other end. All tubing was heated with heating tape. Zero air was passed through the U-tube to the Tedlar ™bag at 1 L/min. The U- tube was held at room temperature for 1 minute, and then immersed in an oil bath, which was heated to 50°C for 1 minute. The temperature of the oil bath was then increased in successive 25°C intervals to a final temperature of 200°C. At the end of each interval, the temperature was held constant for 1 minute. The bag was then filled to 200 L with UHP zero air.

Air was sampled from the Tedlar™ bag at a flow-rate of 1 standard liter per minute (SLPM; (Standard Liters Per Minute calibrated at 0°C, 1 atm), diluted with UHP zero air to a final flow rate of ~30 SLPM. All the experiments were conducted by collecting air into two mist chambers in series.

K. Calculation of Characteristic Times to Support Establishment of "Effective" Henry's Law Equilibrium.

We conducted the following analysis to explain the observation of a relationship between the "effective" Henry's law constant (K_H) and the collection efficiency of the mist chamber, and to support the choice of operational parameters that have the potential to increase the collection efficiency. The calculations provided herein, do not afford precise characteristic times to achieve the "effective" Henry's law equilibrium. They provide a rough approximation of the times, which are sufficient to suggest the potential for equilibrium to be established, and to explain the experimental observation of a relationship between the K_H and the collection efficiency. A more precise and rigorous analysis is beyond the scope of this work, and not necessary to accomplish the stated objective.

The contact time between the air and the water during sample collection, τ_{scr}, is 0.36 seconds when using a 190-mL mist sampler, containing 10 mL of aqueous solution, operated at an air flow rate of 30 L min^{-1}. Thus, Henry's law equilibrium to be established during sample collection, equilibrium must be established in ≤ 0.36 seconds. Establishment of the "effective" Henry's law equilibrium between air containing an analyte (the sample) and a body of water that does not contain the analyte (the collecting solution in the sampler) involves: 1) diffusion of the analyte in the gas phase to the surface of the droplet (τ_{dg}), 2) transport of the analyte across the air-liquid interphase (τ_i), 3) diffusion of the analyte in the aqueous phase (τ_{da}), and 4) hydration of the analyte to form a gem-diol (τ_{hyd}). It is possible for equilibrium conditions to exist during sample collection, if the sum of these processes is ≤ 0.36 seconds. The characteristic time for each of the processes was estimated, for representative compounds for which constants were available, using equations 1 – 7 (Schwartz, 1983, Buschmann et al., 1982, Seinfeld and Pandis, 1998). Constants used are given in Table 3, and calculated values are presented in Table 4. For all compounds, we use a gas-phase diffusion constant, D_g, of 0.1cm^2 s^{-1}; an aqueous-phase diffusion constant, D_a, of 2 x 10^{-5} cm^2 s^{-1}; a droplet radius, a, of 10 μm; a liquid water content, ω_L, of 5.6 x 10^{-3} (1 mL H_2O present as droplets/180 mL air in scrubber); and a hydrogen ion concentration of 10^{-3} M (pH=3). The calculations were performed at a temperature of 298°K.

The calculated characteristic times for each of the mass transport processes, τ_{dg}, τ_i, and τ_{da}, is at least an order of magnitude faster than the time of contact between air and liquid in the scrubber. The characteristic times for hydrolysis, τ_{hyd}, however, vary from 0.06 to 10 seconds. The establishment of the "effective" Henry's law equilibrium thus should not be limited by mass transport, but may be limited by the hydration reaction for some compounds. The rate and extent of hydration is dependent on the analyte, and hydration constants are not available for many of the analytes of interest to this research. However, for carbonyls that are hydrated rapidly or for which little hydration occurs, Henry's law equilibrium can affect the collection efficiency of the mist chamber. Further evidence that Henry's law equilibrium is established during sample

collection is presented in the results and discussion, as a comparison of sample collection efficiencies estimated using the Henry's law constants and measured empirically.

$$\tau_{dg} = \frac{K_H RT \omega_L a^2}{3D_g} \quad (1)$$

$$C = \sqrt{\frac{8RT}{\pi M}} \quad (2)$$

$$\tau_i = \frac{K_H RT \omega_L 4a}{3C\alpha} \quad (3)$$

$$\tau_{da} = \frac{a^2}{\pi^2 D_a} \quad (4)$$

$$\tau_{hyd} = \left[\left(1 + K_{hyd}^{-1}\right)\left(k_{hyd,0} + k_{hyd,H}\left[H^+\right]\right)\right]^{-1} \quad (5)$$

$$RCOR' \overset{k_{hyd}}{\leftrightarrows} RC(OH)_2R' \quad (6)$$

$$K_{hyd} = \frac{\left[RC(OH)_2 R'\right]}{\left[RCOR'\right]} \quad (7)$$

τ_{dg} = characteristic time for gas-phase diffusion

τ_i = characteristic time for interfacial transport

τ_{da} = characteristic time for aqueous-phase diffusion

τ_{hyd} = characteristic time for hydration reaction

a = droplet radius

D_g = gas-phase diffusion constant

D_a = aqueous-phase diffusion constant

C = mean molecular speed of gas

K_H = Henry's law equilibrium constant

α = accommodation coefficient

ω_L = liquid water content

R = ideal gas law constant

T = temperature

M = molecular weight of analyte

K_{hyd} = hydration equilibrium constant

$k_{hyd,0}$ = hydration rate constant

$k_{hyd,H}$ = acid-catalyzed hydration rate constant

Table 2.3. Constants used for calculation of characteristic times of mass transport and reaction processes required to support establishment of the effective Henry's law equilibrium.

Compound	K_H (M atm^{-1})	K_H (M Pa^{-1})	C (cm s^{-1})	α	K_{hyd}[f]	$k_{hyd,0}$ (s^{-1})	$k_{hyd,H}$ (s^{-1})
2,3-butanedione	57[a]	5.64 x 10^{-4}	2.71 x 10^4	0.004[c]	2.1	0.063[f]	16[f]
Formaldehyde	2970[b]	2.94 x 10^{-2}	4.59 x 10^4	0.02[d]	2273	12[g]	6136[g]
Glycolaldehyde	41400[b]	4.10 x 10^{-1}	3.24 x 10^4	0.02[d]	9.1	0.087[h]	0.3[h]
Pyruvic Acid	6730[a]	6.66 x 10^{-2}	2.68 x 10^4	0.02[e]	1.8	7.5[f]	5.9[e]

[a]Meylan and Howard, 1991; [b]Betterton and Hoffman, 1988; [c]Duan *et al.*, 1993, used value for acetone at 298K; [d]Jayne *et al.*, 1992, used value for formaldehyde at 267K; [e]Jayne *et al.*, 1991, used value for acetic acid at 298K; [f]Buschmann *et. al.*, 1982; [g]Bell and Evans, 1966; [h]Sorensen, 1972.

Table 2.4. Characteristic times for representative carbonyl compounds to reach effective Henry's law equilibrium.

Compound	τ_{dg} (s)	τ_i (s)	τ_{da} (s)	τ_{hyd} (s)
2,3-butanedione	2.6 x 10^{-5}	9.5 x 10^{-5}	5.1 x 10^{-3}	8.6
Formaldehyde	1.3 x 10^{-3}	5.9 x 10^{-4}	5.1 x 10^{-3}	0.055
Glycolaldehyde	1.9 x 10^{-2}	1.2 x 10^{-2}	5.1 x 10^{-3}	10
Pyruvic Acid	3.0 x 10^{-3}	2.3 x 10^{-3}	5.1 x 10^{-3}	0.086

L. Sorption of analytes to the Zefluor™ (Teflon™) filters.

As stated in the description of the mist chamber, aqueous droplets strike a hydrophobic membrane, prior to return of the droplets to the reservoir. If analytes from the water partition to the filter, the concentration in the water would be low and the collection efficiency would appear artificially low. The air also passes through the filter before exiting the first mist chamber and entering the second scrubber. If analytes from the air stream sorb to the filter, they would not make it to the second scrubber. In this case, the concentration measured in the second scrubber would be low and the collection efficiency would appear artificially high. Therefore, to evaluate whether sorption occurs during sample collection, we conducted experiments (n=3) in which we measured the analytes in the filters and in the aqueous phase.

M. Optimization Experiments.

1. Effect of the pH on the Collection Efficiency.

A Tedlar™ bag experiment (n=2), and an experiment in the ambient environment (n=5) were conducted to investigate the effect of the pH of the collecting solution on the collection efficiency. The PFBHA solution without any addition of buffer is a pH=3. In the laboratory, the pH of the PFBHA solution was altered to pH = 1, 5, or 7 by adding H_3PO_4 and NaH_2PO_4 to a final PO_4^{3-} concentration of 2 mM, and by adjusting the pH with NaOH. For experiments conducted in the ambient environment, a PFBHA solution of pH = 5 was prepared by addition of NaH_2PO_4 to a final PO_4^{3-} concentration of 5 mM, and adjusting the pH with NaOH. The pH of the solution analyzed after collection of samples was within ± 0.5 pH units of the initial pH. NaCl was added as needed to equalize the conductivity in all samples.

2. Effect of the Temperature on the Collection Efficiency.

A Tedlar™ bag experiment (n=3) was conducted to determine the effect of temperature of the PFBHA solution on the collection efficiency. The temperature was decreased by wrapping the mist chamber in a plastic bag containing ice and KCl. The temperature of the PFBHA solution was measured after completion of the experiment and was 16°C for the experiment conducted at room temperature, and 11°C for the experiment in which the temperature of the solution was lowered.

3. Effect of the Addition of Tetraalkylammonium on the Collection Efficiency.

A Tedlar™ bag experiment was conducted to determine the effect of tetraalkylammonium salt additions on the collection efficiency. Air was collected into scrubbers containing: 1) aqueous PFBHA; 2) aqueous PFBHA containing 0.25 molal tetramethylammonium bromide; or 3) aqueous PFBHA containing 0.25 molal tetrapropylammonium bromide.

4. The Effect of the Volume of the PFBHA Solution on the Collection Efficiency.

To evaluate the effect of the volume of the collecting solution on the collection efficiency, Mist chambers containing 10 and 20 mL of 1mM aqueous PFBHA solution were utilized to collect air in the Blodgett Forest. Replicate (n=4) samples were collected. An additional 10 mL of 1-mM PFBHA solution was added to the 10-mL samples after sample collection.

5. Determination of the stability of PFBHA Derivatives in CH_2Cl_2.

We investigated the stability of the PFBHA derivatives in CH_2Cl_2 under refrigeration (4°C) to determine the time period that the derivatives could be stored prior to analysis. Methacrolein, hydroxyacetone, methylgloxal and pyruvic acid were employed as the model compounds,

representing a carbonyl, a hydroxycarbonyl, a dicarbonyl, and a keto-acid. We also examined the stability of $^{13}C_3$-acetone, 4-fluorobenzaldehyde, and 4-hydroxybenz-$^{13}C_6$-aldehyde, the internal standards used for quantification.

For this experiment, Day 0 is defined as the first day of analysis. days prior to this day, 70 mL of an aqueous solution containing approximately 300 pg/μL methacrolein, hydroxyacetone, pyruvic acid, methylglyoxal, $^{13}C_3$-acetone, 4-fluorobenzaldehyde, and 4-hydroxybenz-$^{13}C_6$-aldehyde and 2 mM PFBHA was prepared. The PFBHA was allowed to react with the analytes for 24 hours. On the day prior to day 0, the analytes were extracted with 28 mL of methylene chloride. The final concentration was ~750 pg/μL for each compound. Aliquots (1 mL) of the extract were transferred to twenty-four 2-mL amber silanized vials. For 21 of these vials, the head space was evacuated with N_2(g) and the vials were stored at 4°C until BSTFA-derivatization and analysis. From each of the remaining 3 vials, 2 aliquots of 200 μL were transferred to silanized auto-sampler inserts. One aliquot was evaporated to dryness, reconstituted in 100% BSTFA, and heated to 42°C for 12 hours. To each aliquot, 10 μL of a 20 ng/μL solution of 2,2'-difluorobiphenyl, the internal standard, was added. The BSTFA-derivatized aliquot was analyzed for the PFBHA/BSTFA derivatives of hydroxyacetone, pyruvic acid, and $^{13}C_6$-hydroxybenzaldehyde on day 0. The other aliquot was analyzed for the PFBHA derivatives of methacrolein, methylglyoxal, $^{13}C_3$-acetone, and fluorobenzaldehyde.

On days 6, 16, 24, 32, 37, 51, and 65, three aliquots (200 μL) were reacted with BSTFA. On days 7, 17, 25, 33, 38, 52, and 66, the internal standard, 2,2'-difluorobiphenyl, was added to these BSTFA-derivatized aliquots and to three 200- μL aliquots of the solution containing the PFBHA derivatives prior to analysis by GC/ITMS. Two days prior to each data of analysis, a new set of standard solutions was reacted with aqueous PFBHA. One day prior to each analysis date, these standard solutions were extracted and reacted with BSTFA.

N. Interferences from Ozone.

Removal of ozone by using a KI-coated annular denuder was investigated. KI-coated annular denuders were constructed from a 12" x 1/8" o.d. stainless steel tube inside a 12" x ¼" o.d. stainless steel tube. The denuders were coated with KI by passing a saturated aqueous KI solution through the annular denuder three times, and drying the denuder under a stream of $N_2(g)$.

The ability of the KI-coated annular denuder to remove ozone was tested by passing O_3 through the denuder. Ozone was produced in animal exposure chambers at the UCD Primate Center from vaporized liquid, medical grade oxygen by electric discharge ozonizers. Both the ozone and oxygen were conveyed through Teflon™ lines to the mixing inlet of the exposure chamber. The ozone mixing ratio was monitored at the inlet and the outlet of the mist chamber every 30 seconds with an ultraviolet ozone analyzer (Model 1003-AH, Dasibi Corp., Glendale, CA). Calibration of the ozone analyzers was performed according to the national reference method (US CFR, Title 40, pp. 667-683; 1988) and is traceable to National Institute of Standards and Technology absolute ozone photometer serial number 4 located at the California Air Resources Board Quality Assurance Laboratory in Sacramento, CA. Air containing 120 ppbv O_3 was passed through the denuder at a 30 SLPM flow-rate. The mean and standard deviation of (n=6) measurements were 91 ± 2%.

1. Theoretical Calculations of Negative Interferences.

Ozonation of the analytes in the collecting solution will result in negative interferences - lower concentrations of the analytes due to their oxidation during sampling. Since no information exists regarding aqueous ozonolysis of the analytes, we estimated the rate of reaction based on the maximum concentration of ozone in the Blodgett Forest and the maximum concentration of ozone in the mist chamber, based on the assumption that the K_H gives an accurate prediction of

the aqueous-phase concentration of ozone. Using $K_H(O_3) = 0.0113$ M atm^{-1} (Seinfeld and Pandis, 1997) and a maximum mixing ratio of 100 ppbv for O_3 (Gunnar Schade, personal communication), the maximum aqueous concentration of ozone in the mist chamber was calculated to be 1.3×10^{-9} M. The rates of reaction for hydroxyacetone, formaldehyde, 2-hydroxy-2-methylpropanal, glycolaldehyde, glyoxal, and methylglyoxal were calculated using the equation $-d[\text{carbonyl}]/dt = k_{oz+carb}*[O_3]*[\text{carbonyl}]$ for the rate of destruction of carbonyls in the scrubber, where $k_{oz+carb}$ is 100 M^{-1} s^{-1} (Lee, 1985), and [carbonyl] is the concentration of analyte in the collection solution at the detection limit. We examined the effects of aqueous ozonolysis on the analytes of interest at the detection limit or at the lowest concentration measured at Blodgett. We did this because the low concentrations are more susceptible to interference. For example, if 200 pptv glycolaldehyde is destroyed or produced by aqueous ozonolysis, this is only 11% interference at the highest concentration measured (~ 1900 pptv), but it is 25% interference at the low concentration measured (~ 800 pptv) and 417% interference at the detection limit (48 pptv). Because the analytes are allowed to react with PFBHA in the collection solution for approximately 24 hours, we calculated the amount of each analyte destroyed in 24 hours by multiplying the reaction rate by 24 hours.

2. Theoretical Calculations of Positive Interferences.

The maximum formation of the analytes or products (formaldehyde, glycolaldehyde, hydroxyacetone, 2-hydroxy-2-methylpropanal, glyoxal, and methylglyoxal) due to aqueous ozonolysis (positive artifacts) was calculated by using the highest mixing ratios for the parent compounds, isoprene (10 ppbv), 2-methyl-3-buten-2-ol (10 ppbv), methacrolein (5 ppbv), and methyl vinyl ketone (10 ppbv) measured at the Blodgett Forest (Lamanna and Goldstein, 1999, Schade and Goldstein, 2000). We estimated the concentration of the parent compounds in the Cofer by using Henry's law constants to predict the partitioning of the gas- phase compounds to the liquid phase (Allen et al, 1998, Nirmalakahandan and Speece, 1988, Altschuh et al, 1999). We again assumed that the aqueous concentrations of these compounds can be predicted using

their Henry's law constants (Allen et al, 1998, Nirmalakahandan and Speece, 1988, Altschuh et al, 1999). We calculated the rates of reaction of the parents using -d[parent]/dt = $k_{oz+parent}$*[O_3]*[parent]. Because these compounds are unsaturated, they react with ozone more rapidly than analytes discussed previously (10^4- 10^5 $M^{-1}s^{-1}$ vs. 10^2 $M^{-1}s^{-1}$) and will quickly deplete the aqueous ozone in the sample (Pedersen and Sehested, 2001, Hoigne et. al., 1983). Therefore, the total amount of each parent compound that can react with ozone was calculated as the sum of the amount that will react during the 10-minute sampling period and the amount that will react with the remaining ozone present at the end of the sampling period. However, we do not have information on the products of aqueous ozonolysis of isoprene, 2-methyl-3-buten-2-ol, methacrolein, and methyl vinyl ketone, or on the yields of the products. We therefore summed the total amount of each parent that would react with ozone in 24 hours, and assumed that 100% of the product could consist of any one of the analytes of interest. Again, because interference will be greatest at the low concentrations, we compared the potential concentration of analyte formed to the detection limit of each analyte.

3. Air Sampling in the Absence and Presence of a KI-Coated Stainless Steel Annular Denuder.

Six air samples (n=2 for each sample) were collected in the Blodgett Forest, CA, on July 29, 2000, between the hours of 12:00 p.m. and 4:45 p.m., Pacific Standard Time, in the absence and presence of a KI-coated stainless steel annual denuder. Ozone mixing ratios during the sampling period ranged from 49 to 95 ppbv, which are typical summer levels.

4. Sorption of Analytes to the Stainless Steel Annular Denuder.

A Tedlar™ bag experiment was conducted to investigate sorption of the analytes to the stainless steel. Analytes were collected from the bag into a mist chamber fitted with a stainless

steel annular denuder at the inlet. After each sample, the sorbed analytes were extracted by rinsing the annular denuder with 20 ml of a 1mM aqueous PFBHA solution.

5. *Aqueous Ozonation of Isoprene, Methacrolein, Methyl Vinyl Ketone, and 2-methyl-3-buten-2-ol.*

Experiments were conducted to determine whether aqueous ozonation of isoprene, methyl vinyl ketone, methacrolein, and 2-methyl-3-buten-2-ol (unsaturated compounds known to be present at Blodgett in high concentrations) yields sufficient concentrations of the analytes of interest to affect quantification. We collected air containing 150 ppbv of ozone through a mist chamber that contained 20 ml of 1-mM aqueous PFBHA for 10 minutes at 28 SLPM. After collection of ozonated air, the collection solution was enriched with 7 μg isoprene, 5 μg methacrolein, 8 μg methyl vinyl ketone, and 8 μg 2-methyl-3-buten-2-ol. This is equivalent to 280L of air containing approximately 8 ppbv isoprene, 6 ppbv methacrolein, 9 ppbv methyl vinyl ketone and 7 ppbv 2-methyl-3-buten-2-ol, representing high concentrations in the Blodgett Forest, (Lamanna and Goldstein, 1999; Schade and Goldstein, 2000), and assuming 100% dissolution of each.

O. Field Site.

The Blodgett Forest field site is in a ponderosa pine plantation, owned and operated by Sierra Pacifica Industries. The plantation is located (38°53'42,9' N, 120°37'57.9' W, 1315m) adjacent to the Blodgett Forest Research Station, a research forest of the University of California, Berkeley.

P. Statistical Analyses.

All statistical analyses were accomplished by using MINITAB Statistical Software for Windows, Release 13 (Minitab Inc., State College, PA). A student t-test was used to compare

means for experiments conducted in which two parameters were varied. The t-test was used to compare collection efficiencies at two temperatures and to compare collection efficiencies with two volumes of scrubbing solution. When the experiment contained more than two variables, analysis of variance (ANOVA) was used to test for differences between means. The ANOVA tests the null hypothesis that means for all variables are equal. If the null hypothesis is rejected by the ANOVA, a multiple comparison test must be used to determine which variables are not equal. For this, we used Tukey's pair-wise comparison, which is a widely accepted and robust multiple comparison test (Zar, 1984). ANOVA and Tukey's pair-wise comparison were used to compare collection efficiencies at different pH, to compare collection efficiencies with different salts added to the collection solution, to compare the efficiencies of different solvents for extraction of PFBHA derivatives, and to compare different protocols for silylation of hydroxyl groups. We performed the t-test, ANOVA, and Tukey's pair-wise comparisons using 95% confidence intervals.

III. Results and Discussion.

A. Sorption of Analytes to the Zefluor™ (Teflon™) Membrane Filter.

Because collection efficiencies and analyte concentrations measured in the mist chamber could be affected by sorption of the analytes to the Zefluor™ filter during sample collection, we evaluated whether sorption to the filter was significant. After collection of gas-phase standards, the concentration of model carbonyl compounds sorbed to the Zefluor™ filter were compared to the concentration measured in the scrubber as described by Rao *et al.*, 2001. To determine the efficiency of the extraction method, we also extracted carbonyls from Zefluor™ filters that were enriched with a solution containing the compounds. The average recoveries from the enriched filters were 91% for glycolaldehyde (n=1), 77% for hydroxyacetone (n=1), 100% for pyruvic acid (n=1), 134 ± 42% for glyoxal, and 80 ± 25% for methylglyoxal (n=2), indicating that these compounds can be extracted efficiently from the Zefluor™ membrane filter. The average

recovery of formaldehyde was 34 ± 6% (n=2). Formaldehyde concentrations measured on Zefluor™ filters, after sample collection, were corrected to account for the low recoveries. The recoveries for acetone, methacrolein, and methyl vinyl ketone were ≤ 1%. Therefore, sorption of these compounds onto the filters was not apparent.

The distribution of carbonyls between the aqueous collecting solution and the Zefluor™ filters after collection of gas-phase samples in the mist chamber is presented in Table 2.5. The fraction in the aqueous phase ranged from 87 to 99% of the total collected. We consider ± 20% to be acceptable error for the method, and thus sorption of formaldehyde, hydroxycarbonyls, dicarbonyls, and keto-acids on the Zeflour™ membrane filter during sample collection is essentially zero.

B. Relationship Between Collection Efficiency and Henry's Law Constant (K_H).

If Henry's law equilibrium is established for carbonyl compounds during sample collection in the mist chamber, the collection efficiency (CE) for these compounds can be estimated using a gas/aqueous-phase distribution calculation (equation 8), where the CE represents the

$$CE = \frac{K_H R T w_L}{1 + K_H R T w_L} \qquad (8)$$

fraction of analyte that is present in the aqueous phase at equilibrium (Seinfeld and Pandis, 1998). The theoretical CE was calculated using equation 8, where K_H is the Henry's law equilibrium constant (M atm^{-1}), R is the ideal gas law constant, T is the temperature, and w_L is the liquid water content (volume water/volume air). For all the carbonyls, except methacrolein and methyl vinyl ketone, we used the "effective" K_H, determined from the total amount of carbonyl that dissolves in water (including the gem-diol) (Betterton and Hoffman, 1988). For methacrolein and methyl vinyl ketone, we used the "physical" K_H determined as the amount of

Table 2.5. Distribution of analytes between the Zefluor™ filter and the aqueous PFBHA solution in the mist chamber.

Compound	Sample Number	Concentration (pg/μL)		Percent of Total		Percent of Total in Solution
		Filter	Aqueous Solution	Filter	Aqueous Solution	Mean ± S.D (% RSD)
Formaldehyde	1	ND	2447	0	100	99 ± 1
	2	35	1602	2	98	(1)
	3	ND	6013	0	100	
Glycolaldehyde	1	ND	509	0	100	89 ± 11
	2	165	1304	11	89	(12)
	3	153	542	22	78	
Hydroxyacetone	1	5	668	1	99	93 ± 12
	2	ND	2149	0	100	(12)
	3	12	49	20	80	
Glyoxal	1	17	832	2	98	87 ± 14
	2	104	273	28	72	(17)
	3	32	816	4	96	
Methylglyoxal	1	86	2329	4	96	91 ± 9
	2	224	973	19	81	(10)
	3	55	1504	4	96	
Pyruvic Acid	1	5	600	1	99	99 ± 1
	2	ND	477	0	100	(1)
	3	10	654	2	98	

carbonyl dissolved in its native form (without inclusion of the gem-diol), because to our knowledge, "effective" K_H are not available (Allen et al., 1998). However, we expect, as with other aldehydes and ketones, that minimal gem-diol formation would occur for methacrolein and methyl vinyl ketone (Buschmann et al., 1980, Buschmann et al., 1982). For example, if we

assume that the hydration equilibrium constants for methacrolein and methyl vinyl ketone are within the hydration constants for acetone ($K_{hyd} = 2\times10^{-3}$) and butyraldende ($K_{hyd}= 0.83$), the K_H would increase by a factor less than two. For hydroxyacetone and pyruvic acid, we estimated the K_H from solubility and vapor pressure because experimental values were not available (Yalkokowsky and Dannenmfelser, 1992, Perry and Green, 1984, Neely and Blau, 1985).

The results of initial experiments indicate a relationship between the collection efficiency and the Henry's law constant. These results are presented as a plot of the collection efficiency versus each compound in the order of increasing K_H. (See Figure 2.3). The mean collection efficiencies, in order of increasing K_H, are 0.06 ± 0.28 for methacrolein, -0.02 ± 0.27 for methyl vinyl ketone, 0.74 ± 0.19 for hydroxyacetone, 0.83 ± 0.12 for formaldehyde, 0.82± 0.20 for glycolaldehyde, 0.97± 0.07 for pyruvic acid, 0.88± 0.15 for glyoxal, and 0.73± 0.14 for methylglyoxal.

To explain empirical observations, and to support the choice of operational parameters that may increase the collection efficiency by altering the K_H, we evaluated the potential for Henry's law equilibrium to be established during sample collection. The analysis is not precise, but is sufficient to suggest the potential for equilibrium to be established. A more rigorous analysis is beyond the scope of this work.

When collecting air at 30 L min^{-1} in a 190-mL mist chamber containing 10 mL of aqueous solution, the contact time between the air and the water is 0.36 seconds. Therefore, for equilibrium conditions to apply, equilibrium must be established in ≤ 0.36 seconds.

Establishment of the "effective" Henry's law equilibrium between air containing an analyte and an aqueous solution that does not contaning the analyte, involves: 1) gas-phase diffusion of the analyte to the surface of the mist droplet, 2) transport of the analyte across the interface of the droplet, 3) aqueous-phase diffusion of the analyte through the droplet, and 4) hydration of the carbonyl to form a gem-diol. The calculations, which are not meant to predict precise times,

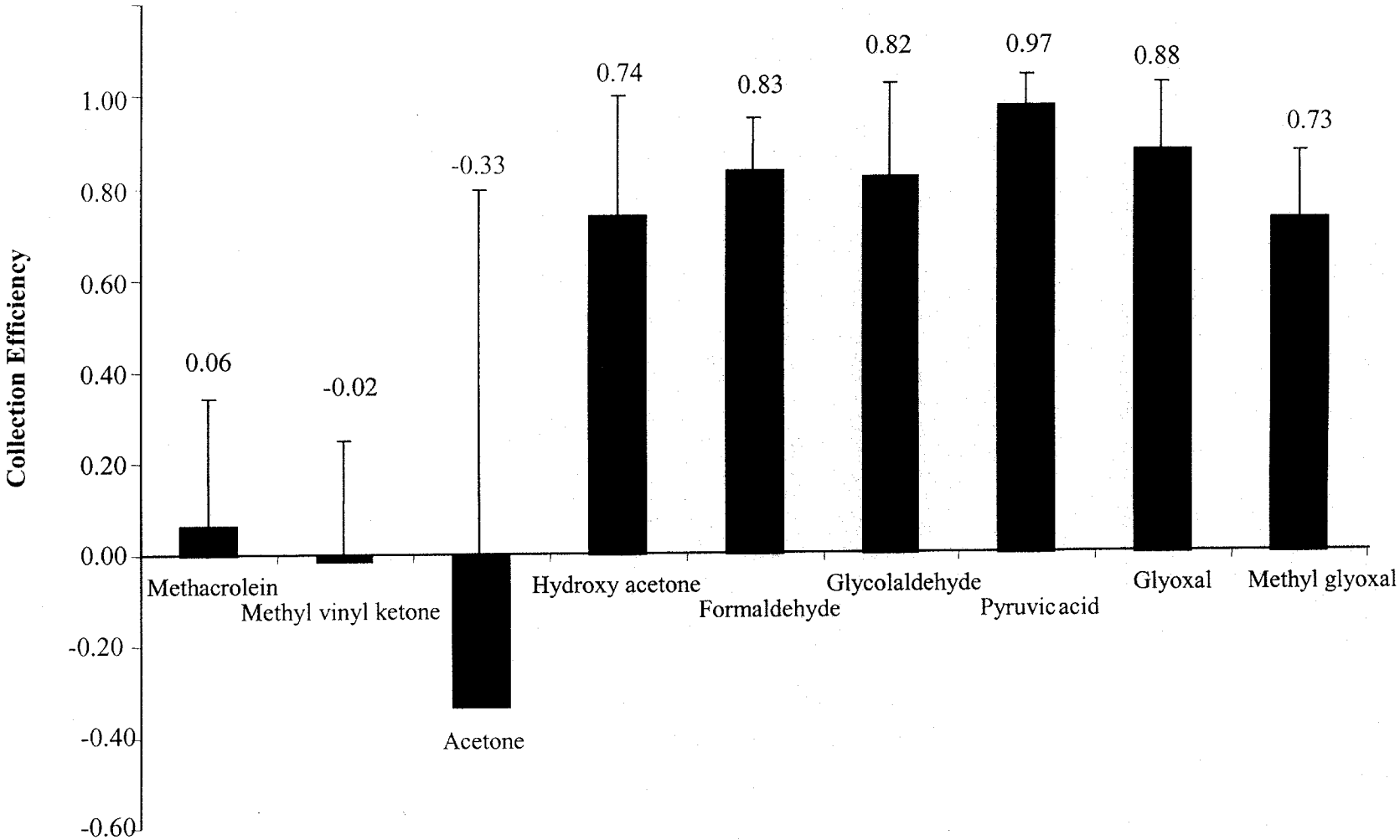


Figure 2.3. Mean collection efficiency plotted in increasing order of Henry's law constant (K_H).

indicate that the time for each transport process will be at least an order of magnitude less than 0.36 sec for carbonyls, hydroxycarbonyls, dicarbonyls, and keto-acids. However, the time for hydration can range from 0.06 to 10 sec. Therefore, establishment of the "effective" Henry's law equilibrium compounds may be limited by the rate of hydration. The rate and extent of hydration can vary considerably for different carbonyl compounds, and constants are not available for most of the analytes of interest. However, for compounds that become hydrated rapidly or for which little hydration occurs, Henry's law equilibrium may dictate the collection efficiency of the mist chamber and equation 1 should provide a reasonable approximation of the collection efficiency.

For two samplers in series, such as in our experiments, the empirical collection efficiency can be calculated by the equation $[1- C_1/C_2]$, where C_1 is the concentration in the first scrubber and C_2 is the concentration in the second scrubber. The theoretical CE was compared to the empirical CE, to evaluate whether Henry's law was controlling collection efficiency for the analytes. This approach was also used by other researchers to calculate the empirical and theoretical CE (Lee and Zhou, 1993).

The results of experiments conducted to evaluate the relationship between the collection efficiency and K_H are presented in Table 2.6, as the theoretical and empirical collection efficiencies for model carbonyl compounds in the mist chamber. For all compounds except acetone good agreement ($\leq$ 22% difference) was obtained between the theoretical and empirical collection efficiencies. The difference between theoretical and empirical collection efficiencies for acetone (0.02 vs. -1.02) is likely a result of analytical errors that arise from measuring acetone near the limit of detection.

The data indicate that Henry's law equilibrium is established for carbonyls, hydroxycarbonyls, dicarbonyls, and keto-acids during sample collection in the mist chamber, and that the collection efficiency of a given carbonyl compound can be predicted using equation 1 when effective

Henry's law constants are available. The data also suggest that the method is suitable for sampling water-soluble species with $K_H \geq 10^3$.

Table 2.6. Comparison of theoretical and empirical collection efficiencies for sampling carbonyls in a mist chamber (n=4).

		Collection Efficiency		
Compound	**"effective" K_H at 298K (M atm^{-1})**	**Theoretical**	**Empirical Mean ± S.D.**	**Difference**
Methacrolein	4.3[a]	0.00	0.08 ± 0.36	+0.08
Acetone	26[b]	0.02	-1.02 ± 2.05	-1.00
Methyl vinyl ketone	46[a]	0.04	0.06 ± 0.36	+0.02
Hydroxyacetone	2927[c,d]	0.70	0.84 ± 0.14	+0.14
Formaldehyde	2970[b]	0.71	0.84 ± 0.12	+0.13
Pyruvic Acid	6730[c,e]	0.85	0.94 ± 0.12	+0.12
Glycolaldehyde	41400[b]	0.97	0.93 ± 0.06	-0.04
Glyoxal	>300000[b]	1.00	0.78 ± 0.20	-0.22
Methylglyoxal	371000[b]	1.00	0.85 ± 0.04	-0.15

[a] "physical" K_H from Allen *et al.*, 1998.
[b] "effective" K_H from Betterton, 1992.
[c] K_H estimated from solubility, Yalkowsky and Dannenfelser, 1992.
[d] and vapor pressure, Neely and Blau, 1985 and [e]Perry and Green, 1984.

C. Evaluation of Operational Parameters.

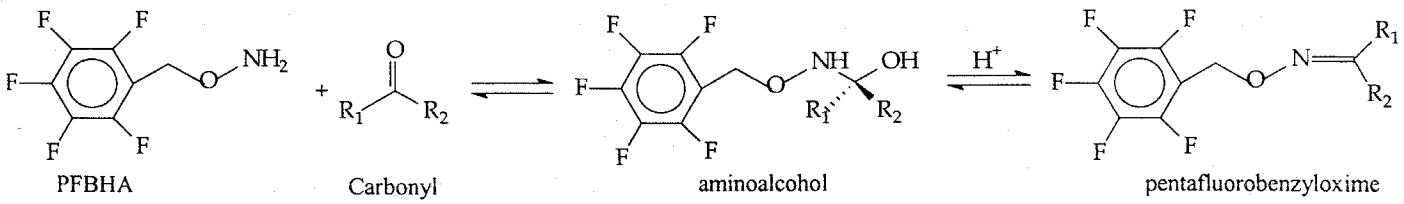
Given the correlation between the collection and the Henry's law constant, we hypothesized that we could increase the collection efficiency by altering operational parameters that would affect the K_H. Accordingly, we investigated the effect of pH, temperature, and addition of organic salts on the collection efficiency.

1. The Effect of the pH on the Collection Efficiency.

In theory, removal of the aqueous-phase species by formation of the PFBHA derivative would shift the Henry's law equilibrium to enable more of the gas-phase compound to dissolve, and thus increase the "effective Henry's law constant," (H^*) as shown by the following equation:

$$\text{Carbonyl (g)} \xrightleftharpoons{H^* \text{ carbonyl}} \text{Carbonyl(aq)} \xrightleftharpoons{\text{PFBHA}} \text{PFBHA-oxime (aq)}$$

To our knowledge, kinetic and mechanistic data do not exist regarding the reaction of carbonyls with PFBHA. Limited data do exist, however, for the reaction of carbonyls with hydroxylamine (Jencks, 1964). These data demonstrate that the formation of an oxime from reaction of hydroxylamine with a carbonyl is a two-step process. In the first step of the reaction, shown here (using PFBHA), the hydroxylamine reacts with the carbonyl through nucleophilic attack on the carbonyl carbon by the lone electron pair on the nitrogen to form an aminoalcohol. The rate of this reaction increases as the pH rises above the pK_a of the hydroxylamine (pH 6 for hydroxylamine, pH 3.2 for PFBHA), and the hydroxylamine becomes unprotonated (Jencks, 1964; Cancilla et. al., 1992). The second step is dehydration of the aminoalcohol, which leads to formation of an oxime. The dehydration reaction is faster at low pH, where the aminoalcohol is easily protonated (Jencks, 1964).



For the reaction of hydroxylamine with acetone, the overall reaction rate is a bell-shaped curve, with the maximum rate between pH 4 and 5. We expect the kinetics for PFBHA to be similar, but do not know the pH at which the fastest rate of the reaction occurs for the analytes of interest. We hypothesized that by changing the pH we could increase the rate of reaction of PFBHA with the carbonyls to a rate that would be fast enough to occur within the contact time between air and water in the mist chamber. The consequence would be an increase in the effective Henry's law constant for the carbonyls and, thus, an increase in the collection efficiency.

The pK_a of PFBHA is between 3.0 and 3.2 (Cancilla *et al.,* 1992). Therefore, formation of the aminoalcohol should be fast above pH 3. On the other hand, the dehydration reaction should be fast at lower pH. However, it is not necessarily important that both steps of the reaction occur quickly. It is only necessary for the carbonyl compound to react, thereby shifting the Henry's law equilibrium to the right. Therefore, instead of attempting to understand the kinetics of the reaction in detail, we chose to examine the effect of different pH on collection efficiency in the mist chamber.

The data are presented as a plot of the mean collection efficiencies (n=2) obtained in the laboratory vs. pH in Figure 2.4. Methacrolein could not be detected at any of the pH, and thus the mean collection efficiency and standard deviation are 0.00 ± 0.00 at pH=1,3,5,and 7. For methyl vinyl ketone, acetone, and formaldehyde an increase in the collection efficiency was observed between pH=1 and pH=5, and then decreased at pH=7.0. The mean collection

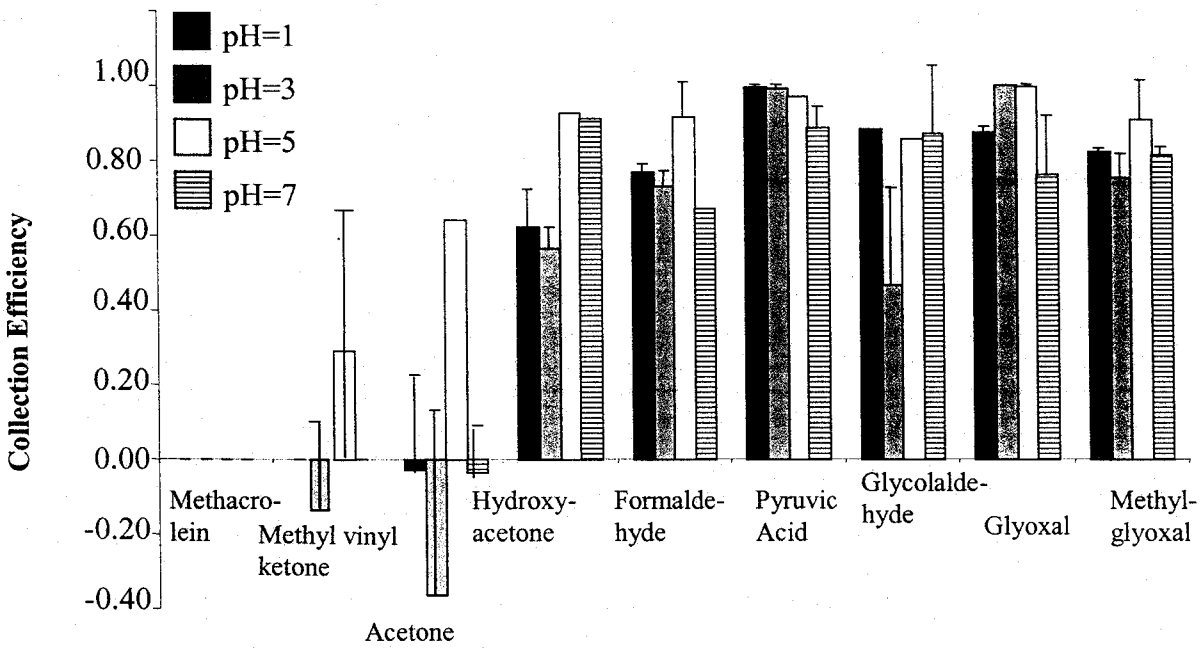


Figure 2.4. Collection efficiencies of analytes for samples collected from a Tedlar™ bag at pH=1, 3, 5, and 7 of the PFBHA aqueous solution in the mist chamber (n=2, error bars = 1σ).

efficiency and the standard deviation for methyl vinyl ketone were 0.00± 0.00 (pH=1), -0.18 ± 0.25 (pH=3), 0.29 ± 0.41 (pH=5), and 0.00 ± 0.00 (pH=7). For acetone, the collection efficiencies were -0.02 ± 0.25 (pH=1), -0.36 ± 0.49 (pH=3), 0.64 ± 0.32 (pH=5), and -0.03 ± 0.12 (pH=7), and for formaldehyde the collection efficiencies were 0.77 ± 0.02 (pH=1), 0.73 ± 0.04 (pH=3), 0.91 ± 0.10 (pH=5), and 0.67 (n=1; pH=7). The collection efficiency for hydroxy acetone was similar at pH=1, and pH=3, and increased to similar values at pH=5.0 and pH=7.0. The collection efficiencies were 0.62 ± 0.10 (pH=1), 0.57 ± 0.06 (pH=3), 0.93 ± 0.00 (pH=5), and 0.91 (n=1; pH=7). For pyruvic acid and methyl glyoxal, the collection efficiency did not appear to be affected by pH. The mean collection efficiencies and standard deviations for pyruvic acid were 0.99 ± 0.01 (pH=1), 0.99 ± 0.01 (pH=3), 0.97 ± 0.00 (pH=5), and 0.89 ± 0.06 (pH=7), and 0.82 ± 0.01 (pH=1), 0.76 ± 0.06 (pH=3), 0.91 ± 0.10 (pH=5), and 0.81 ± 0.02 at

pH=7 for methyl glyoxal. For glycolaldehyde, the mean collection efficiency at pH=1,3 and 7 were similar, with mean collection efficiencies and standard deviations of 0.88 ± 0.00 (pH=1), 0.47 ± 0.26 (pH=3), 0.85 ± 0.00 (pH=5), and 0.87 ± 0.18 (pH=7.0). For glyoxal, the mean collection efficiency appeared higher at pH=3 and pH=5.0 than at pH=1.0 and pH =7.0. The mean collection efficiencies and standard deviations were 0.87 ± 0.01 (pH=1), 1.00 (n=1; pH=3), 0.99 ± 0.01 (pH=5), and 0.76 ± 0.16 (pH=7).

Although no clear trend was observed among the compounds, visual inspection of the data indicate an optimum pH= 5 for methyl vinyl ketone, acetone, formaldehyde, glyoxal, and methylglyoxal, and pH=5 or 7 for hydroxyacetone. Further the data appear to follow a bell-shape curve that represents the balance in the rate of the PFBHA reaction between nucleophilic attack and dehydration. When the data were analyzed by ANOVA, however no significant differences (p=0.050) were observed among the different pH. This may be due to the low number of replicates (2), and the large standard deviation between the replicates for some compounds (*e.g.*, a relative standard deviation > 100% among replicate measurements for methyl vinyl ketone and acetone).

To resolve differences between the conclusions reached by visual inspection and statistical analysis of the data, an additional experiment was conducted in the ambient environment. In this experiment, we compared collection efficiencies at pH=3, the pH of the PFBHA solution without any pH adjustment, and pH=5. The results are presented as a plot of the mean collection efficiency for each compound at pH=3 and pH=5 in Figure 2.5.

For 2-hydroxy-2-methyl-propanal, 3-hydroxy-2-butanone, and glyoxal, the mean collection efficiencies were 1.00 ± 0.00 at both pH. For glycolaldehyde and hydroxy acetone, the mean collection efficiencies were nearly the same with mean collection efficiencies of 0.98 ± 0.05 (pH=3) and 0.99 ± 0.03 (pH=5) for glycolaldehyde, and mean collection efficiencies of 0.96 ± 0.08 (pH=3) and 1.00 ± 0.00 (pH=5) for hydroxy acetone. Methyl glyoxal was the only

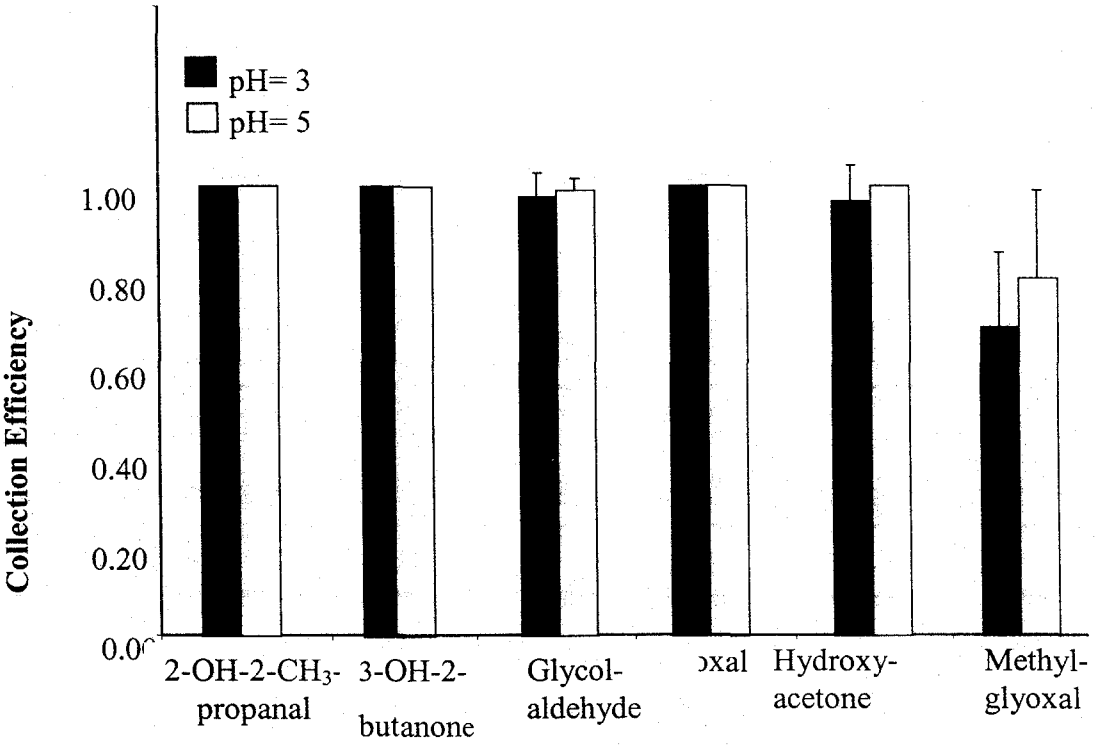


Figure 2.5. Collection efficiencies of the analytes sampled in the Blodgett Forest at a pH=3 and pH=5 of the PFBHA aqueous solution (n=5; error bars = 1σ).

compound for which the collection efficiency appears to be affected by pH. For this analyte collection efficiencies were 0.68 ± 0.17 (pH=3) and 0.79 ± 0.19 (pH=5). The means of the collection efficiencies at pH=3 and pH=5 were compared by using a two-sample t-test. No significant differences (p=0.05) were observed between the collection efficiencies at pH=3 and pH=5.

In summary, the results of the experiments conducted in the laboratory and in the ambient environment do not suggest that the pH of the collecting solution has an effect on the collection efficiency. This indicates that the reaction of the analytes with PFBHA does not occur at a fast enough rate to significantly increase the effective Henry's law equilibrium. Accordingly, we chose to collect subsequent samples at pH=3 (no pH adjustment).

2. The Effect of the Temperature on the Collection Efficiency.

For most organic compounds, decreasing the temperature will decrease the vapor pressure significantly, while only affecting the solubility slightly. The solubility can decrease or increase with decreased temperature. However, since the decrease in vapor pressure generally outweighs the change in solubility, the result is an increase in the Henry's law constant (Schwartzenbach, et al., 1992). This is demonstrated by the integrated van't Hoff equation:

$$\frac{1}{T_2} = \frac{1}{T_1} - \frac{R}{\Delta K_H} \ln \frac{K_H(T_2)}{K_H(T_1)}$$

where T_1 and T_2 are the original and modified collecting solution temperatures, respectively, and K_H is the reaction enthalpy for dissolution of an analyte from the gas phase into water at constant temperature and pressure (Seinfeld and Pandis, 1998). Because ΔK_H is negative for most compounds, decreasing the temperature will increase K_H, and thereby increase dissolution. We therefore attempted to increase K_H and thus the collection efficiency by decreasing the temperature of the collecting solution.

The mean collection efficiencies (n=3) for each analyte at 16°C (control) and 11°C (water temperature lowered by KCl ice bath) are presented in Figure 2.6. The mean collection efficiencies ± standard deviation are 0.02 ± 0.03 at 16°C and 0.00 ± 0.00 at 11°C for methacrolein; 0.83 ± 0.06 at 16°C and 0.78 ± 0.09 at 11°C for hydroxy acetone; 0.99 ±0.01 at 16°C and 0.98 ±0.09 at 11°C for pyruvic acid; 0.86 ± 0.07 at 16°C and 0.90 ± 0.06 at 11°C for glycolaldehyde; at 11°C; 0.51 ± 0.08 at 16°C and 0.49 ± 0.05 at 11°C for glyoxal; and 0.73 ± 0.03 at 16°C and 0.66 ± 0.06 at 11°C for methyl glyoxal. For methyl vinyl ketone, acetone and

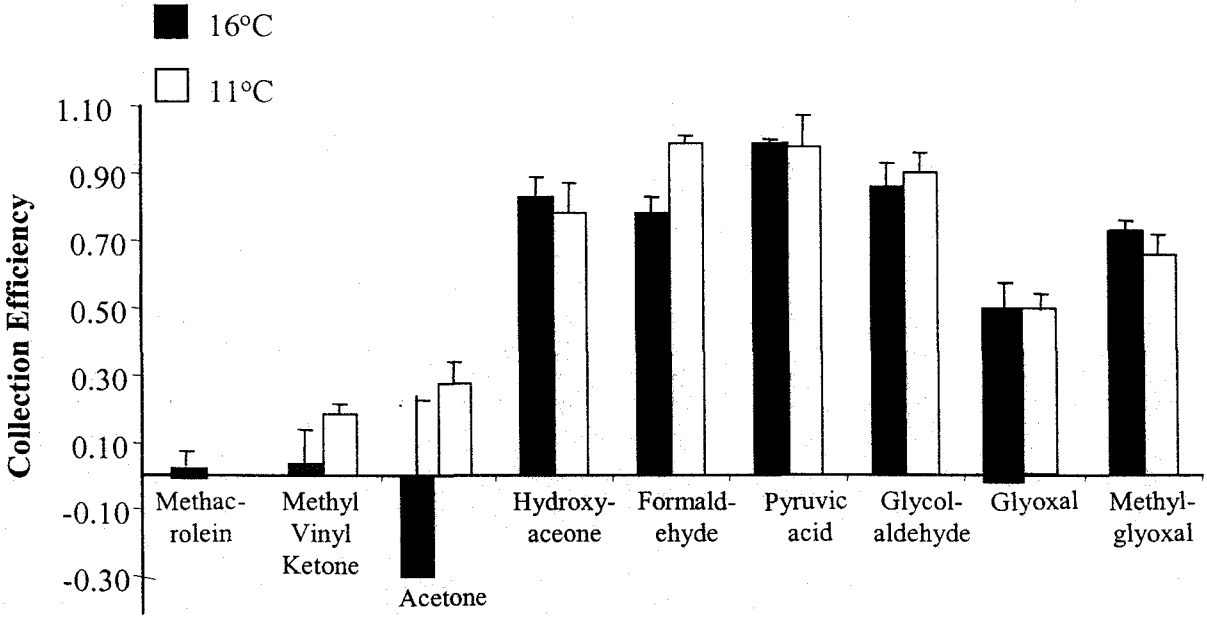


Figure 2.6. Collections efficiencies of analytes for samples collected from a Tedlar™ bag at temperatures of the collecting solution of 16°C and 11°C (n=3; error bars=1σ).

formaldehyde, the collection efficiency appeared to increase at the lower temperature. The mean collection efficiencies were 0.04± 0.10 at 16°C and 0.19± 0.03 at 11°C for methyl vinyl ketone; 0.29 ± 0.50 at 16°C and 0.27 ± 0.07 at 11°C for acetone; 0.78 ± 0.04 at 16°C and 0.99 ± 0.02 at 11°C for formaldehyde.

Statistical analysis of the data by using a t-test was conducted to determine if significant differences exist between the mean collection efficiencies at 16°C and 11°C. Statistical differences (p=0.05) were observed between the collection efficiencies at 11°C and 16°C only for formaldehyde.

To assist in explaining these results, the theoretical K_H at 16°C (289K) and 11°C (284K) were calculated according to the van't Hoff equation. (See Table 2.7). The K_H at 16°C (289K) and

Table 2.7. Henry's law equilibrium constants at 25°C (298K), 16°C (289K) and 11° (284K).

Compound	K_H at 298K (M atm^{-1})	ΔK_H (KJ mol^{-1})	K_H at 289K (M atm^{-1})	K_H at 284K (M atm^{-1})
Methacrolein	4.3	-41.7	7.3	9.9
Acetone	25.6	-37.2	40.9	53.7
Methyl Vinyl Ketone	46	-62.3	101	159
2,3-butanedione	57	-50	107	154
Hydroxyacetone	129		209	278
Formaldehyde	2.97×10^3	-53.6	5.83×10^3	8.63×10^3
Pyruvic Acid	6.73×10^3		1.32×10^4	1.96×10^4
Glycolaldehyde	4.14×10^4	-38.5	6.72×10^4	8.91×10^4
Glyoxal	3.00×10^5		6.60×10^5	1.04×10^6
Methylglyoxal	3.71×10^5	-62.7	8.16×10^5	1.29×10^6

11°C (284K), respectively are 7.3 and 9.9 for methacrolein; 40.9 and 53.7 for acetone; 101 and 159 for methyl vinyl ketone; 107 and 154 for 2,3-butanedione; 209 and 278 for hydroxy acetone; 5.83×10^3 and 8.63×10^3 for formaldehyde; 1.32×10^4 and 1.96×10^4 for pyruvic acid; 6.72×10^4 and 8.91×10^4 for glycolaldehyde; 6.60×10^5 and 1.04×10^6 for glyoxal; and 8.16×10^5 and 1.29×10^6 for methyl glyoxal. The theoretical and empirical collection efficiencies at 16°C (289K) and 11°C (284K) and a comparison of the predicted change to the measured change are presented in Table 2.8 and Table 2.9.

Overall, good agreement (< 20% relative difference) was obtained between the theoretical and empirical collection efficiencies, except for glyoxal and methyl glyoxal. Methylglyoxal and glyoxal might not reach Henry's law equilibrium, as mentioned above, due to slower equilibrium reactions, and thus exhibit lower than expected collection efficiencies. The predicted and

Table 2.8. Comparison of theoretical and empirical collection efficiencies at 16°C and 11°C.

Compound	Collection efficiency at 16°C (298K) Mean ± S.D.			Collection efficiency at 11°C (284K) Mean ± S.D.		
	Theoretical	Empirical	% Relative Difference	Theoretical	Empirical	% Relative Difference
Methacrolein[1]	0.01	0.02 ± 0.03	+10	0.01	0.00 ± 0.00	-1
Acetone[2]	0.03	-0.28 ± 0.50	-33	0.04	0.27 ± 0.07	+23
Methyl Vinyl Ketone[1]	0.07	0.04 ± 0.10	-3	0.11	0.19 ± 0.03	+8
2,3-butanedione[2]	0.08	-0.04 ± 0.10	-12	0.11	-0.08 ± 0.23	-19
Formaldehyde[2]	0.82	0.78 ± 0.04	-4	0.87	0.99 ± 0.02	+12
Pyruvic Acid[3]	0.91	0.99 ± 0.01	+8	0.94	0.98 ± 0.09	+4
Glycolaldehyde[2]	0.98	0.86 ± 0.07	-12	0.99	0.90 ± 0.06	-9
Methylglyoxal[2]	1.00	0.73 ± 0.03	-27	1.00	0.66 ± 0.06	-34

[1]Allen *et. al.*, 1998; [2]Betterton,, 1992; [3]Meylan and Howard, 1997, estimated value for K_H; *Used ΔH for glycolaldehyde
*Used ΔH for methylglyoxal

measured changes in the collection efficiency, with the exception of acetone, are also in good agreement (< 20% relative difference). The change in the predicted collection efficiency between 16°C and 11°C (0-13% relative difference) is less than the error of the method.

In conclusion, the change in the collection efficiency between 16°C and 11°C, as predicted from theory or from experimental results is too small to warrant lowering the temperature of the collecting solution in the ambient environment. The protocol that we used to lower the temperature (i.e., submersing the scrubbers in an ice bath) is quite cumbersome and unwieldy. Based on the results and this consideration, we decided to sample air at the ambient temperature of the collecting solution.

Table 2.9. Comparison of theoretical and empirical changes in the collection efficiency due to changing the temperature of collecting solution from 16°C to 11°C.

Compound	Collection Efficiency	
	Predicted Change (% relative difference)	**Measured Change (% relative difference)**
Methacrolein	+ 0.00 (+ 0)	- 0.01 (- 100)
Acetone	+ 0.01 (+ 33)	+ 0.55 (+ 196)
Methyl Vinyl Ketone	+ 0.04 (+ 57)	+ 0.15 (+ 375)
2,3-butanedione	+ 0.03 (+ 38)	- 0.04 (- 100)
Hydroxyacetone	+ 0.04 (+ 29)	- 0.05 (- 6)
Formaldehyde	+ 0.05 (+ 6)	+ 0.11 (+ 11)
Pyruvic Acid	+ 0.03 (+ 3)	+ 0.05 (+ 5)
Glycolaldehyde	+ 0.01 (+ 1)	+ 0.04 (+ 5)
Glyoxal	+ 0.00 (+ 0)	+ 0.02 (+ 4)
Methylglyoxal	+ 0.00 (+ 0)	+ 0.07 (+ 10)

3. The Effect of Addition of Tetraalkylammonium Salts to the Collecting Solution on the Collection Efficiency.

Dissolution of an organic compound in water involves: 1) breaking of interactions between organic molecules, 2) breaking of interactions between water molecules, and 3) formation of interactions between the organic molecules and the water molecules. The first two processes are endothermic (+ΔH), while the third is exothermic (-ΔH). Because organic:organic interactions and water:water interactions are generally stronger than organic:water interactions, the overall process is generally endothermic. Therefore, organic compounds are often only slightly soluble in water. Addition of an inorganic salt to water causes the water molecules to become more polarized and the solution to become more structured. The water:water interactions are stronger and require more energy to break. This makes dissolution of an organic compound more

endothermic, thus decreasing the solubility of the organic compound, which is commonly known as "salting out." Addition of a large organic salt, such as a tetraalkylammonium salt, to water also increases the structure of the water molecules and increases the strength of the water:water interactions. However, the large alkyl portion of the salt will allow "co-dissolution" of an organic compound by forming favorable interactions between the organic compound and the alkyl portion of the salt. This process is exothermic and can off-set the endothermic processes of breaking organic:organic and water:water interactions. If -ΔH for formation of organic:tetraalkly interactions is greater that the excess +ΔH of breaking water:water interactions caused by addition of the tetraalkylammonium salts, the organic compound will become more soluble, which is commonly known as "salting in" (Desnoyers *et al.,* 1978; Conway and Novak, 1974).

" Salting in" of alkanes and alcohols by tetraalkylammonium salts has been demonstrated, and Setchenow, or "salting," constants have been calculated for some of these compounds (Desnoyers,et at., 1965; Wen and Hung, 1970). However, to our knowledge, data on the effect of tetraalkylammonium salts on the solubility of carbonyl, dicarbonyl, hydroxycarbonyl, and keto-acid compounds is not available in the literature. We investigated the effect of the addition of tetraalkylammonium salts on the collection efficiency in the mist chamber and, thus, on the solubility of multifunctional carbonyl compounds. We measured collection efficiency after addition of 0.25 molal tetramethylammonium bromide or 0.25 molal tetrapropylammonium bromide to the collecting solution in the mist chamber. The control was 0.5 mg/mL aqueous PFBHA.

The results are presented in Figure 2.7 as the mean (n=2) collection efficiency versus the analyte for the three conditions employed. Collection efficiencies for control samples, tetramethylammonium bromide samples, and tetrapropylammonium bromide samples were 0.00 ± 0.00 for all three conditions for methacrolein; -0.46 ±0.34, -0.40 ± 0.27, –1.28 ± 1.36 for acetone; -0.07 ±0.10, -0.07 ± 0.18, and 0.04 ± 0.06 for methyl vinyl ketone; 0.79 ± 0.03, 0.83 ± 0.00, and 0.80 ± 0.02 for hydroxyacetone; 0.92 ± 0.01, 0.94 ± 0.09, and 0.90 ±0.09 for

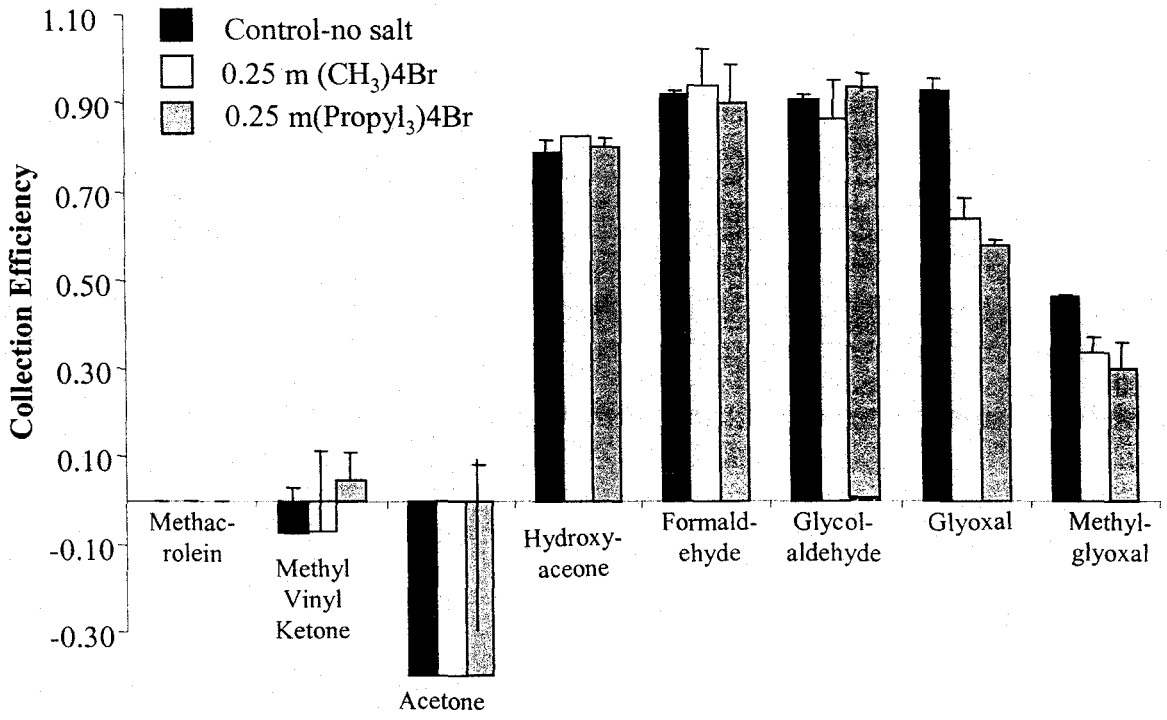


Figure 2.7. Collection efficiencies of analytes sampled from a Tedlar™ bag after addition of salts to the PFBHA aqueous solution (n=2; error bars=1σ).

formaldehyde; 0.99 ± 0.01, 1.00 ± 0.00, and 1.00 ± 0.00 for pyruvic acid; 0.91 ± 0.01, 0.87 ± 0.09, and 0.93 ± 0.04 for glycolaldehyde; 0.93 ± 0.03, 0.64 ± 0.05, and 0.58 ±0.01 for glyoxal; and 0.47 ± 0.00, 0.34 ± 0.04, and 0.30 ± 0.06 for methylglyoxal. No significant differences (p=0.05) were observed for methacrolein, methyl vinyl ketone, acetone, hydroxyacetone, methacrolein, methyl vinyl ketone, acetone, hydroxyacetone, formaldehyde, pyruvic acid, and glycolaldehyde by analysis of variance. According to analysis by Tukey's pair-wise comparison, for glyoxal and methylglyoxal the collection efficiency in 0.25 m tetrapropylammonium bromide was significantly lower than the collection efficiency in tetramethylammonium bromide, which

was significantly lower than the collection efficiency in the control (p=0.05). The reason for the latter result is unclear. However, quaternary ammonium salts have been shown to decrease the solubility of some alkanes and alcohols in water (Desnoyers,et at., 1965; Wen and Hung, 1970; Desnoyers et al., 1978). Additionally, glyoxal and methylglyoxal owe their high water solubilities to the formation of gem-diols (Betterton, 1992). Interaction of glyoxal and methylglyoxal with the alkyl portion of the tetraalkylammonium salts might partially inhibit the formation of the gem-diols, thus decreasing the solubility of these compounds, and glyoxal and methylglyoxal might interact more strongly with the larger propyl group of tetrapropylammonium bromide, inhibiting gem-diol formation to a greater degree. This would explain why the solubility of these dicarbonyls decreases more with addition of tetrapropylammonium bromide than with addition of tetramethylammonium bromide.

5. The Effect of Scrubber-Solution Volume on the Collection Efficiency.

The volume of the liquid in the mist chamber could affect the partitioning of the analyte between the gas- and liquid phases by changing ω_L in the equation for X_{aq}. Accordingly, we compared the collection efficiency for analytes sampled in the Blodgett Forest with either 10 mL or 20 mL of PFBHA solution in the mist chambers (n=4). The data are presented in Figure 2.8. For glycolaldehyde, hydroxy acetone, 3-hydroxy-2-butanone, 2-hydroxy-2-methyl propanal and glyoxal the mean collection efficiency collection efficiency did not differ between 10 mL or 20 mL of 1mm PFBHA. The mean ± standard deviation collection efficiency was 0.94± 0.07 for glycolaldehyde, 0.93± 0.08 for hydroxy acetone; 1.00± 0.00 for 3-hydroxy-2-butanone; 1.00± 0.00 for 2-hydroxy-2-methyl propanal; and 1.00± 0.00 for glyoxal. For methyl glyoxal, a mean collection efficiency of 0.89± 0.08 and 0.87± 0.09 was measured for 10 mL and 20 mL of the 1 mM PFBHA solution, respectively. Statistical analysis was conducted by ANOVA to verify no significant differences existed between the mean values. As expected, no significant differences were observed (p=0.05). The data thus indicate that doubling the volume of the liquid phase is not a sufficient volume increase to significantly increase collection efficiency.

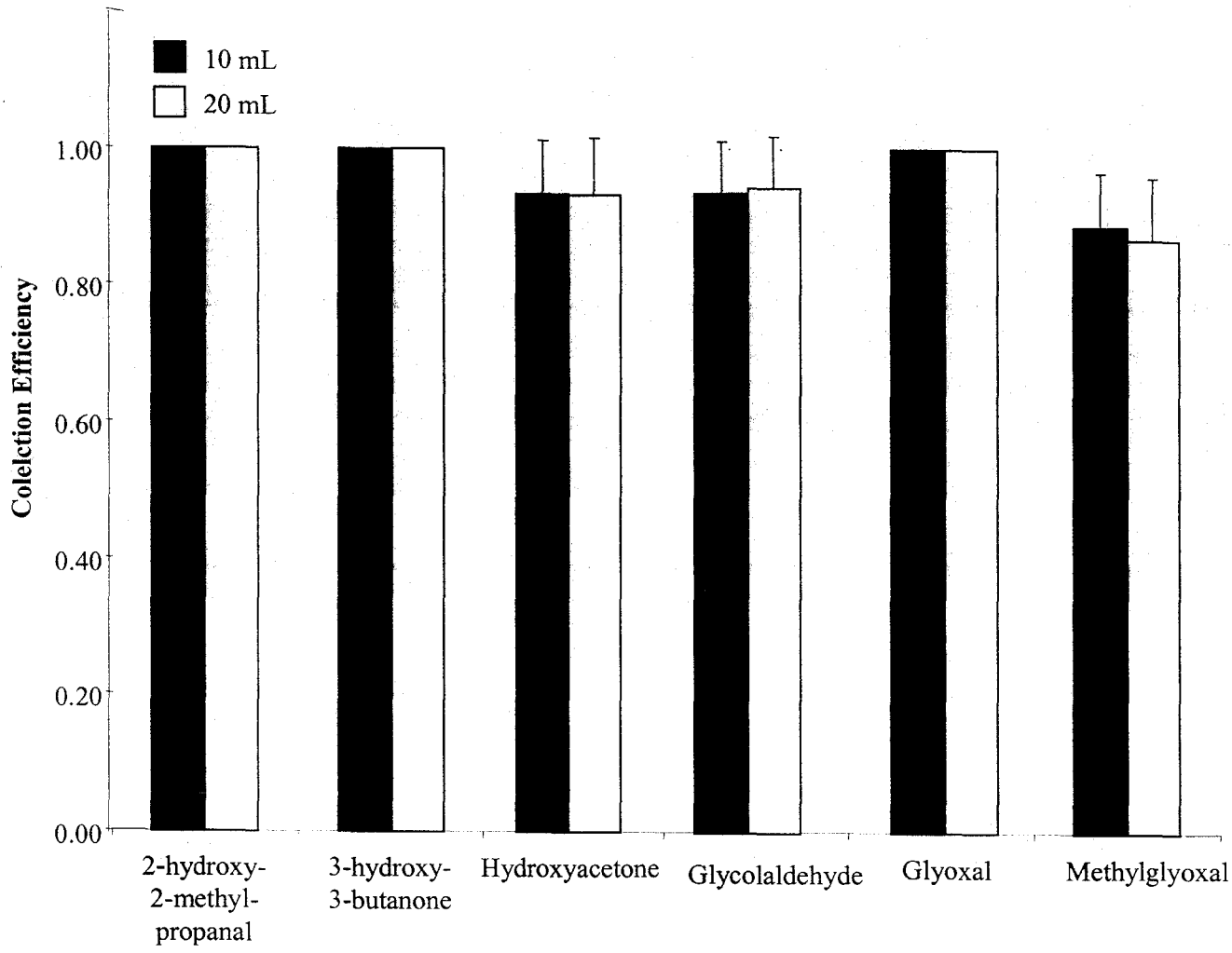


Figure 2.8. Collection efficiencies of analytes for samples colleted in the Blodgett Forest with 10 or 20 mL of PFBHA aqueous solution in the mist chamber (n=4; error bars=1σ).

6. Stability of PFBHA Derivatives in CH_2Cl_2.

In the chamber experiments and previous ambient air studies (Spaulding *et al.*, 1999), the PFBHA derivatives were extracted on site after 24 hours of reaction, and the extracts were stored on ice or under refrigeration at 4°C until we returned to the laboratory. However, the subsequent sample treatment and GC/ITMS analyses were time consuming. If a large number of samples are collected, the samples might require storage for several months before the instrumental analysis is complete. Fan *et. al.* (1998) determined the stability of PFBHA derivatives of aldehydes and ketones in water and methanol over the period of two weeks. To our knowledge, data on the stability of PFBHA derivatives of mono- and multifunctional carbonyls in CH_2Cl_2 do not exist in the literature. Therefore, we explored the stability of the PFBHA derivatives of representative carbonyl and multi-functional carbonyl compounds (i.e., methacrolein, hydroxyacetone, methyl glyoxal, pyruvic acid) and the internal standards (4-hydroxybenz-$^{13}C_6$-aldehyde, 4-fluorobenzaldehyde, and $^{13}C_3$-acetone) used to quantify the compounds, in methylene chloride at 4°C. The results are presented as a plot of the concentration measured, normalized to the concentration measured on day 0, for methacrolein, hydroxy acetone, methyl glyoxal and pyruvic acid in Figure 2.9, and for the internal standards $^{13}C_6$-hydroxy benzaldehyde, 4-fluorobenzaldehye and $^{13}C_3$-acetone in Figure 2.10.

The stability of the derivatives is indicated by a normalized concentration that is within ± 20% relative difference of the initial concentration of the derivatives over a 66-day period, or a normalized concentration that exceeds 1.20 or is less than 0.80. The PFBHA derivatives of the internal standards are within this margin. For methyl glyoxal, the normalized concentration of the PFBHA derivative exceeds 1.20 on days 33 and 38, but no clear trend is observed regarding degradation of the derivative. The PFBHA derivatives of methacrolein and pyruvic acid are the only PFBHA derivatives for which the normalized concentration is equal to or less than 0.80 after 52 days. The mean normalized concentration ± standard deviation for the PFBHA

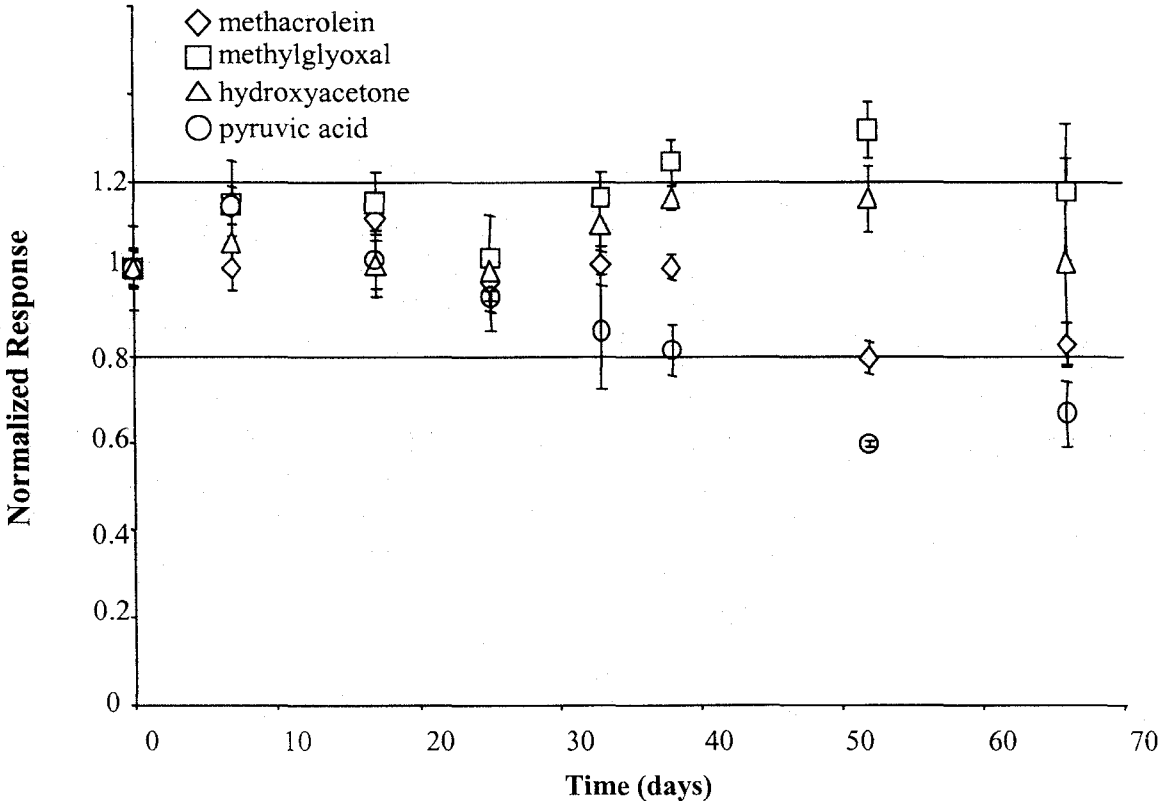


Figure 2.9. Concentrations of the PBFHA derivatives of a model carbonyl (methacrolein), dicarbonyl (methylglyoxal), hydroxycarbonyl (hydroxyacetone), and a keto-acid (pyruvic acid) in CH_2Cl_2 stored under refrigeration (4°C) over 66 days, normalized

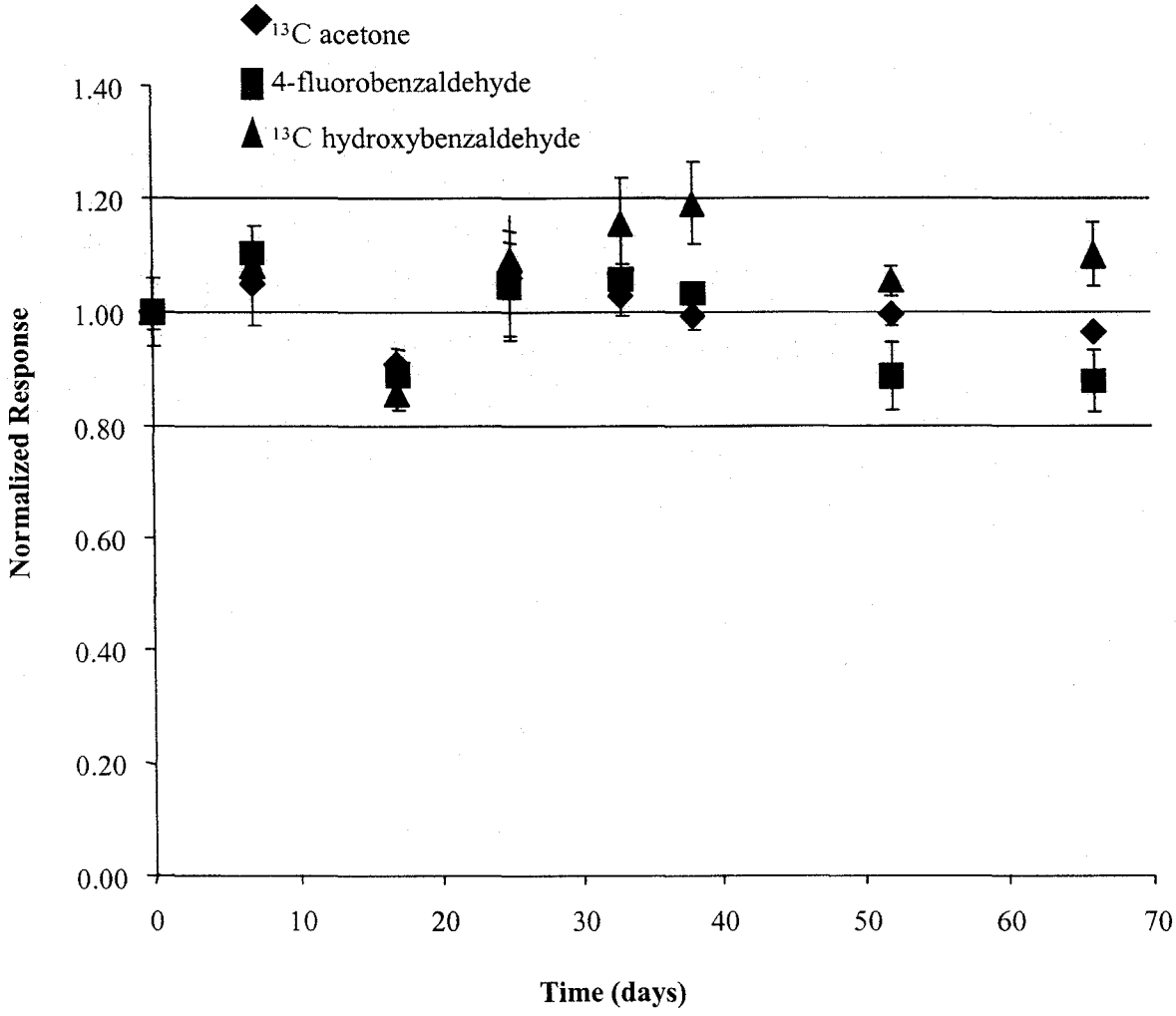


Figure 2.10. Concentrations of the PFBHA derivatives stored in CH_2Cl_2 under refrigeration (4°C) of an internal standards employed in quantification of carbonyls over 66 days, normalized to the concentration measured on day 0 (n = 3; error bars = 1σ).

derivative of methacrolein was 0.79± 0.04, and 0.80± 0.05 on days 52 and 66, respectively, and the mean normalized concentration ± standard deviation for the PFBHA derivative of pyruvic acid was 0.60± 0.01 and 0.67 ± 0.08 on days 52 and 66, respectively. Methacrolein is more reactive than saturated carbonyls due to the double bond, and thus unsaturated carbonyls may degrade at a faster rate than saturated carbonyls. The data clearly indicate degradation of the PFBHA derivative of pyruvic acid, and weakly suggest the degradation of the PFBHA derivative of methacrolein. Overall, the variability among the concentrations for the hydroxycarbonyls, dicarbonyls, and internal standards are within experimental error. We thus conclude that the PFBHA derivatives of hydroxycarbonyls and dicarbonyls are stable for at least 66 days when stored in the refrigerator. The PFHBA derivatives of unsaturated carbonyls and keto-acids appear to degrade after day 40. Methacrolein is more reactive than saturated carbonyls due to the double bond, and thus the data suggest that PFBHA derivatives of unsaturated carbonyls are only stable for about 40 days. Because the concentrations of some of the compounds show more variability with increasing storage time, storage time between sample collection and analysis should be minimized.

D. Interferences from Ozone.

Atmospheric ozone has been shown to cause interferences in the measurement of carbonyl compounds collected in the presence of a derivatizing reagent. The types of interference caused by ozone are: 1) depletion of the analytes (negative interference), and 2) formation of the analytes (positive interference, or artifact formation), (Helmig, 1997). Depletion of analytes could occur by reaction of ozone with the derivatized or native carbonyls in the collecting solution, and formation of the analytes in aqueous solution could occur by the through reaction of ozone with other unsaturated compounds, such as terpenes, isoprene, and unsaturated carbonyls and alcohols in the collecting solution. Both positive and negative interferences were observed during collection of carbonyls using 2,4-dinitrophenylhydrazine (DNPH) and dansylhydrazine (DNSH) derivatizing reagents (Helmig, 1997, Slemr, 1991, Rodier and Birks,

1994). Collection on DNPH-coated solid sorbents appears to be more susceptible to ozone interference than is collection in solution containing DNPH (Helmig, 1997, Arnts and Tejada, 1989). We previously found a difference between concentrations of carbonyls collected with and without ozone removal when using PFBHA solution in impingers for collection, but did not investigate the reason for the differences (Spaulding et al., 1999). Following, we address interferences by ozone by conducting theoretical and experimental studies. The conditions used in these studies represent conditions utilized in the field: a sampling time of 10 minutes, followed by a 24-hour period, the time allowed for PFBHA derivatization of the carbonyls under which the aqueous solutions are kept at room temperature (25°C).

1. Negative Interference (Depletion of the Analytes by Aqueous Ozonolysis of the Analytes).

To evaluate the plausibility that negative interferences might arise from aqueous ozonolysis of the analytes, the concentration of the analytes that might be destroyed over a 24 hour period was calculated under conditions the represent the worst case scenario – high levels of ozone in the atmosphere (100 ppbv) and a mixing ratio of the analytes at the limit of detection (LOD). The concentration of ozone in solution, and the concentration of the analytes in the mist chamber was estimated based on the Henry's law constant and a sampling time of 10 minutes at a flow rate of 25 SLPM. The concentration of the analytes at the LOD was employed because at this concentration the relative error will be the greatest as a consequence of calculating a difference from a small value. The concentration of the analytes predicted to be collected in the mist chamber under these conditions was 8. 4x 10^{-9} M (15 pptv), hydroxyacetone, 4.7 x 10^{-7} M (843 pptv) formaldehyde, 2.4 x 10^{-9} M (4 pptv) 2-hydroxy-2-methylpropanal, 2.7 x 10^{-18} M (48 pptv) glycolaldehyde, 1.5 x 10^{-9} M glyoxal (2.7 pptv), and 4.3 x 10^{-9} methylglyoxal (7.7 pptv). (See Table 2.10). Assuming a rate constant of 1 x 10^{2} for aqueous ozonolysis, provided by Lee, 1985,

Table 2.10. Theoretical calculation of negative interferences: analyte concentrations arising from the reaction of the parent compounds with ozone during sample collection in the Blodgett Forest with the mist chamber (25 SLPM for 10 min.; 100 ppbv ozone).

Compound	Mixing Ratio at LOD[1] (pptv)	[Analyte] Scrubber at LOD[2] (M)	Rate Constant[3] (k) (M^{-1} s^{-1})	Reaction Rate[4] (M s^{-1})	Maximum [Analyte] Reacted[5] (M)	[6]Relative Amount Reacted
Hydroxyacetone	15	8.4×10^{-9}	1×10^{2}	9×10^{-16}	8×10^{-11}	1%
Formaldehyde	843	4.7×10^{-7}	1×10^{2}	5×10^{-14}	1×10^{-9}	0.2%
2-hydroxy-2-methylpropanal	4	2.4×10^{-9}	1×10^{2}	3×10^{-16}	2×10^{-11}	1%
Glycolaldehyde	48	2.7×10^{-8}	1×10^{2}	3×10^{-15}	3×10^{-10}	1%
Glyoxal	3	1.5×10^{-9}	1×10^{2}	2×10^{-16}	1×10^{-11}	1%
Methylglyoxal	8	4.3×10^{-9}	1×10^{2}	5×10^{-16}	4×10^{-11}	1%

[1]mixing ratio (pptv) = $([Analyte]_{chamber,LOD})*(0.02L\ solution/250\ air)*(1\ L\ air/0.04463\ mole\ air)*1x10^{12}$; [2]$[Analyte]_{chamber,LOD} = 3\sigma_{blank}$; results from samples collected at Blodgett Forest on July 29, 2000; [3]Lee, 1985; [4]Reaction rate = $k*([Analyte]_{chamber,LOD})*([O_3]_{chamberr})$; $[O_3]_{chamber} = 1.13x10^{-9}$ M; [5]$[Analyte]_{reacted}$ = Reaction rate x 24 hours; [6]Realtive amount reacted = $100*[Analyte]_{reacted}/[Analyte]_{chamber,\ LOD}$

the reaction rates were calculated as:

$$k * [\text{analyte}] * [O_3]$$

where, k= rate constant, [analyte]= concentration of the analyte and $[O_3]$=concentration of ozone or 1.13×10^{-9} M (100 ppbv).

Using this reaction rate, we estimated that 8×10^{-11} M hydroxyacetone, 1×10^{-9} M formaldehyde, 2×10^{-11} M 2-hydroxy-2-methylpropanal, 3×10^{-10} M glycolaldehyde, 1×10^{-11} M glyoxal, and 4×10^{-11} methylglyoxal would react with ozone. The results indicate that the concentration of each analyte expected to react with ozone is $\leq 1\%$ of the concentration at the limit of detection for each analyte. These data therefore indicate that aqueous ozonolysis of the analytes will not affect the measured concentration.

2. *Positive Interference (Formation of the Analytes from Aqueous Ozonolysis of Parent Precursors).*

a. Theoretical Calculations.

To evaluate the plausibility of positive interferences, the concentration of the analytes formed by aqueous ozonolysis of the parent precursors of the analytes was calculated under conditions that represent the worst-case scenario. The highest mixing ratio reported in the Blodgett Forest by Lamanna and Goldstein, 1999 and an ozone concentration of 100 ppbv was utilized. We also assumed that the yield of a specific product could be 100% of the total concentration of the parent molecules that reacted with ozone in the mist chamber. We recognize that this approach will result in an overestimate of the concentration of the product in the mist chamber since it is improbable that aqueous ozonolysis of a parent will yield one product. It is also improbable that aqueous ozonolysis of each parent will yield 100% of the same product. We estimated that 1.3×10^{-10} M (10 ppbv) of isoprene, 3.0×10^{-8} M (5 ppbv) of methacrolein, 3.4×10^{-7} M of methyl

vinyl ketone (10 ppbv), and 4.8 x 10^{-7} M of 2-methyl-3-buten-2-ol (10 ppbv) would be collected in the mist chamber (See Table 2.11).

Table 2.11. Theoretical calculation of positive interferences: reaction of the parent compounds with ozone during sample collection in the Blodgett Forest with the mist chamber (25 SLPM for 10 min.; 100 ppbv ozone) and their subsequent destruction.

Compound	Mixing Ratio (ppbv)	K_H (M atm^{-1})	Concentration in Scrubber (M)	Maximum Amount Destroyed (M)	Relative Amount Destroyed
Isoprene	10[1]	0.013[3]	1.3 x 10^{-10}	1.1 x 10^{-9}	100%
Methacrolein	5 [1]	5.9[4]	3.0 x 10^{-8}	3.1 x 10^{-9}	11%
Methyl Vinyl Ketone	10[1]	34[4]	3.4 x 10^{-7}	2.4 x 10^{-8}	7%
2-methyl-3-buten-2-ol	10 [2]	48[5]	4.8 x 10^{-7}	3.4 x 10^{-8}	7%

[1]Lamanna and Goldstein, 1999; [2]Schade and Goldstein, 2000; [3]Nirmalakahandan and Speece, 1988; [4]Allen et. al., 1998; [5]Altschuh et. al., 1999.

The concentration of each of the parent species that would react with ozone in the mist chamber was estimated by using rate constants for aqueous ozonolysis from Altschuh et al., (1999), and reaction rates were calculated as previously described. The concentration that would react to produce the analytes was estimated to be 1.2 x 10^{-9} M isoprene, 1.6 x 10^{-9} M methacrolein, 1.1x 10^{-8} M methyl vinyl ketone, and 3.4 x 10^{-8} M 2-methyl-3-buten-2-ol, with at total of 4.8 x 10^{-8} M. (See Table 2.12). In the next part of this exercise, we assumed that the total amount could produce 4.8 x 10^{-8} M of each product. In this case, artificial formation of the analytes would produce 4.8 x 10^{-8} M of any given product. Relative to the detection limit, the fraction of the total due to aqueous ozonolysis of the parent species would be 100% of the total concentration for all compounds except formaldehyde. Therefore, at analyte concentrations at the limit detection of the method, the measure concentration might be due entirely to aqueous ozonolysis. For formaldehyde, the concentration in the mist chamber due to aqueous ozonolysis would be

Table 2.12. Calculation of the reaction of the parent compounds with ozone to yield positive interferences under conditions of sample collection at the Blodgett Forest with the mist chamber (25 SLPM for 10 min.; 100 ppbv ozone).

Compound	**Maximum Mixing Ratio[1,2] (ppbv)**	**K_H (M atm^{-1})[3,4,5]**	**[Analyte] in Scrubber[6] (M)**	**Rate Constant [7,8] (k) (M^{-1} s^{-1})**	**Reaction Rate[9] (M s^{-1})**	**Maximum [Analyte] Reacted [10] (M)**
Isoprene	10	0.013	1.3×10^{-10}	4.0×10^{5}	5.9×10^{-14}	1.2×10^{-9}
Methacrolein	5	5.9	3.0×10^{-8}	2.4×10^{4}	8.0×10^{-13}	1.6×10^{-9}
Methyl Vinyl Ketone	10	34	3.4×10^{-7}	4.4×10^{4}	1.7×10^{-11}	1.1×10^{-8}
2-methyl-3-buten-2-ol	10	48	4.8×10^{-7}	1.0×10^{5}	5.4×10^{-11}	3.4×10^{-8}
Total Amount Reacted						**4.8×10^{-8}**

[1]Lamanna and Goldstein, 1999; [2]Schade and Goldstein, 2000; [3]Nirmalakahandan and Speece, 1988; [4]Allen et. al., 1998; [5]Altschuh et. al., 1999; [6]Concentration in the scrubber = (K_H)*(mixing ratio); [7]Pedersen and Sehested, 2001; [8]Hoigne et. al., 1983; [9]Reaction rate = k*[analyte]*[O_3]; [O_3] = 1.13×10^{-9} M; [10]Maximum amount reacted = (reaction rate)*(600 sec) + [O_3]; [O_3] = 1.13×10^{-9} M.

insignificant, accounting for 10% of the total. This is due primarily to the high detection limit for formaldehyde due to the presence of formaldehyde in the reagents. (See Table 2.13).

b. Experimental Studies.

1. Air Sampling in the Absence and Presence of a KI-Coated Stainless Steel Annular Denuder.

To further evaluate the effect of negative or positive ozone interferences on quantification of the analytes, we sampled air at the Blodgett Forest, in the presence and absence of a KI-coated stainless steel annular denuder that removed 91 ± 2% of ~120 ppbv O_3 at 30 SLPM (Standard Liters Per Minute, 0°C, 1 atm). A comparison of concentrations measured with and without the denuder is presented in Figure 2.11 as a plot of the normalized concentration for each analyte in the presence and absence of a KI-coated stainless steel annular denuder. For each pair of samples (n=6), the concentrations were normalized to the concentration measured without the annular denuder. Data are presented in this manner because the absolute concentrations vary from one sampling period to another. The absolute concentrations and the relative difference between the concentrations are presented in Table 2.14.

Formaldehyde and pyruvic acid were not quantified due to high levels of contamination in field blanks. The mean % relative difference ± standard deviation are <10% for hydroxyacetone and glycolaldheyde, -66± 22% for glyoxal and -36 ± 15% for methyl glyoxal. No significant differences (p=0.05) between the normalized concentration of 2-hydroxy-2-methyl-propanal, hydroxyacetone, and glycolaldehyde in the presence and absence of the KI-coated annular denuder were observed by using a paired-sample t-test. Differences were statistically significant for glyoxal and methylglyoxal. Lower concentrations of methylglyoxal and glyoxal in the denuder were observed by using a paired-sample t-test.

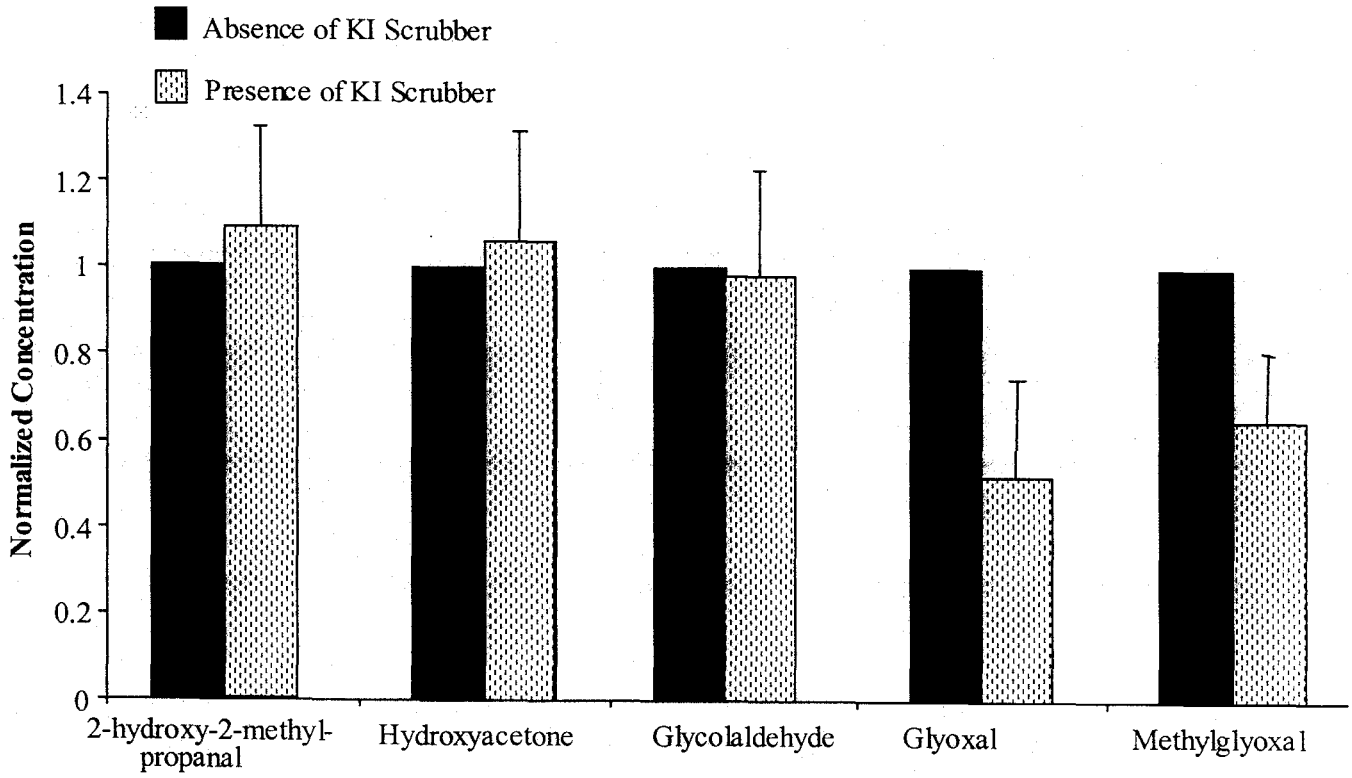


Figure 2.11. Comparison of analyte concentrations normalized to concentrations obtained in the absence of a KI scrubber for removal of ozone (n=6; error bars=1σ).

Table 2.13. Calculation of artifact formation from aqueous ozonolysis of the parent species under conditions of sample collection at the Blodgett Forest with the mist chamber (25 SLPM for 10 min.,100 ppbv ozone).

Compound	Mixing Ratio at LOD (ppt)[1]	[Analyte] in Scrubber at LOD (M) [1,2]	Potential [Artifact] in Scrubber[3] (M)	$\frac{[Analyte]_{ART}}{[Analyte]_{Total}}$[4]
Hydroxyacetone	15	0.84×10^{-8}	4.8×10^{-8}	5.7
Formaldehyde	843	47×10^{-8}	4.8×10^{-8}	0.10
2-hydroxy-2-methylpropanal	4	0.24×10^{-8}	4.8×10^{-8}	20
Glycolaldehyde	48	2.7×10^{-8}	4.8×10^{-8}	1.8
Glyoxal	3	0.15×10^{-8}	4.8×10^{-8}	32
Methylglyoxal	8	0.43×10^{-8}	4.8×10^{-8}	11

[1]mixing ratio (pptv) = $([Analyte]_{chamber,LOD})*(0.02L\ solution/250\ air)*(1\ L\ air/0.04463\ mole\ air)*1x10^{12}$; [2]$[Analyte]_{chamber,LOD} = 3\sigma_{blank}$; results from samples collected at Blodgett Forest on July 29, 2000; [3]From Table 13; Artifacts relative to LOD = $[Analyte]_{artifactr}/[Analyte]_{chamber,\ LOD\ +\ artifact}$.

Table 2.14. Concentration of analytes sampled in the Blodgett Forest, CA. collected in the absence and presence of a KI-coated stainless steel annular denuder to remove ozone. Samples collected on July 29, 2000.

Analyte	Mixing Ratio (pptv)		% Relative Difference	% Relative Difference Mean ± S.D.
	KI-coated Annular Denuder Absent	KI-coated Annular Denuder Present		
Glycolaldehyde	1062	1166	+10	-2 ± 25%
	1397	804	-42	
	1930	1757	-9	
	1552	1487	-4	
	1264	1700	+34	
	1277	1278	0	
Hydroxyacetone	498	697	+40	+6 ± 25%
	945	672	-29	
	1481	1450	-2	
	1048	1021	-3	
	879	1142	+30	
	879	890	+1	
Glyoxal	32	4	-88	-66 ± 22%
	59	16	-73	
	24	17	-29	
	20	5	-75	
	24	9	-63	
Methylglyoxal	167	75	-55	-36 ± 15%
	232	173	-25	
	297	240	-19	
	265	165	-38	
	247	194	-21	
	390	182	-53	

2. Sorption of Analytes to the Stainless Steel Annular Denuder.

To determine whether sorption to the stainless steel annular denuder was occurring, we collected samples from a Tedlar™ bag into a mist chamber fitted with a stainless steel annular denuder. To ensure that sorption of the analytes onto the stainless steel denuder would not affect the results, initial experiments were conducted to determine the recovery of carbonyls from the denuder. The results are presented in Table 2.15. Recoveries of 128 ± 11, 139 ± 5% , 147 ±11%, 128 ± 11%, 91 ± 3%, 90 ± 21% were obtained for hydroxy acetone, pyruvic acid, glycolaldehyde, glyoxal and methylglyoxal,, respectively (n=2), thereby demonstrating our ability to accurately and precisely quantify analytes sorbed on the denuder.

In the sample extracts obtained from air samples collected from the Tedlar™ bag, we measured 4.3 ± 1.7%, 55 ± 13%, 1.6± 0.4, 32 ± 6%, and 17 ± 5% for hydroxyacetone, pyruvic acid, glycolaldehyde, glyoxal, and methylglyoxal, respectively, on the stainless steel annular denuder (n=2) (see Table 2.16). For hydroxy acetone, formaldehyde, glycolaldehyde and methyl glyoxal, these concentrations constitute < 20% of the total amount measured in the mist chamber and the denuder. Significant (>20%) amounts of pyruvic acid, glyoxal, and methylglyoxal were measured on the denuder, indicating that these compounds are sorbed on the stainless steel annular denuder during sample collection.

3. Aqueous Ozonation of Isoprene, Methacrolein, Methyl Vinyl ketone, and 2-methyl-3 -buten- 2-ol.

To further explore whether positive interferences could arise from aqueous ozonolysis of the parent species, we conducted an experiment in which air containing 150 ppbv ozone was passed through an aqueous 1-mM PFBHA solution enriched with 5.1 x 10^{-6} M of isoprene, 3.5 x 10^{-6} M of methacrolein, 5.7 x 10^{-6} M of methyl vinyl ketone and 4.7 x 10^{-6} M of 2-methyl-3-buten-2-ol. through an aqueous 1-mM PFBHA solution enriched with 5.1 x 10^{-6} M of isoprene, 3.5 x 10^{-6} M

Table 2.15. Recovery of carbonyls sorbed onto a stainless steel annular denuder.

Compound	**Amount Sorbed (ng)**	**Amount Measured (ng)**	**% Recovery**	**% Recovery Mean ± S. D.**
Hydroxyacetone	390 390	527 469	135 120	128 ± 11 %
Formaldehyde	1347 1347	1578 1491	117 111	114 ± 5%
Pyruvic Acid	422 422	599 571	142 135	139 ± 5%
Glycolaldehyde	406 406	629 564	155 139	147 ± 11 %
Glyoxal	405 405	361 377	89 93	91 ± 3%
Methylglyoxal	415 415	366 376	88 91	90 ± 2%

Table 2.16. Distribution of carbonyl compounds on the stainless steel annular denuder and in solution after sampling with a stainless steel denuder fitted to a mist chamber.

Compound	Amount on Denuder (ng)	Amount in Mist chamber (ng)	% of Total Sorbed on Denuder	% of Total Sorbed on Denuder Mean ± S.D.
Hydroxyacetone	18.1 11.5	879 646	3.1 5.5	4.3 ± 1.7
Formaldehyde	0.0 0.0	146 0.0	0.0 0.0	0.0
Pyruvic Acid	39.9 44.3	47.2 25.1	46 64	55 ± 13
Glycolaldehyde	11.2 10.8	849 574	1.3 1.9	1.6 ± 0.4
Glyoxal	18.8 22.4	49.1 39.4	28 36	32 ± 6
Methylglyoxal	39.1 63.3	256 240	13 21	17 ± 5

of methacrolein, 5.7 x 10^{-6} M of methyl vinyl ketone and 4.7 x 10^{-6} M of 2-methyl-3-buten-2-ol. Assuming 100% dissolution from 300 L of air, these concentrations correspond to 8.2 ppbv isoprene, 5.7 ppbv methacrolein, 9.2 ppbv, methyl vinyl ketone and 7.4 ppbv 2-methyl-3-buten-2-ol in air. The concentration of the analytes (products) measured in the mist chamber was 6.1 ± 1.4 x 10^{-7} M hydroxyacetone, 7.8 ± 3.1 x 10^{-7} M glycolaldehyde, and 3.8 ± 0.6 x 10^{-7} M methyl glyoxal. These concentrations in the scrubber correspond to ambient air concentrations of 10± 2 pptv of hydroxyacetone, 12 ± 5 pptv of glycolaldehyde and 6.1 ± 1 pptv of glyoxal. (See Table 2.17). Glyoxal and 2- hydroxy-2-methylpropanal were not detected, and formaldehyde and

Table 2.17. Generation of analytes due to aqueous ozonolysis of isoprene, 2-methyl-3-buten-2-ol, methacrolein, and methyl vinyl ketone and relative contribution .

		Concentration arising from Aqueous Ozonolysis of Parent and Relative Contribution to [Analyte] at the LOD and at the Lowest [Analyte] Reported in the Blodgett Forest.			
Compound	**Mixing Ratio (pptv)**	**LOD (pptv)**	**Contribution Relative to the LOD**	**Lowest [Analyte] Reported (pptv)**	**Contribution Relative to Lowest [Analyte] Reported (pptv)**
Glycolaldehyde	12 ± 5	48	25%	515	2%
Hydroxyacetone	10 ± 2	15	67%	271	4%
3-hydroxy-2-butanone and 2-hydroxy-2-methylpropanal	ND	5.4	-	267	-
Glyoxal	ND	2.7	-	20	-
Methylglyoxal	6.1 ±1.0	7.7	79%	69	9%

pyruvic acid could not be quantified due to high levels of formaldehyde in the reagent blank. We again compared the concentrations measured to the detection limits for each of the analytes, and the lowest concentration measured in the Blodgett Forest on July 29, 2000. For hydroxy acetone and methyl glyoxal, these concentrations would contribute 67% and 79% of the total measured concentration, whereas for glycolaldehyde the concentration would constitute 25% of the measured concentration. However, at the lowest concentrations collected at Blodgett on July 29, 2000, these values would only constitute artifact formation of 4% for hydroxyacetone, 2% for glycolaldehyde and 9% for methylglyoxal. These results agree with conclusions reached from the theoretical study that positive artifact formation may constitute a significant fraction of the measured concentration for hydroxy acetone, glycolaldehyde, and methylglyoxal near the detection limit. However the data also demonstrate that positive interferences do not constitute a large fraction of the measured concentration at the lowest levels in the Blodgett Forest.

In summary, the theoretical and experimental studies conducted herein establish aqueous ozonolysis of isoprene, methacrolein, methyl vinyl ketone, and 2-methyl-3-buten-2-ol will not significantly affect quantification at mixing ratios lower than about 100-150 pptv for glycolaldehyde and hydroxyacetone, 70 pptv for methylglyoxal, and at any level for glyoxal and 2-hydroxy-2-methylpropanal. At mixing ratios lower than those specified, artifact formation could constitute ≥ 20% of the hydroxyacetone, glycolaldehyde, and methyl glyoxal measured. In addition, the experimental studies demonstrate that sorption of glycolaldehyde, glyoxal and methyl glyoxal onto a stainless steel denuder will result in lower measured concentrations when a KI-coated stainless steel denuder is employed to remove ozone. For this reason, ambient air sampling for these compounds was conducted in the absence of a KI-coated stainless steel denuder. We suggest that future studies be conducted to investigate different material (*e.g.* silanized glass wool coated with KI) for removal of ozone from the sampling stream.

E. Application of the Method to Measurement of Multi-functional Carbonyls in the Ambient Environment (Blodgett Forest).

The method was tested and evaluated by sampling air in a ponderosa pine plantation near the Blodgett Forest on July 29, 2000. Samples were collected from 9:00 a.m. to 6:00 p.m. We quantified glyoxal, methyl glyoxal, hydroxy acetone and glycolaldehyde, and we identified 2-hydroxy-2-methylpropanal in the sample extracts.

a. Comparison of Laboratory and Field Collection Efficiency.

We present a comparison of the collection efficiencies for laboratory samples (pH=3.0 and no salts added; n=11) to the collection efficiencies for samples collected at the Blodgett Forest on July 29, 2000 (n=8) in Table 2.18. Overall, there was good agreement (<15% relative difference) between the collection efficiencies obtained in laboratory and ambient air experiments. The % relative difference between the collection efficiencies obtained in the

Table 2.18. Comparison of collection efficiency in laboratory and ambient air experiments.

Analyte	Laboratory Experiments		Ambient Air Experiments		% Relative Difference
	Collection Efficiency	Mean ± S.D. (RSD)	Collection Efficiency	Mean ± S.D. (RSD)	
Glycolaldehyde	0.99 0.85 0.93 0.95 0.28 0.65 0.90 0.92 0.87 0.78 0.92	0.82 ± 0.20	0.86 1.00 0.95 0.92 0.90 0.90 1.00 1.00 1.00 0.94	0.95 ± 0.05	+13
Hydroxyacetone	0.90 0.86 0.93 0.92 0.59 0.53 0.77 0.81 0.84 0.77 0.88	0.80 ± 0.13	0.87 0.95 0.93 0.89 0.89 0.84 0.86 0.87 0.87 0.88	0.88 ± 0.04	+8
Glyoxal	0.97 0.94 0.57 0.66 1.00 ND 0.91 0.94 0.97 0.96 0.86	0.88 ± 0.15	0.61 .074 1.00 0.87 0.86 0.85 1.00 1.00 0.90 1.00	0.88 ± 0.13	0

Table 2.18. Comparison of collection efficiency in laboratory and ambient air experiments. (continued).

	Laboratory Experiments		Ambient Air Experiments		
Analyte	**Collection Efficiency**	**Mean ± S.D. (RSD)**	**Collection Efficiency**	**Analyte**	**% Relative Difference**
Methylglyoxal	0.89	0.73 ± 0.14	0.74	0.85 ± 0.06	+12
	0.81		0.86		
	0.83		0.84		
	0.87		0.80		
	0.80		0.83		
	0.71		0.91		
	0.46		0.83		
	0.47		0.94		
	0.75		0.85		
	0.70		0.92		
	0.74				

laboratory and air were 15% for glycolaldehyde, 8% for hydroxy acetone, -2% for glyoxal and 14% for methyl glyoxal. The mean collection efficiency and standard deviation in the laboratory and the field, respectively was 82 ± 20% and 95 ± 5% for glycolaldehyde, 80 ± 13% and 88 ± 4% for hydroxy acetone, 88 ±15% (n=10) and 88 ± 13% for glyoxal, and 73 ± 14% and 85 ± 6% for methyl glyoxal.

b. Calibration curve data.

A calibration curve was generated after the analysis of five standard solutions before and after the analysis of sample extracts. Two mid-point standard solutions were analyzed after every five samples to check the stability of the calibration curve. For concentrations ranging from approximately 102 – 4064 pg/μL, the relative deviation of the relative response factors were 22 – 68% for glycolaldehyde (concentration range = 102 – 4064 pg/μL), 19 – 21% for hydroxyacetone, 20 – 36% for glyoxal, and 13 – 23% for methylglyoxal. For glycolaldehyde the

RRF exceeded 25% only for calibration curves used to quantify compounds in the second scrubber, which is less important than the first scrubber, therefore the quantification results were 0.986 for hydroxyacetone, 0.925 to 0.976 for glyoxal, and 0.902 to 0.984 for methylglyoxal. The percent of the actual concentration measured for each of these mid-point standards was 74 to 125% for glycolaldehyde, 76 to 131% for hydroxyacetone, 82 to 117% for glyoxal, 83 to 114% for methylglyoxal, and 54 to 129% for formaldehyde. Formaldehyde and pyruvic acid were not quantified in the sample extracts due to problems related to contamination of the reagent blank.

c. Accuracy and Precision of the Method.

The % recovery calculated by the analysis of extracts from PFBHA solutions enriched with approximately 400 pg/μl of each compound (1347 pg/μL for formaldehyde) in the ambient environment, at the beginning and end of sample collection was 74 and 98% for glycolaldehyde, 87 and 110% recovery of hydroxyacetone, 79 and 111% recovery of glyoxal, and 85 and 99% recovery of methylglyoxal. Measured concentrations for duplicate samples collected at Blodgett Forest are presented in Table 2.19. Excellent precision is indicated by a % relative standard deviation of generally ≤ 25%. The % relative standard deviation between duplicate samples was 24% for glycolaldehyde, 8% for hydroxy acetone, 14% for glyoxal, and 6% for methyl glyoxal.

d. Limits of Detection.

The limits of detection were calculated as $3\sigma_{blank} + ave_{blank}$, where σ_{blank}, calculated from the standard deviation of the environment at the beginning and end of sample collection, was 74 to 98% for glycolaldehyde, 87 to 110% recovery of hydroxyacetone, 79 – 111% recovery of glyoxal, and 85 to 99% recovery of methylglyoxal. The mean response factor for each compound in the field blanks (n=2), and ave_{blank} is the average response factor for each compound in field blank (n=2). The limits of detection measured on July 29, 2000 are 48 pptv for glycolaldehyde, 15 pptv for hydroxyacetone, 2.7 pptv for glyoxal, and 7.7 pptv for

Table 2.19. Isoprene Photooxidation Products in the Blodgett Forest on 7/29/00.

Compound	Concentration (pptv) Sample No. 1	Sample No. 2	Mean ± S.D. (% RSD)	Matrix Spike Recovery
Glycolaldehyde	515	807	661 ± 206 (31%)	98%, 74%
	1209	1003	1106 ± 146 (13%)	
Hydroxyacetone	271	309	290 ± 27 (9%)	110%, 87%
	801	726	764 ± 53 (7%)	
Glyoxal	40	28	34 ± 8 (25%)	79%, 11%
	26	28	27 ± 712 (5%)	
Methylglyoxal	83	69	76 ± 10 (13%)	99, 85%
	345	359	352 ± 10 (3%)	

methylglyoxal. We compare the detection limits to other methods that utilize impingers, solid sorbents and a coil scrubber with DNPH or PFBHA derivatization in Table 2.20.

Overall, the method developed herein provides detection limits that are an order of magnitude more sensitive than other methods for the measurement of glyoxal and hydroxy acetone, and similar detection limits for glycolaldehyde and methylglyoxal. In addition, the method affords a shorter sampling time, 10 minutes compared to 1hr. to 4 hr. sampling times utilized by other methods. For glycolaldehyde, Lee and Zhou, 1993 reported a detection limit of 20 pptv using a coil scrubber along with DNPH derivatization, and in previous research, we reported a limit of detection of 67 pptv by using a method that collected air in 400 ml impingers and derivatized glycolaldehyde with PFBHA/BSTFA. For glyoxal and methyl glyoxal, a detection limit of 20 pptv was obtained by using methods that employ C_{18} cartridges and a coil scrubber with DNPH derivatization. In previous work, we report a detection limit of 13 pptv for methylglyoxal and

Table 2.20. Comparison of limits of detection (LOD) for methods measuring multifunctional carbonyls in air.

Sampler	Derivatizing Reagent(s)	Flow Rate (L/min.)	Sampling Time (min.)	Analytes	Limit of Detection (pptv)
C_{18}-cartridges[1]	DNPH	0.2 – 1.2	100 -500	Glyoxal Methylglyoxal	20 20
Coil scrubber[2,3]	DNPH	2.3	20	Glycolaldehyde Glyoxal Methylglyoxal Glyoxylic acid Pyruvic acid	20 20 20 20 20
Coil scrubber[4]	$NaHSO_3$-OPA*	2.0	15	Hydroxyacetone	400
Mist chamber [5]	DNPH	10	60 - 120	Glyoxal Methylglyoxal	20 50
400-mL impingers[6]	PFBHA-BSTFA	0.5	180 - 240	Glycolaldehyde Hydroxyacetone Methylglyoxal	67 200 13
This study (cofer scruuber)	PFBHA-BSTFA	23 - 25	10	Glycolaldehyde Hydroxyacetone 2-hydroxy-2-methylpropanal Glyoxal Methylglyoxal	48 15 5.4 2.7 7.7

[1]Zhou & Mopper, 1990; [2]Lee & Zhou, 1993; [3]Lee et. al., 1995; [4]Klotz *et. al.*, 1999; [5]Munger et. al., 1995; [6]Spaulding et. al., 1999. *OPA = *o*-phthaldialdehyde

200 pptv for hydroxy acetone. The method developed in this work thus marks a drastic improvement in the detection of water-soluble carbonyls. Another advantage of the method is that it obviates any ambiguities regarding the identification of unknowns. The complementary information gleaned from the EI, methane CI and PFBOH CI mass spectra affords unambiguous molecular weight determinations, and the employment of PFBHA instead of DNPH abolishes errors associated with identification and quantification due to conversion of α-hydroxycarbonyls

to the corresponding dicarbonyls when derivatized with DNPH in organic solvent (*i.e.,* hydroxyacetone is converted to methylglyoxal and glycolaldehyde is converted to glyoxal). Another strength of the method is the fact that it is selective to the measurement of compounds with $K_H > 10^2$. On the other hand, it can be desirable to use one method to collect a broad range of carbonyls, and thus a limitation of the method could be its selectivity to the collection of water soluble compounds with $K_H > 10^2$. Another limitation of the current method is the contamination of field blanks with formaldehyde and pyruvic acid. Both of these limitations can be addressed in further work.

e. Isoprene and 2-hydroxy-2-methylpropanal Photooxidation Products in the Blodgett Forest.

The sample data are plotted, along with isoprene mixing ratios (Gunnar Schade, personal communication), in Figure 2.12, as the mixing ratio measured vs. the time the sample was collected. Overall, isoprene photooxidation products follow the same trend as isoprene, with the maximum mixing ratios of the photooxidation products and isoprene occurring around 13:00 - 14:00 local standard time. This observation is consistent with transport of isoprene and its photooxidation products from a source 2 - 3 hours upwind. A rise in the isoprene mixing ratio earlier in the morning is likely due to local emissions and therefore is not accompanied by an increase in the photooxidation products, whose generations lags several hours behind isoprene emissions due to reaction times. Experiments in smog chambers establish reaction rates and yields of glycolaldehyde, hydroxyacetone, and methylglyoxal from isoprene and glyoxal from glycolaldehyde (Niki et al., 1987, Carter and Atkinson, 1996, Alvarado et al. 1999, Feronato et al., 1998). Smog chamber data also establish photolysis rates and reaction rates with ·OH for the product compounds (Plum et al., 1983, Koch and Moortgat, 1998, Orlando et al., 1999 Bacher and Orlando, 2001). The smog chamber data predict that when isoprene is the dominant source of these compounds in the atmosphere, glycolaldehyde will be the highest concentration, followed by hydroxyacetone, methylglyoxal, and glyoxal, which is in fact demonstrated in the data presented here.

III. Conclusions.

Herein, we report the development and application of a mist chamber to measure water-soluble organics in air. The mist chamber enables collection of trace levels of organic compounds at pptv detection limits with short (10 minute sampling) times. In combination with PFBHA- and BSTFA- derivatization and ion trap mass spectrometry, the mist chamber can be used to collect, identify, and quantify multi-functional carbonyls and keto-acids, which have not previously been well-characterized in ambient air due to the difficulty in their measurement. We used the method to identify 2-hydroxy-2-methylpropanal, a product of hydroxyl radical oxidation of 2-methyl-3-buten-2-ol, in both smog chambers and in ambient air. To our knowledge, the measurement of this compound has not been reported in the literature, although MBO is an important biogenic reactant in the photochemistry of rural Western North America. We also applied the method to characterize compounds that are generated from hydroxyl radical oxidation of isoprene, which is arguably the most important biogenic compound globally. It is now possible to further characterize isoprene and MBO photochemistry in rural environments by using a mist sampler along with PFBHA and PFBHA/BSTFA derivatization and gas chromatography/ion trap mass spectrometry. The method will also play an important role in characterization of polar organics in urban atmospheres, where alkyl benzene photochemistry is important.

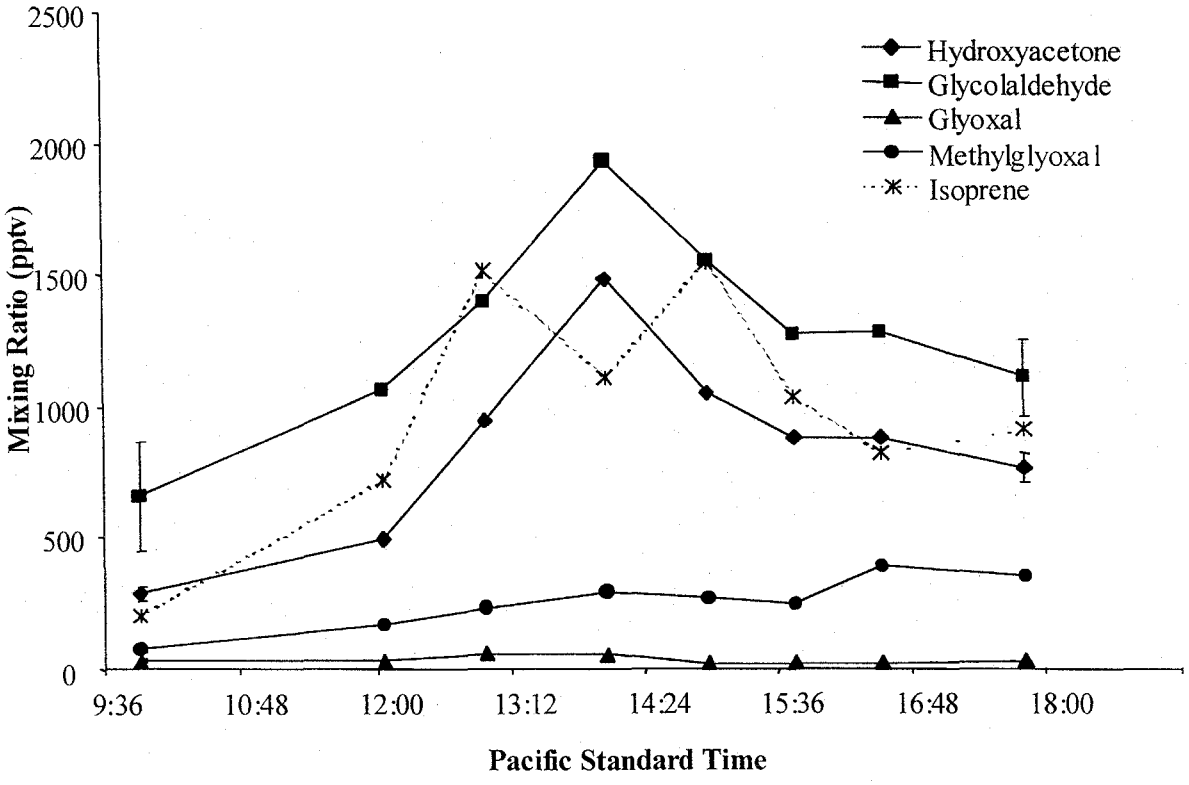


Figure 2.12. Mixing ratios of isoprene and its photooxidation products, glycolaldehyde, hydroxyacetone, methyl glyoxal, and glyoxal sampled above a ponderosa pine plantation near the Blodgett Forest, CA. on July 29, 2000.

V. References Cited

Allen, J. M., W. X. Balcavage, B. R. Ramachandran, and A. L. Shrout, 1998. *Environ. Toxicol. Chem.*, 17, 1216-221.

Altschuh, J., R. Bruggemann, H. Santl, G. Eichinger, and O. G. Piringer, 1999. *Chemosphere*, 39, 1871-1887.

Alvorado, A., E. C. Tuazon, S. M. Aschmann, J. Arey, and R. Atkinson, 1999. *Atmos. Environ.*, 2893-2905.

Andreae, M. O. and P. J. Crutzen, 1997. Atmospheric Aerosols. *Science*, 276, 1052-1058.

Arnts, R. R. and S. B. Tejada, 1989. *Environ. Sci. Technol.*, 23, 1428-30.

Aschmann, S. M., Y. Shu, J. Arey, and R. Atkinson, 1997. *Atmos. Environ.*, 31, 3551-3560.

Atkinson, R., 2000. *Atmos. Environ.*, 34, 2063-2101.

Atkinson, R. and S. M. Aschmann, 1995. *Environ. Sci. Technol*, 29, 528-536.

Bacher, C., G. S. Tyndall, and J. J. Orlando, 2001. *J. Atmos. Chem.*, Accepted.

Bell, R. P. and P. G. Evans, 1966*Proc. Roy. Soc. (London) Ser. A*, 291, 297-323.

Betterton, E. A., 1992. In Gaseous Pollutants. Characterization and Cycling, J. O. Nriagu, Ed.

Betterton, E. A., Y. Erel, and M. R. Hoffmann, 1988. *Environ. Sci. Technol.*, 22, 92-99.

Biesenthal, T. A., Q. Wu, P. B. Shepson, H. A. Wiebe, K. G. Anlauf, and G. I. Mackay, 1997. *Atmos. Environ.*, 2049-2058.

Blau, K. and J. Halket, Eds., 1993. In Handbook of Derivatives for Chromatography. John Wiley & Sons.

Buschmann, H. J., H. H. Fueldner, and W. Knoche, 1980. *Ber. Bunsenges. Phys. Chem.*, 84, 41-4.

Buschmann, H.-J., E. Dutkiewicz, and W. Knoche, 1982. *Ber. Bunsenges. Phys. Chem.*, 86, 129-134.

California Air Resources Board, 1998. Air Quality Data.

Cancilla, D. A., C.-C. Chou, R. Barthel, and S. S. Que Hee, 1992. *J. of AOAC International*, 75, 842-854.

Carter, W. P. L. and R. Atkinson, 1996. *Inter.l Jour. Chem. Kinetics*, 28, 497-530.

Chameides, W. L., R. W. Lindsay, J. Richardson, and C. S. Kiang, 1988. *Science*, 241, 1473-1475.

Chien, C.J., M. J. Charles, K. G. Sexton, and H. E. Jeffries, 1998. *Environ. Sci. Technol.*, 32, 299-309.

Cofer, W. R. I., V. G. Collins, and R. W. Talbot, 1985. *Environ. Sci. Technol.*, 19, 557-560.

Conway, B. E. and D. M. Novak, 1975. In Chemistry and physics of aqueous gas solutions, W. A. Adams, Ed., The Electrochemical Society, 115-134.

Desnoyers, J. E., G. E. Pelletier, and Jolicoeur, 1965. *Canadian Jour. Chem.*, 43, 3232-3237.

Desnoyers, J. E., G. Perron, S. Leger, B. Y. Okamotoa, T. H. Lilley, and R. H. Wood, 1978. *Jour. Solution Chem.*, 7, 165-178.

Duan, S. X., J. T. Jayne, P. Davidovits, D. R. Worsnop, M. S. Zahniser, and C. E. Kolb, 1993. *J. Phys. Chem.*, 97, 2284-2288.

Fan, Z.H., M. R. Peterson, R. K. M. Jayanty, and F. W. Wilshire, 1998. Abstracts of Air and Waste Management Asoociation Annual Meeting, San Diego, CA.

Fantechi, G., N. R. Jensen, J. Hjorth, and J. Peeters, 1998. *Int. J. Chem. Kinet.*, 30, 589-594.

Ferronato, C., J. J. Orlando, and G. S. Tyndall, 1998. *J. Geophys. Res.*, 103, 25579-25586.

Frazey, P., X. Rao, R. Spaulding, B. Beld, and M. J. Charles, 1999. *International Journal of Mass Spectrometry.*, 190/191, 343-357.

Grosjean, D., E. Grosjean, and E. L. I. Williams, 1994. *Environ. Sci. Technol.*, 28, 186-196.

Grosjean, D., E. Grosjean, and A. W. Gertler, 2001. *Environ. Sci. Technol.*, 35, 45-53.

Helmig, D., 1997. *Atmos. Env.*, 31, 3635-3651.

Hoigne, J. and H. Bader, 1983. *Water Res.*, **17,** 173-183.

Jayne, J. T., S. X. Duan, P. Davidovits, D. R. Worsnop, M. S. Zahniser, and C. E. Kolb, 1992. *J. Phys. Chem.*, **96,** 5452-5460.

Jayne, J. T., S. X. Duan, P. Davidovits, D. R. Worsnop, M. S. Zahniser, and C. E. Kolb, 1991. *J. Phys. Chem.*, 95, 6329-6336.

Jencks, W. P., 1964. *Adv. Phys. Org. Chem.*, 63-123.

Jenkin, M. E. and K. C. Clemitshaw, 2000. *Atmos. Environ.*, 34, 2499-2527.

Kleinman, L., Y. N. Lee, S. R. Springstown, L. Nunnermacker, X. Zhou, R. Brown, K. Hallock, P. Klotz, D. Leahy, J. H. Lee, and L. Newman, 1994. *J. Geophys. Res.*, 99, 34693482.

Klemm, O. and R. W. Talbot, 1991. *J. Atmos. Chem.*, 13, 325-342.

Klotz, P. J., E. S. C. Kwok, X. Zhou, J. H. Lee, and Y.-N. Lee, 1999. BNL-66932, Brookhaven National Laboratory.

Koch, G. and G. K. Moortgat, 1998. *J. Phys. Chem. A*, 102, 9142-9153.

Kwok, E. S. C., J. Arey, and R. Atkinson, 1996a. *J. Phys. Chem.*, 100, 214-219.

Kwok, E. S. C., R. Atkinson, and J. Arey, 1996b. *Environ. Sci. Technol.*, 30, 1048-1052.

Lamanna, M. S. and A. H. Goldstein, 1999. *J. Geophys. Res.*, 104, 21247-21262.

Lee, Y.N., 1985. BNL-36220, Brookhaven National Laboratory..

Lee, Y.N. and X. Zhou, 1993. *Environ. Sci. Technol.*, 27, 749-756.

Lee, Y. N., X. Zhou, and K. Hallock, 1995. *J. Geophys. Res.*, 100, 25,933-25,944.

Lee, Y.N. and X. Zhou, 1996. *J. Geophys. Res.*, ***101,*** 29075-29080.

Lee, Y. N., X. Zhou, L. I. Kleinman, L. J. Nunnermacker, S. R. Springston, P. H. Daum, L. Newman, W. G. Keigley, M. W. Holdren, C. W. Spicer, V. Young, B. Fu, D. D., Parrish, J. Holloway, J. Williams, J. M. Roberts, T. B. Ryerson, and F. C. Fehsenfeld, 1998. *J. Geophys. Res.*, 103, 22,449-22462.

Li, S. M., C. M. Banic, W. R. Leatich, P. S. K. Liu, G. A. Isaac, X. L. Zhou, and Y. N.

Lee, 1996. *J. Geophys. Res.*, 101, 29,111-29,121.

Lipari, F. and S. J. Swarin, 1982. *J. Chromatogr.*, 247, 297-306.

Martin, R. S., H. Westberg, E. Allwine, L. Ashman, J. C. Farmer, and B. Lamb, 1991. *J. Atmos. Chem.*, 13, 1-32.

Meylan, W. M. and P. H. Howard, 1991. *Environ. Toxicol. Chem.*, 10, 1283-1293.

Montzka, S. A., M. Trainer, P. C. Goldan, W. C. Kuster, and F. C. Fehsenfeld, 1993. *J. Geophys . Res.*, 98, 1101-1111.

Munger, J. W., D. J. Jacob, B. C. Daube, L. W. Horowitz, W. C. Keene, and B. G. Heikes, 1995. *J. Geophys. Res.*, 100, 9325-9333.

Neely, W. B. and G. E. Blau, 1985. **In** Environmental Exposure From Chemicals. *Volum2 1.* CRC Press.

Niki, H., P. D. Maker, C. M. Savage, and M. D. Hurley, 1987. *J. Phys. Chem.*, 91, 2174-2178.

Nirmalakhandan, N. and R. E. Speece, 1988. *Environ. Sci.Technol.*, 22, 606-615.

Orlando, J. J., G. S. Tyndall, J.-M. Fracheboud, E. G. Estupinan, S. Haberkorn, and A. Zimmer, 1999. *Atmos. Environ.*, 33, 1621-1629.

Pedersen, T. and K. Sehested, 2001. *International Journal of Chemical Kinetics*, **33,** 182-190.

Perry, R. H. and D. Greem, 1984. In Perry's Chemical Handbook. Physical and Chemical Data; 6th ed. McGraw Hill.

Pierce, T., C. Geron, L. Bender, R. Dennis, G. Tonnesen, and A. Guenther, 1998. *J. Geophys. Res.*, 103, 25611-25629.

Plum, C. N., E. Sanhueza, R. Atkinson, W. P. L. Carter, and J. Pitts, J. N., 1983. *Environ. Sci. Technol.*, 17, 479-484.

Possanzini, M. and V. DiPalo, 1996. *Chromatographia*, 43, 433-435.

Rao, X., R. Kobayashi, R. White, R. Spaulding, P. Frazey, and M. J. Charles, 2001. *JAOAC*, 84, 699-705.

Rodier, D. R. and J. W. Birks, 1994. *Environ. Sci. Technol.*, 28, 2211-15.

Rudich, Y., R. Talukdar, J. B. Burkholder, and A. R. Ravishankara, 1995. *J. Phys. Chem.*, 99, 12188-12194.

Schade, G. W., A. H. Goldstein, D. W. Gray, and M. T. Lerdau, 2000. *Atmos. Environ.*, 34, 3535-3544.

Schwartz, S. E., 1983. In Chemistry of Multiphase Atmospheric Systems, J. W, Ed., Springer-Verlag, 415-471.

Schwarzenbach, R. P., P. M. Gschwend, and D. M. Imboden, 1993. In Environmental Organic Chemistry. John Wiley & Sons, Inc.

Seinfeld, J. H. and S. N. Pandis, 1998. In Atmospheric Chemistry and Physics, From Air Pollution to Climate Change. John Wiley & Sons, Inc., 1326 pp.

Slemr, J., 1991. *Fresenius J. Anal. Chem.*, 340, 672-677.

Sorensen, P. E., 1972. *Acta* Spaulding, R. S., P. Frazey, X. Rao, and M. J. Charles, 1999. *Anal. Chem.*, 71, 3420-3427.

Stroud, C. A., J. M. Roberts, P. D. Goldan, W. C. Kuster, P. C. Murphy, E. J. Williams, D. Hereid, D. Parrish, D. Sueper, M. Trainer, F. C. Fehsenfeld, E. C. Apel, D. Riemer, B. Wert, B. Henry, A. Fried, M. Martinez-Harder, H. Harder, W. H. Brune, G. Li, H. Xie, and V. L. Young, 2001. *J Geophys. Res.*, 106, 8035-8046.

Tanner, R., L. and Z. Meng, Meng, 1984. *Environ. Sci. Technol.*, 18, 723-726.

Trainer, M., E. J. Williams, D. D. Parrish, M. P. Buhr, E. J. Allwine, H. H. Westberg, F. C. Fehsenfeld, and S. C. Liu, 1987. *Letters to Nature*, 329, 705-707.

Trainer, M. E., E. Hsie, S. McKeen, R. Tallamraju, D. Parrish, F. Fehsenfeld, and S. Liu, 1987. *J. Geophys. Res.*, 92, 11879-11894.

Tuazon, E. C. and R. Atkinson, 1989. *Inter. Jour. Chem. Kinet.*, 21.

U.S. Environmental Protection Agency. National Air Quality Emissions Trends Report, 1999. Office of Air Quality Planning and Standards. Research Triangle Park, North Carolina.

Vairavamurthy, A., J. M. Roberts, and L. Newman, 1992. *Atmos. Environ.*, 26A, 1965-1993.

Wen, W.Y. and J. H. Hung, 1970. *J. Phys. Chem.*, 74, 170-180.

Yalkowsky, S. H. and R. M. Dannenfelser, 1992. In Aquasol Database of Aqueous Solubility. College of Pharmacy, University of Arizona, TuscoN.

Yokouchi, Y., 1994. *Atmos. Environ.*, 28, 2651-2658.

Yu, J. and H. E. Jeffries, 1997. *Atmos. Environ.*, 31, 2281-2287.

Yu, J., H. E. Jeffries, and R. M. LeLacheur, 1995. *Environ. Sci. Technol.*, 29, 1923-1932.

Yu, J., H. E. Jeffries, and K. G. Sexton, 1997. *Atmos. Environ.*, 31, 2261-2280.

Yu, J., R. C. Flagan, and J. H. Seinfeld, 1998. *Environ. Sci. Tech.*, 32, 2357-2370.

Zar, J. H. 1984. In Biostatistical Analysis. 2nd Edition. Prentice-Hall, Inc. Englewood Cliffs, N. J.

Zhou, X. L. and K. Mopper, 1990. *Environ. Sci. Technol.*, 24, 1482-1485.

Chapter 3

Advances in the Analytical and Atmospheric Chemistry of 2-hydroxy-2-methylpropanal, a Proposed Photooxidation Product of 2-methyl-3-buten-2-ol.

Table of Contents

Page No.

List of Tables.

List of Figures.

Abstract

In the western United States, in areas where emissions of the biogenic hydrocarbon, 2-methyl-3-buten-2-ol (MBO) are high, MBO contributes significantly to the oxidative capacity of the atmosphere. Hydroxyl radical oxidation of MBO can play an important role in forming tropospheric ozone, and MBO reaction products may contribute to the formation of secondary organic aerosols (Saxena and Hildemann, 1996, Lamanna and Goldstein, 1999, Kenkin and Clemitshaw, 2000). Although 2-hdyroxy-2-methylpropanal was tentatively identified as a product from the reaction of MBO with ·OH in indoor chamber studies, the identity of the compound was not confirmed due to the lack of an authentic standard. Further, no data exists on the atmospheric generation and fate of 2-hydroxy-2-methylpropanal in the ambient environment. Herein, we provide further evidence that 2-hydroxy-2-methylpropanal is generated by ·OH reaction with MBO by identifying 2-hydroxy-2-methylpropanal in an indoor chamber experiment and in ambient air sampled in the Blodgett Forest, where MBO emissions are high. We analyzed 2-hydroxy-2-methylpropanal by using a method that relies on *O*- (2,3,4,5,6-pentafluorobenzyl)hydroxylamine (PFBHA) and *bis*-(trimethylsilyl) trifluoroacetamide (BSTFA) derivatization along with ion-trap mass spectrometry. Tentative identification of 2-hydroxy-2-methylpropanal was possible by using knowledge gained in this study regarding the mass spectrometry of PFBHA-BSTFA derivatives of carbonyls with primary, secondary, and tertiary -OH groups, and aldo- and keto-acids. The identification was confirmed by comparing the methane CI mass spectra and relative gas chromatographic retention time obtained by analyzing 2-hydroxy-2-methylpropanal in a sample extract and a synthesized authentic standard. Since the standard became available at the end of this study (after all samples were analyzed), we also developed a method for semi-quantification of 2-hydroxy-2-methylpropanal, with a detection limit of 27 pptv in air. We used the method to provide the first ambient air measurements of 2-hydroxy-2-methylpropanal. The analyte is not commercially available, and hence other researchers who have not synthesized an authentic standard can employ the method.

I. Introduction

Biogenic volatile organic compounds (VOC) play an important role in tropospheric ozone and secondary organic aerosol formation in rural and urban areas, and can dominate the oxidative capacity of the atmosphere in rural areas (Saxena and Hildemann, 1996, Lamanna and Goldstein, 1999, Jenkin and Clemitshaw, 2000. On a global scale, biogenic emissions exceed anthropogenic emissions by approximately 10 times (Atkinson. 1997). Isoprene is the dominant biogenic hydrocarbon and constitutes about 30% of the biogenic volatile organic compounds (VOCs) in North America (Atkinson, 1997). Although 2-methyl-3-buten-2-ol (MBO) comprises only 5% of the biogenic VOCs in North America, MBO concentrations were measured at 2 to 7 times the concentrations of isoprene in the Blodgett Forest, CA, and at Niwot Ridge, CO. (Lamanna and Goldstein, 1999, Goldan et al, 1993) due to emission from ponderosa and lodgepole pines, trees that are endemic to western North America (Harley et al., 1998). Hydroxyl radical oxidation is the dominant loss mechanism for MBO during daytime (Ferronato et al., 1998, Fantechi et al., 1998). Therefore, in order to reduce tropospheric ozone in atmospheres that are affected by MBO emissions, it is essential that we gain insight into atmospheric processes affecting ·OH oxidation of MBO, and the generation and fate of the reaction products.

Laboratory (chamber) studies establish that ·OH oxidation of MBO yields acetone and glycolaldehyde (50-60% yield), and formaldehyde (30-35% yield) (Ferronato et al., 1998, Fantechi et al., 1998, and Alvarado et al., 1999). A fourth product, 2-hydroxy-2-methylpropanal was also proposed. The identification of this product was based on: 1) the proposed reaction mechanism of MBO with ·OH (Figure 3.1) and a gas chromatographic (GC) retention index for the 2,4-dinitrophenylhydrazine (DNPH) derivative (Fantechi, et al., 1998); 2) identification of an ion in the chemical ionization mass spectra that corresponds to the $(M\text{-}H_2O)^+$ ion of a C_4-hydroxycarbonyl or a C_3-oxo-acid DNPH derivative (Fantechi et al., 1998); and 3) identification of absorption bands corresponding to C-H, C=O, and $(CH_3)_3Si\text{-}OR$ stretches in the GC-infrared spectrum and an ion corresponding to $(M\text{-}CH_3)^+$ in the electron ionization MS of a trimethylsilyl

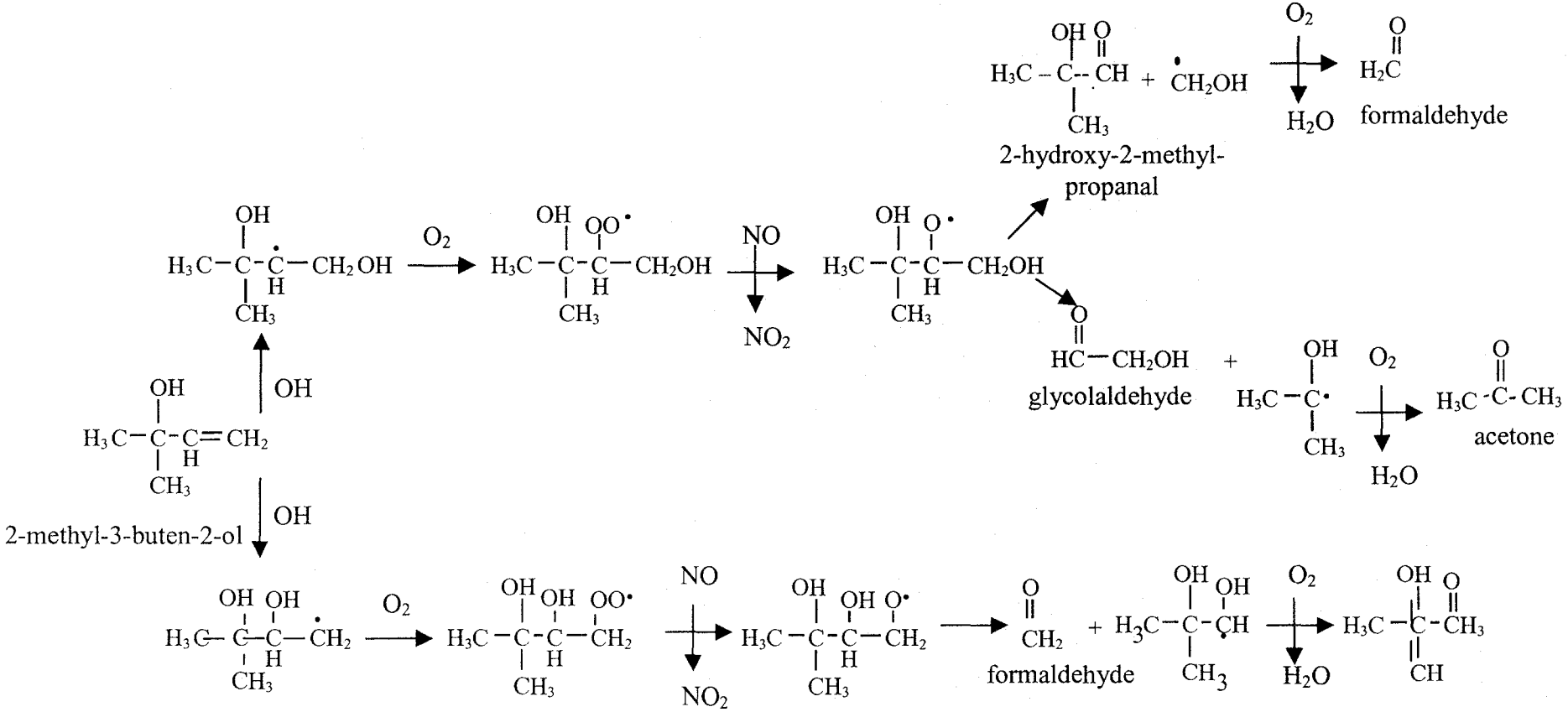


Figure 3.1. Mechanism for reaction of MBO with ·OH proposed by Fantechi et al., 1998.

derivatized sample extract (Alvarado et al., 1999). The yield is assumed to be equal to that of formaldehyde (Ferronato et al., 1998). However, Alvarado et al., 1999 estimated a yield of 19 ± 7%, compared to the formaldehyde yield of 29 ± 3%. Although experimental evidence indicates a C_4-hydroxycarbonyl, confirmation of 2-hydroxy-2-methylpropanal was not possible due to the absence of an authentic standard. Further, no ambient air data exists that relates concentrations of 2-hydroxy-2-methylpropanal to MBO emissions. The lack of information regarding the atmospheric generation and fate of 2-hydroxy-2-methylpropanal is in part due to the absence of a suitable analytical method to identify and quantify this compound in air.

We recently developed a method using a mist chamber for collection of compounds with a Henry's law constant > 10^3 M atm^{-1} (Sapulding et al., 2002) *O*-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine (PFBHA) in combination with *bis*-(trimethylsilyl) trifluoroacetamide (BSTFA) were used to derivatize carbonyl and hydroxyl/carboxyl groups, respectively. Detection and quantification were accomplished using gas chromatography/ion trap mass spectrometry (GC/ITMS) (Yu et al., 1997, Yu et al., 1998, Spaulding et al., 1999, Frazey et al., 1999, Rao et al., 2001). The power of ion trap mass spectrometry to facilitate identification of carbonyl and multifunctional carbonyl derivatives was presented in previous studies (Spaulding et al., 1999, Frazey et al., 1999, Rao et al., 2001). Herein, we describe the utility of ion trap mass spectrometry to identify 2-hydroxy-2-methylpropanal in chamber studies and in air sampled in the Blodgett Forest, CA. We confirm the identification by comparing the mass spectrum and GC retention time of the analyte in an extract of air to that of an authentic standard. In addition, we provide a method for semi-quantification of 2-hydroxy-2-methylpropanal in air. An authentic standard is not commercially available, and hence other researchers who have not synthesized an authentic standard can use the method.

II. Experimental

A. Gas chromatography/ion trap mass spectrometry.

A Varian Star 3400 CX gas chromatograph (GC), with a temperature-programmable injector port interfaced to a Saturn 2000 ion trap mass spectrometer (Varian Assoc., Walnut Creek, CA)

was employed. Gas chromatographic separation was accomplished by using a capillary column coated with either (50%-phenylmethyl) polysiloxane (DB-17ms) or a formula with equivalent polarity to (12%-phenylmethyl) polysiloxane (DB-XLB). The dimensions of the columns were 30 m x 0.25 mm i.d., 0.25 μm film thickness (J&W Scientific, Inc., Folsom, CA). A 5-m integrated guard column was used prior to the DB-XLB analytical column. The injector temperature was held at 280°C for 1 min, increased to 310°C at a rate of 50°C min^{-1}, held at 310°C for 25 min, then decreased to 280°C. The column temperature was held at 70°C for 1 min, increased to 100°C at 5°C min^{-1}, increased to 280°C at 10°C min^{-1}, increased to 310°C at 30°C min^{-1}, then held at 310°C for 10 min. The injection volume was 2 μL.

For the electron-ionization (EI), methane chemical ionization (CI), and pentafluorobenzyl alcohol (PFBOH) CI mass spectra, we employed a filament current of 10 μA and an ion trap temperature of 150°C. The EI mass spectra were acquired by scanning from m/z 65 to m/z 650, using automatic gain control with a target total ion current (TIC) of 20,000 and a maximum ionization time of 25,000 μs. We acquired the methane CI mass spectra by scanning from m/z 150 to m/z 550, using automatic reaction control with a target TIC of 5000, a maximum ionization time of 500 μs, and a maximum reaction time of 80 ms. PFBOH was introduced into the ion trap as described by Frazey *et al*, 1999. The PFBOH CI mass spectra were acquired by scanning from m/z 230 to m/z 650, using automatic reaction control with a target TIC of 5000, a maximum ionization time of 2000 μs, and a maximum reaction time of 128 ms.

B. Reagents and Glassware.

HPLC grade water (Fisher Scientific, Fairlawn, NJ) was purified by distillation in glass in the presence of $KMnO_4$ to oxidize any organic contaminants. Other solvents were purchased in the highest purity available (≥ 99.9%), and further purified by distillation in glass. *O*-(2,3,4,5,6-pentafluorobenzyl) hydroxylamine hydrochloride (PFBHA) (≥ 98% purity), *O*-(2,3,4,5,6-pentafluorobenzyl) alcohol (PFBOH) (≥ 98% purity), trimethylchlorosilane (TMCS), and carbonyl standards (≥ 95% purity) were purchased from Aldrich Chemical Company, Inc (Milwaukee, WI.). *Bis*-(trimethylsilyl) trifluoroacetamide (BSTFA) was purchased from

Supelco Chromatography Products (Bellefonte, PA.). The PFBHA was recrystallized two times in 2-propanol. Other chemicals were used without further purification.

All glassware was soaked overnight in 15% (v/v) dichlorodimethylsilane in toluene. The glassware was then rinsed with toluene, methanol, and dichloromethane (three times for each solvent), and dried at 150°C.

C. PFBHA and BSTFA Derivatization.

PFBHA derivatization using a 1mM aqueous PFBHA solution was allowed to proceed for 24 hours at room temperature. The PFBHA derivatives were extracted with dichloromethane. Two drops of concentrated H_2SO_4 and 5 mL of water were added to the sample extract to remove excess PFBHA (Cancilla et al, 1992), and the organic fraction was filtered through a 70 mm x 7 mm o.d. column of anhydrous Na_2SO_4(s) to remove water. The eluate was collected and evaporated under a stream of N_2(g) to a final volume of 2.0 mL for chamber studies, and 200 μL for ambient air studies. Each time a vial was opened to add reagent or transfer the extract to another vial, the headspace was purged with N_2(g) before it was sealed. Hydroxyl and carboxyl groups were derivatized with BSTFA containing 10% trimethylchlorosilane (TMCS). Twenty μL of BSTFA:TMCS (90:10) was added to a vial containing 200 μL of the PFBHA-derivatized sample extract, and the vial was sealed with a teflon-coated cap. The BSTFA was allowed to react for 12 hours at 42°C, after which the derivatives were analyzed by GC/ITMS.

D. Semi-Quantification of 2-hydroxy-2-methylpropanal.

Semi-quantification of 2-hydroxy-2-methylpropanal in ambient air samples was accomplished by using 3-hydroxy-3-methyl-2-butanone standard as a surrogate and 4-hydroxybenz-$^{13}C_6$-aldehyde as the internal standard. The analyses were conducted by using this method because an authentic standard of 2-hydroxy-2-methylpropanal was not available at the time when the analyses were conducted. We were unable to retroactively conduct such analyses due to concerns about degradation of the analyte in the sample extract. We employed 3-hydroxy-3-methyl-2-butanone as the surrogate because it is a carbonyl with a tertiary -OH group. The

standard solutions used to construct the calibration curve contained 46 to 5500 pg/μL (0.451 – 53.9 μM) of 3-hydroxy-3-methyl-2-butanone. The concentration of the internal standard was 1045 pg/μL (8.16 μM). Eight- or 10-point calibration curves were constructed by the analysis of 4 or 5 standard solutions before and after analysis of samples. Recoveries of 3-hydroxy-3-methyl-2-butanone were obtained by the analysis 1 mM aqueous PFBHA solutions enriched with 185 ng (1.81 mmol) of 3-hydroxy-3-methyl-2-butanone at the time of ambient air sample collection (field spikes). The recoveries of the field spikes for the chamber (n=2) and ambient air (n=2) experiments were 90% and 98%, and 113% and 91%, respectively. A mid-point calibration standard (231 or 461 pg/μL; 2.26 or 4.52 μM) was analyzed after every 5 samples. The relative standard deviation among the relative response factors for standard curves was ≤ 28%.

E. Blanks and Limit of Detection (LOD).

For chamber studies, air samples collected from the chamber in impingers before addition of MBO, NO, and NO_2 were used as blanks. For ambient air studies, ultra-high purity (UHP) zero grade air was sampled by using a mist chamber to determine background concentrations of the carbonyls. These samples were employed as blanks, and treated identically to samples. Carbonyl compounds are ubiquitous in air, solvents, and many reagents. Extensive purification procedures, treatment of glassware to reduce contamination, and reducing exposure of glassware, and samples to ambient air, significantly reduce the background concentration, but do not remove carbonyls entirely. We used a standard method for calculating the LOD, which considers the variability among blank samples. The LOD was calculated as $3\sigma_{blnk}$, where σ_{blnk} is the standard deviation of the response factor for the analyte in three or more reagent blanks (Willard et al., 1988). The analyte concentration in the sample was considered significant only if it exceeded the LOD after subtraction of the mean blank concentration.

F. OH Radical Oxidation of 2-methyl-3-buten-2-ol in Chambers.

Alvarado et al., 1999 previously described conditions utilized in the chamber studies. Briefly, a 5800-liter evacuable, Teflon™-coated chamber containing a multiple reflection optical system

interfaced to a Nicolet 7199 Fourier transform infrared (FT-IR) spectrometer was employed. Irradiation was provided by a 24 kW xenon arc filtered through a Pyrex pane to remove wavelengths <300 nm. The experiment was conducted at 298 ± 2 K and 749 ± 2 Torr total pressure. Initial concentrations of reactants were 10 ppm (2.4×10^{14} molecules cm^{-3}) each, MBO, CH_3ONO, and NO. OH radicals were generated by photolysis of CH_3ONO [23]. Three irradiations were performed for 1.5 - 2 minutes. During dark periods, samples were collected in two midget (25 mL) impingers in series, which each contained 20 mL of 1 mM of aqueous PFBHA. Impinger samples were collected on ice for 10 min at an airflow rate of 113 mL min^{-1}. Each sample was enriched with 100 μL 20.1 ng μL^{-1} (157 μM) 4-hydroxybenz-$^{13}C_6$-aldehyde after collection.

G. Collection of ambient air samples.

Ambient air samples were collected above a ponderosa pine plantation on August 17, 2000, between the hours of 6:00 and 21:00, Local Standard Time (LST). The site is located in the western foothills of the Sierra Nevada, near the Blodgett Forest Research Station (38°53', 42.9" N, 120°37', 57.9" W, 1315 m elevation). The pine trees are even aged (9-10 years old), and planted at a density of 0.12 trees m^{-2}, with various coniferous and deciduous trees interspersed. Detailed descriptions of the site can be found elsewhere (Lamanna and Goldstein, 1999, Trainer et al., 1987). Typical daytime mixing ratios of MBO at this site during summer are 1 – 3 ppbv (Trainer et al., 1987).

Ambient air samples were collected in a mist chamber, which was previously described (Spaulding et al., 2002, Cofer et al., 1985, Klemm et al., 1991). For this work, air was sampled for 10 minutes in two mist chambers in series, at a flow rate of approximately 23 – 25 L min^{-1}. The mist chamber reservoir was filled with 20 mL of 1 mM aqueous PFBHA. Each sample was enriched with 50 μL of 4.18 ng μL^{-1} (32.7 μM) 4-hydroxybenz-$^{13}C_6$-aldehyde after collection.

H. Synthesis of 2-hydroxy-2-methylpropanal

The synthesis began with the straight forward 1,2-addition of methyl magnesium bromide in ether (Baeckstrom and Li, 1991). Despite several attempts, subsequent hydrolysis of the acetal in the presence of the secondary alcohol proved to be problematic giving a variety of undesired side products and poor yields of the hydroxy aldehyde. Thus to circumvent these problems the free alcohol was benzyl protected under standard conditions (Fessner et al., 2000), followed by the acid catalyzed hydrolysis of the acetal to readily give aldehydes (Feedman and Dubois, 1976). Then hydrogenation of the benzyl ether under standard conditions gave 2-hydroxy-2-methylpropanal.

III. Results and Discussion

A. Identification of products arising from OH radical oxidation of MBO in chambers.

Previous research conducted in chambers establishes that hydroxyl radical oxidation of MBO yields acetone, glycolaldehyde, formaldehyde, and a C_4-hydroxycarbonyl, tentatively identified as 2-hydroxy-2-methylpropanal (Ferronato et al., 1998, Fantechi et al., 1998, Alvarado et al., 1999). Due to the lack of an authentic standard, the yield was not calculated and the identity of 2-hydroxy-2-methylpropanal (*i.e.* the structure of the C_4-hydroxycarbonyl) was not confirmed.

Electron ionization (EI) of a PFBHA derivative of a carbonyl generates a pentafluorobenzyl cation $[(C_6F_5CH_2)^+]$, which is 181 Daltons (Da) (Spaulding et al., 1999, Frazey et al., 1999, Yu et al., 1995). The presence of an m/z 181 ion in the EI mass spectra of PFBHA derivatives in a sample extract thus denotes the presence of a carbonyl. At least three carbonyls compounds are evident in the m/z 181 ion chromatogram of a sample (—) and blank (-----) extract of air collected from a chamber experiment in which MBO was reacted with ·OH. These products are labeled **I**, **II** and **III** in Figure 3.2. These compounds are significant reaction products because they are present at least 3x the peak area of background levels. By comparing the relative retention times and mass spectra from peaks **I** and **II** to those of PFBHA derivatized standards,

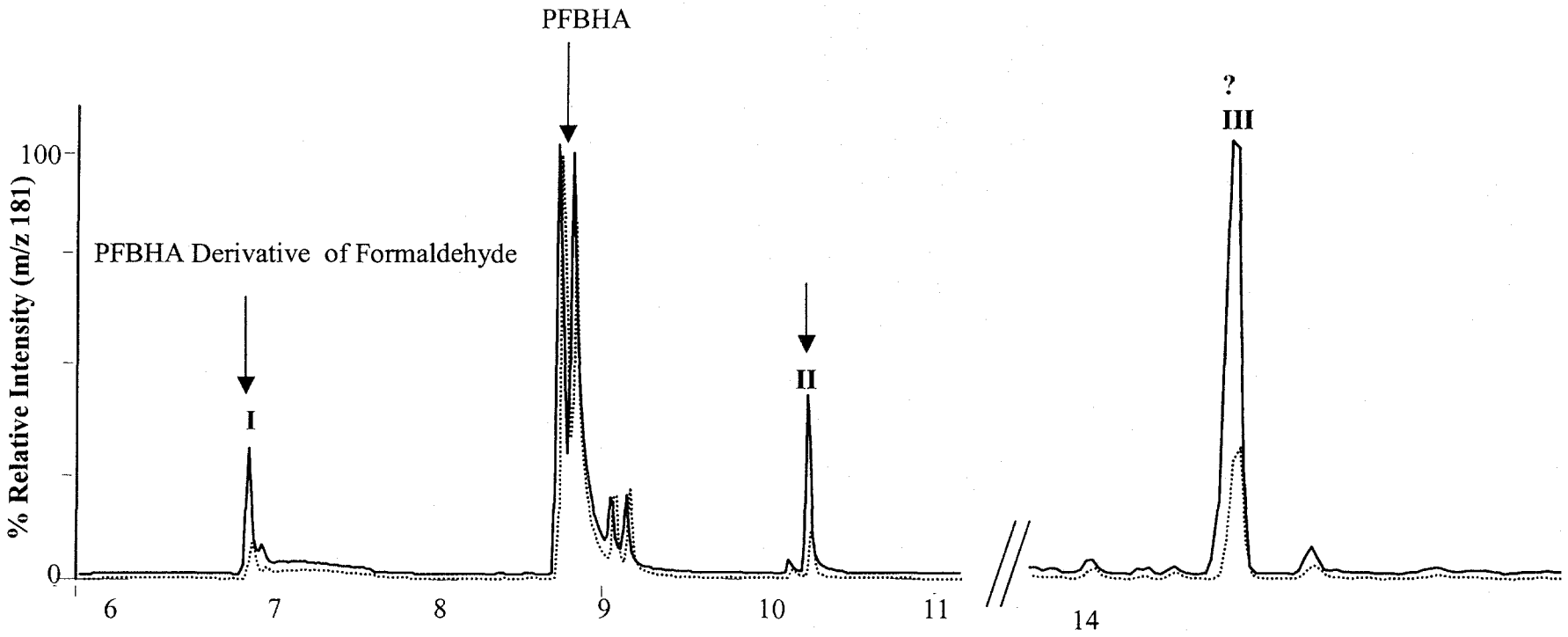


Figure 3.2. m/z 181 ion chromatogram of a PFBHA-BSTFA derivative of products arising from the reaction of MBO with ·OH in an environmental chamber.

we confirmed the identities of formaldehyde (**I**) and acetone (**II**). The large m/z 181 peak that elutes around 9 minutes is due to excess PFBHA reagent.

The EI mass spectrum at the centroid of Peak **III** is presented in Figure 3.3A. The presence of ions at m/z 73, 75, and 181 indicate that the compound is a PFBHA-BSTFA derivative of a hydroxy carbonyl or an aldo- or keto-acid. The m/z 73 and 75 ions are $((CH_3)_3Si)^+$ and $(HO{=}Si(CH_3)_2)^+$ ions that arise from fragmentation of derivatized hydroxyl or carboxyl groups on the molecule. Examination of the mass spectra on the left and right sides of peak **III** revealed the presence of 2 compounds, **IIIA**, with a base peak at m/z 340, and **IIIB**, with a base peak at m/z 312 (see Figure 3.3B). The base peak of a PFBHA-BSTFA hydroxycarbonyl derivative is generally due to an $(M-15)^+$ ion (Spaulding et al., 1999, Frazey et al., 1999). We thus hypothesized that the $(M-15)^+$ ions for compounds **IIIA** and **IIIB** were m/z 340 and 312, respectively. This assumption led to the determination of molecular weights for the PFBHA-BSTFA derivatives of compound **IIIA** and **IIIB** of 355 and 327 Da, respectively. We tentatively identified **IIIB** as the PFBHA-BSTFA derivative of glycolaldehyde, and confirmed the identity by comparing the relative retention time and the EI mass spectra to the PFBHA-BSTFA derivative of an authentic standard.

To assist in identifying the compound in peak **IIIA**, we obtained the methane CI mass spectrum, presented in Figure 3.4A. The methane CI mass spectra of PFBHA-BSTFA derivatives of aliphatic hydroxy carbonyls are characterized by $(M+1)^+$, $(M-15)^+$, and $(M-89)^+$ ions, which are generated by addition of a proton, loss of (CH_3), and loss of $(Si\ (CH_3)_3O)$, respectively (Yu et al., 1998, Spaulding et al., 1999, Frazey et al., 1999). If our hypothesis was correct (*i.e.*, the molecular weight of the derivative in peak **IIIA** is 355 Da), we would expect to observe ions at m/z 356, 340, and 266. However, in this case, the base peak is at m/z 266, with a smaller peak at m/z 340, which could be the $(M-15)^+$ ion. The absence of an ion at m/z 356 makes the identification of the molecular weight inconclusive.

In previous work, interpretation of the PFBOH CI ion trap mass spectra was critical to the identification of compounds for which authentic standards do not exist (*i.e.*, unknowns) (Frazey et al., 1999, Spaulding et al., 1999). The $(M+181)^+$ ion arises from ion-molecule reactions that

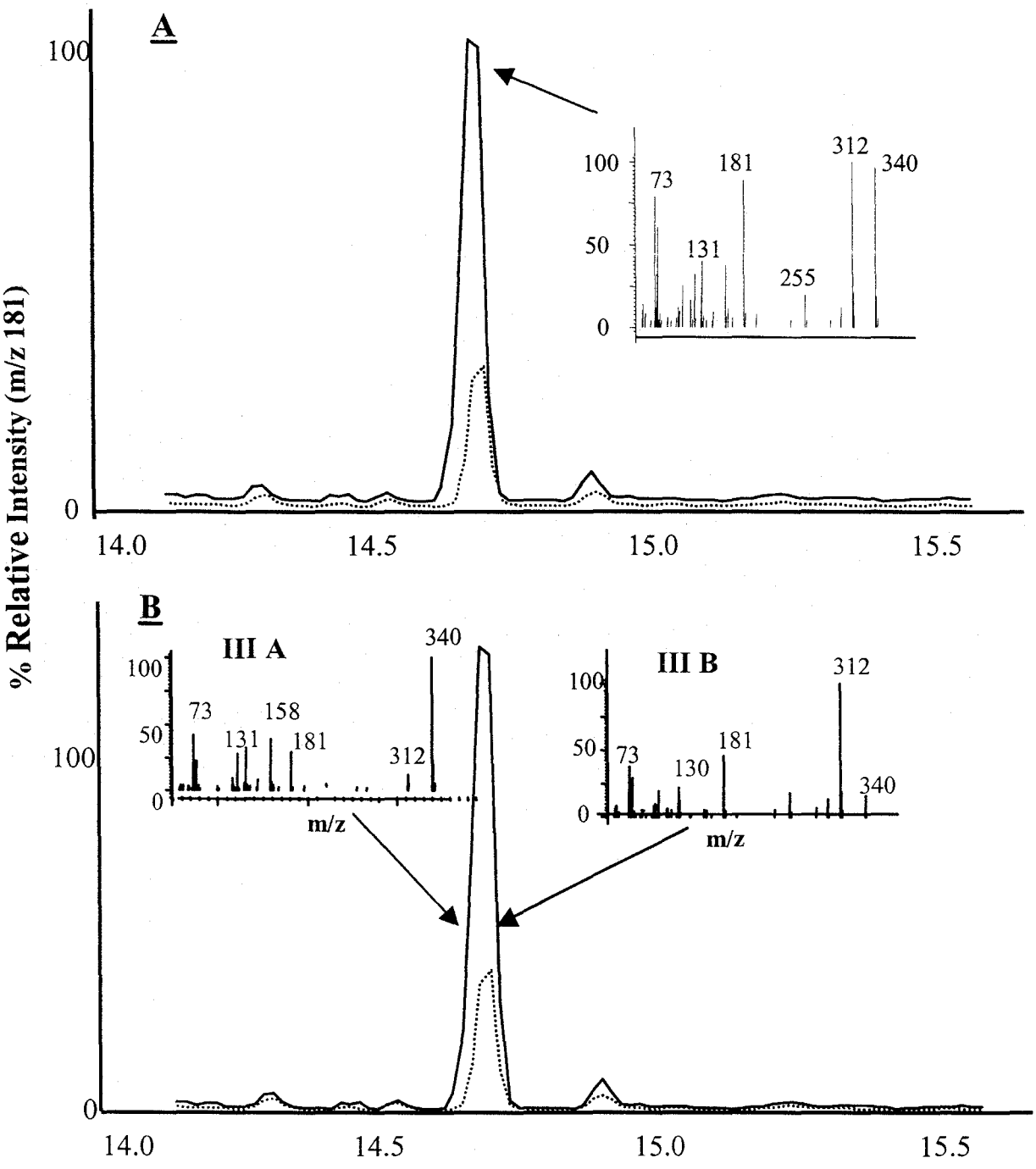


Figure 3.3. Electron ionization mass spectra of a PFBHA-BSTFA derivative of a photooxidation product(s) arising from the reaction of MBO with ·OH in an environmental chamber: Electron ionization mass spectrum at the centroid of peak **III** (A); Electron ionization mass spectra from the left and right sides of peak **III** (B).

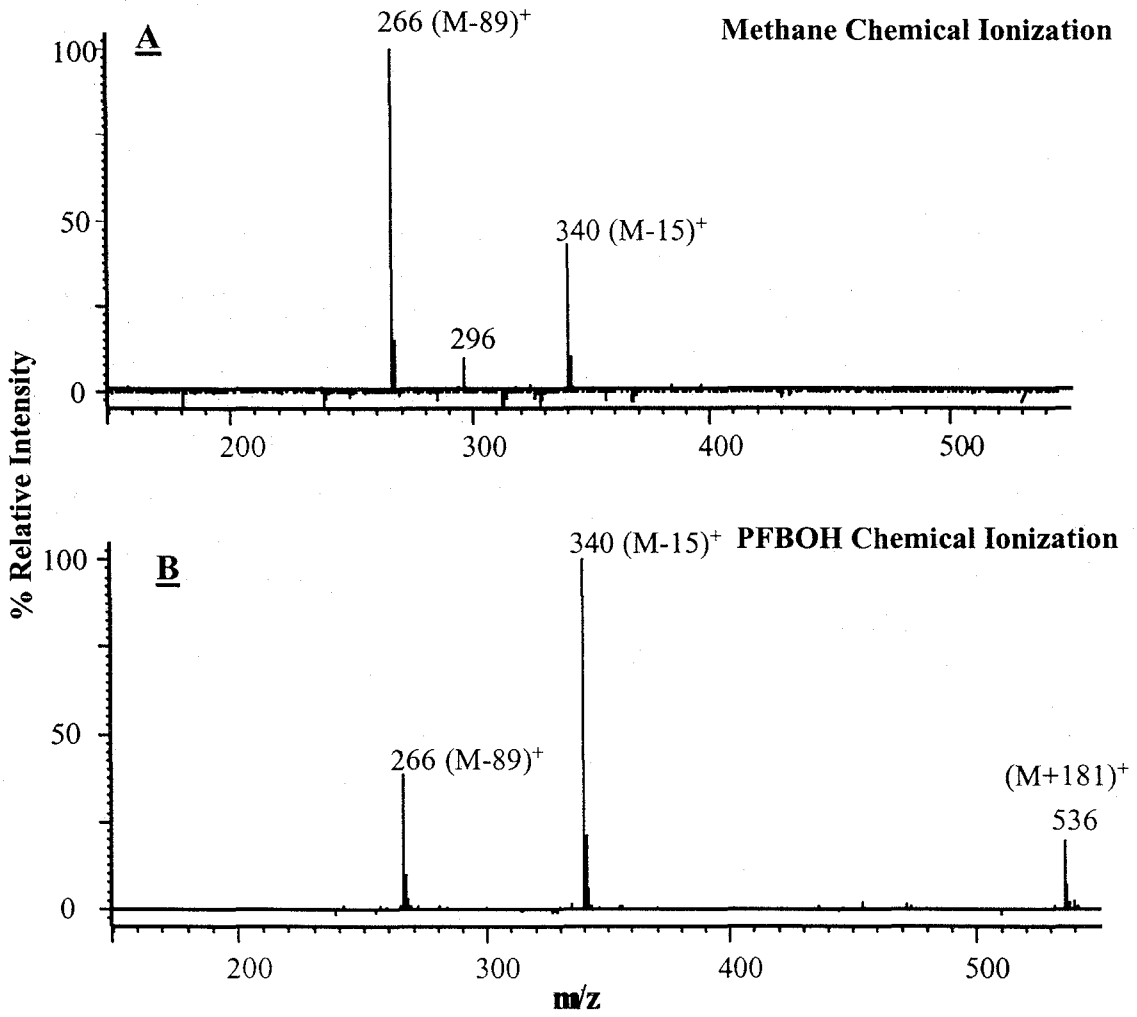


Figure 3.4. Methane chemical ionization (A) and PFBOH chemical ionization (B) mass spectra of the PFBHA-BSTFA derivative in peak **IIIA** of Figure 3.3.

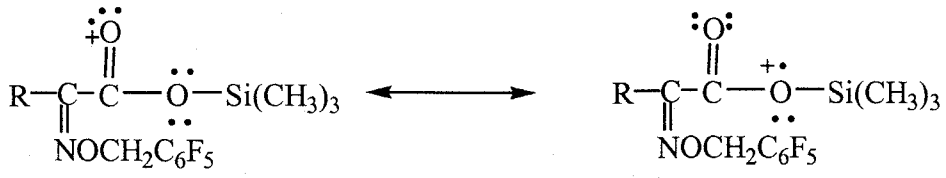
occur in an ion trap mass spectrometer, but not in a conventional quadrupole mass spectrometer (Frazey et al., 1999, Yu et al., 1995, Chien et al., 1998). The relationship between the $(M+H)^+$ and $(M+181)^+$ ions has proven invaluable, in certain cases for identification of the molecular ion (Spaulding et al., 1999, Frazey et al., 1999). In the PFBOH CI mass spectrum of compound **IIIA**, we observe ions at m/z 266, m/z 340, and m/z 536. (See Figure 3.4B). Due to knowledge about the CI and PFBOH CI mass spectra of PFBHA-BSTFA derivatives attained in previous studies (Spaulding et al., 1999, Frazey et al, 1999, Rao et al., 2001), we can assume that the ion at m/z 536 is the $(M+181)^+$ ion of a compound with a molecular weight of 355 daltons. The absence of an $(M+H)^+$ ion at m/z 356 is inconsistent with previously observations regarding the PFBOH CI mass spectra of PFBHA-BSTFA derivatives of multifunctional carbonyls, and indicates that the formation of a stable $(M+H)^+$ ion might be dependent on the structure of the molecule. A molecular weight of 355 daltons for the PFBHA-BSTFA derivative indicates the presence of a C_4-hydroxycarbonyl or a C_3-oxo-acid. The "gold-standard" to distinguish whether the compound was a hydroxy carbonyl or an oxo-acid is to obtain an accurate mass measurement on the molecular or *pseudo*-molecular ion. In this case, the experiment would need to be conducted at a resolving power=10,000 under methane chemical ionization conditions. Under methane CI conditions, the relative intensity of the $(M+H)^+$ ion of the PFBHA/BSTF derivatives is compound dependent and may exist at low relative intensities (<15%) (Spaulding et al., 1999), thereby making it difficult to conduct an accurate-mass measurement on the ion as it elutes from the GC. In contrast, the base peak in the methane CI mass spectra of PFBHA/BSTFA derivatives is typically the $(M-15)^+$ ion. The relative intensity of the $(M+H)^+$ is compound dependent ranges from 11-100% relative intensity for compounds tested in a previous study (Spaulding et al., 1999). Herein, utilize an approach that relies on knowledge of the mass spectrometry of PFBHA-BSTFA derivatives of aldo- and keto-acids, and hydroxy carbonyls to derive the elemental formula of the compound in peak **IIIA**. One advantage of our approach is that it relies on instrumentation that is less expensive than double-focusing mass spectrometers, which are typically employed to perform accurate mass measurements.

B. Characterization of the EI, methane CI, and PFBOH CI mass spectra of aldo- and keto-acids and carbonyls with primary, secondary, and tertiary -OH groups.

The indication that the generation of the $(M+H)^+$ ion may be dependent on the structure of the PFBHA-BSTFA derivative led us to examine the EI, methane CI, and PFBOH CI mass spectra of PFBHA-BSTFA derivatives of aldo- and keto-acids carbonyls with primary, secondary, and tertiary -OH groups. The EI mass spectra of PFBHA-BSTFA derivatives of carbonyls with primary and secondary -OH groups and aldo- and keto-acids are characterized by ions at m/z 73, 75, 181, $(M-15)^+$, and $(M-197)^+$. (See Tables 3.1 and 3.2). The base peak in the EI mass spectra of the compounds investigated is either the $(M-15)^+$ ion, the $(M-197)^+$ ion, m/z 181, or m/z 73. For the hydroxy carbonyls, a consistent trend that can be used to identify substitution of the -OH group is not evident. However, the presence of an $(M)^{+\cdot}$ ion ranging from 7 to 11% relative intensity is unique to the PFBHA-BSTFA derivatives of the aldo- and keto-acids, and the presence of an $(M-17)^+$ ion ranging from 19 to 52% relative intensity is unique to the PFBHA-BSTFA derivatives of the keto-acids [$(M)^{+\cdot}$ and $(M-17)^+$ ions are $\leq$ 3% for hydroxy carbonyls]. The $(M)^{+\cdot}$ ion of a PFBHA-BSTFA derivative of an aldo- or keto-acid is stabilized by charge delocalization, as depicted in Figure 3.5A. The $(M-17)^+$ ion likely results from rearrangement and loss of OH from the derivatized acid. Because the $(M-17)^+$ ion is not observed in the mass spectrum of the aldo-acid, we assume that the alkyl group (CHR_2 in Figure 3.5B) is essential in the rearrangement (CHR_2 = H for an aldo-acid). The proposed fragmentation/rearrangement pathway leading to the formation of an $(M-17)^+$ ion is depicted in Figure 3.5B. Thus, the presence of a low-intensity $(M)^{+\cdot}$ ion in the EI mass spectrum suggests an aldo- or keto-acid, while the presence of an $(M-17)^+$ ion suggests a keto-acid.

The methane CI mass spectra of PFBHA-BSTFA derivatives of aldo- and keto-acids, and hydroxy carbonyls are characterized by $(M+H)^+$, $(M-15)^+$ and $(M-89)^+$ ions. (See Table 3.1,3.2). For the carbonyls with secondary and tertiary –OH groups, the base peak in the mass spectra is the $(M-89)^+$ ion, whereas for the carbonyls with primary –OH groups and the aldo- and keto-acids, the base peak can be the $(M+H)^+$ ion, the $(M-15)^+$ ion, or the $(M-89)^+$ ion. The relative intensity of the $(M+H)^+$ ion from the carbonyls with primary and secondary -OH groups ranges from 9 – 100%. For the aldo- and keto-acids, the relative intensity of the $(M+H)^+$ ion ranges

A. Proposed Mechanism for Stabilization of the PFBHA-BSTFA Derivative of an Aldo- or Keto-Acid.



B. Proposed Pathway for Formation of an $(M-17)^+$ Ion from a PFBHA-BSTFA Derivative of a Keto-Acid.

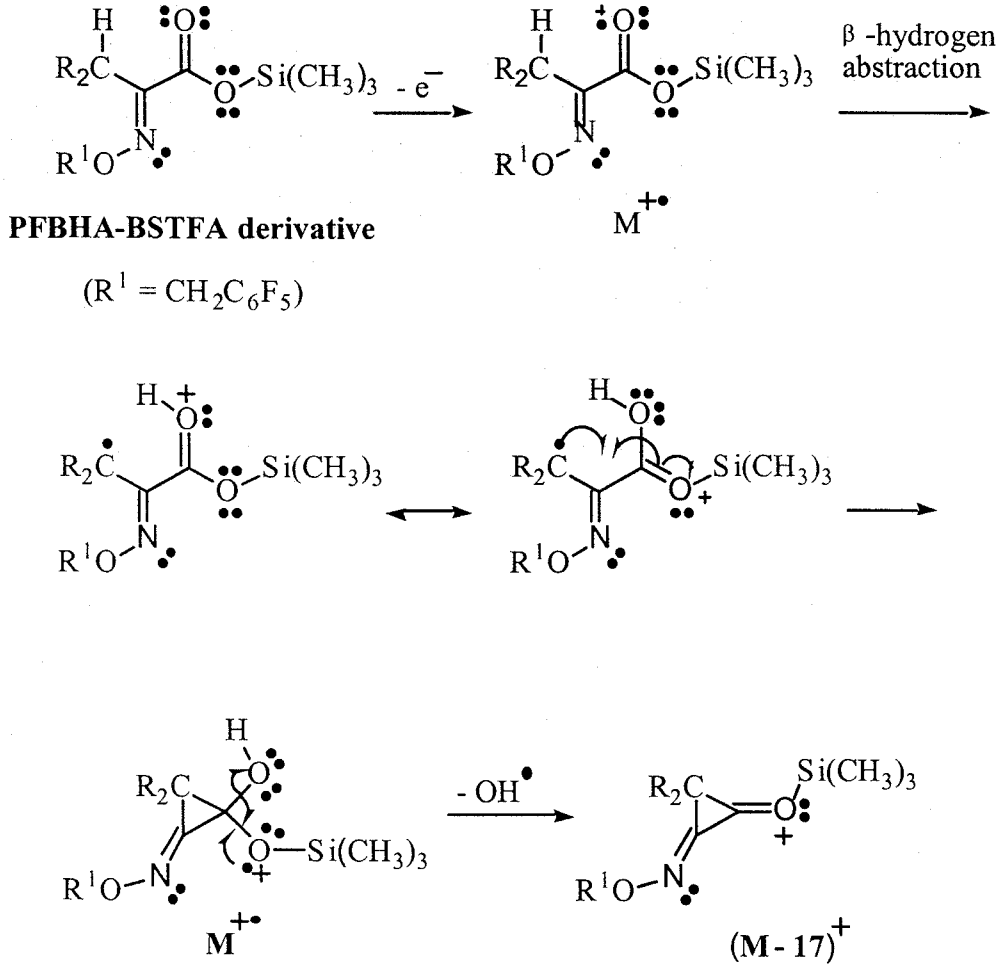


Figure 3.5. Proposed fragmentation pathway of PFBHA-BSTFA derivatives of aldo- and keto-acids under electron ionization conditions in an ion trap mass spectrometer (R = H or alkyl).

Table 3.1. Characterization of the electron ionization, methane chemical ionization, and PFBOH chemical ionization mass spectra for PFBHA-BSTFA derivatives of carbonyls with primary, secondary, and tertiary -OH groups.

	% Relative Intensity									
Compound	**(M+181)**	**(M+H)**	**$(M)^+$**	**$(M-15)^+$**	**$(M-17)^+$**	**$(M-89)^+$**	**$(181)^+$**	**$(M-197)^+$**	**$(75)^+$**	**$(73)^+$**
Electron Ionization										
Primary hydroxycarbonyls										
Glycolaldehyde	0, 0	0, 0	0, 0	82, 100	0, 1	2, 2	100,58	-	3, 1	58, 35
Hydroxyacetone	0	1	2	100	0	1	74	85	24	89
1-hydroxy-2-butanone	1	2	3	73	0	0	75	100	40	77
4-hydroxy-3-methyl-2-butanone	0	0	1	17	0	1	32	4	20	100
5-hydroxy-2-pentanone	0, 0	1, 1	1, 0	1, 5	1, 2	14, 1	69, 35	10, 10	12,17	75,25
Secondary hydroxy carbonyls										
3-hydroxy-2-butanone	0	0	0	57	0	1	58	100	28	72
Tertiary hydroxycarbonyls										
3-hydroxy-3-methyl-2-butanone	0	0	0	23	0	9	100	16	1	0
4-hydroxy-4-methyl-2-pentanone	0	0	0	10	0	0	8	0	84	16
Methane Chemical Ionization										
Primary hydroxy carbonyls										
Glycolaldehyde	0, 0	30, 61	3, 2	20, 100	0, 0	100, 71	15, 14	-	-	-
Hydroxyacetone	1	100	3	88	0	87	5	-	-	-
1-hydroxy-2-butanone	0	100	2	85	0	93	2	3	-	-
4-hydroxy-3-methyl-2-butanone	0	79	2	74	0	100	2	5	-	-
5-hydroxy-2-pentanone	1, 0	9, 13	2, 3	13, 2	5, 0	100,100	9, 25	25, 1	-	-
Secondary hydroxy carbonyls										
3-hydroxy-2-butanone	0	20	2	55		100	1	4	-	-
Tertiary hydroxy carbonyls										
3-hydroxy-3-methyl-2-butanone	0	0	0	54	0	100	3	1	-	-
4-hydroxy-4-methyl-2-pentanone	0	1	1	20	0	100	16	0	-	-

Table 3.1. Characterization of the electron ionization, methane chemical ionization, and PFBOH chemical ionization mass spectra for PFBHA-BSTFA derivatives of carbonyls with primary, secondary, and tertiary –OH groups (continued).

	% Relative Intensity									
Compound	$(M+181)^+$	$(M+H)^+$	$(M)^+$	$(M-15)^+$	$(M-17)^+$	$(M-89)^+$	$(181)^+$	$(M-197)^+$	$(75)^+$	$(73)^+$
PFBOH Chemical Ionization										
Primary hydroxy carbonyls										
Glycolaldehyde	100, 34	41, 28	9, 5	92, 100	2, 1	16, 25	-	-	-	-
Hydroxyacetone	59	51	9	100	1	52	-	-	-	-
1-hydroxy-2-butanone	100	73	19	58	1	36	-	-	-	-
4-hydroxy-3-methyl-2-butanone	100	66	10	24	1	45	-	-	-	-
5-hydroxy-2-pentanone	100, 60	54, 42	9, 7	20, 6	1, 1	41, 100	-	-	-	-
Secondary hydroxy carbonyls										
3-hydroxy-2-butanone	64	45	4	100	1	64	-	-	-	-
Tertiary hydroxy carbonyls										
3-hydroxy-3-methyl-2-butanone	16	2	1	32	1	100	-	-	-	-
4-hydroxy-4-methyl-2-pentanone	0	16	3	100	1	43	-	-	-	-

Table 3.2. Characterization of the electron ionization, methane chemical ionization, and PFBOH chemical ionization mass spectra for PFBHA-BSTFA derivatives of aldo- and keto-acids.

	% Relative Intensity									
Compound	**$(M+181)^+$**	**$(M+H)^+$**	**$(M)^+$**	**$(M-15)^+$**	**$(M-17)^+$**	**$(M-89)^+$**	**$(181)^+$**	**$(M-197)^+$**	**$(75)^+$**	**$(73)^+$**
Electron Ionization										
Aldo-Acids										
Glyoxylic Acid	2	2	8	36	1	0	100	1	6	41
Keto-Acids										
Pyruvic Acid	1	2	9	23	19	1	100	0	6	54
2-ketobutyric Acid	0, 0	2, 2	10, 7	13, 28	46, 45	0, 1	100,100	0, 1	16,13	97, 83
2-oxovaleric Acid	1, 2	4, 8	11,11	11, 51	54, 52	1, 12	100,100	19, 20	12,21	98, 92
Methane Chemical Ionization										
Aldo-Acids										
Glyoxylic Acid	19	100	1	43	1	15	17	-	-	-
Keto-Acids										
Pyruvic Acid	1	100	5	25	1	28	4	1	-	-
2-ketobutyric Acid	0, 1	28, 100	0, 1	3, 21	3, 1	9, 100	100, 17	11, 1	-	-
2-oxovaleric Acid	-	100,100	3, 2	3, 25	4, 0	0, 19	52, 4	0, 7	-	-
PFBOH Chemical Ionization										
Aldo-Acids										
Glyoxylic Acid	100	21	7	22	0	8	-	-	-	-
Keto-Acids										
Pyruvic Acid	100	66	37	30	23	15	-	-	-	-
2-ketobutyric Acid	100, 91	35, 31	0, 19	45, 68	21, 7	0, 27	-	-	-	-
2-oxovaleric Acid	100,100	20, 43	8, 4	7, 37	9, 7	0, 5				

from 28 to 100%. However, the relative intensity of this ion for the carbonyls with tertiary –OH groups was ≤ 1%. While there is no absolute trend in these data, the presence of the $(M-89)^+$ ion as the base peak, and a low intensity $(M+H)^+$ ion (≤1%) in the methane CI mass spectra suggests a PFBHA-BSTFA derivative of a carbonyl with a tertiary –OH group.

The PFBOH CI ion trap mass spectra of PFBHA-BSTFA derivatives are characterized by $(M-89)^+$, $(M-15)^+$, $(M+H)^+$, and $(M+181)^+$ ions. For most of the carbonyls with primary and secondary -OH groups and the aldo- and keto-acids, the base peak is either the $(M+181)^+$ ion or the $(M-15)^+$ ion. For the carbonyls with tertiary -OH groups, the base peak is either the $(M-15)^+$ ion or the $(M-89)^+$ ion. For these carbonyls, both the $(M+H)^+$ ion and the $(M+181)^+$ ion are of low (≤ 16%) relative intensity in the PFBOH CI mass spectra, whereas the $(M+H)^+$ ion in the PFBOH CI mass spectra of the carbonyls with primary and secondary –OH groups and the aldo- and keto-acids ranges from 20 - 73% relative intensity and the $(M+181)^+$ ion ranges from 34 - 100% relative intensity. Accordingly, a base peak at $(M-15)^+$ or $(M-89)^+$ and a low relative intensity for the $(M+H)^+$ and $(M+181)^+$ ions in PFBOH CI (≤ 16%) indicates a PFBHA-BSTFA derivative of a carbonyl with a tertiary -OH group.

These data suggest that interpretation of the EI mass spectra can assist in distinguishing PFBHA-BSTFA derivatives of aldo- and keto-acids from derivatives of hydroxy carbonyls, and that interpretation of the methane CI and PFBOH CI mass spectra can assist in distinguishing the position of the –OH group on hydroxy carbonyls. In the EI mass spectra, an $(M)^{+\cdot}$ ion with a relative intensity ≥ 7% indicates the PFBHA-BSTFA derivative of an aldo- or keto-acid, while an $(M-17)^+$ ion with a relative intensity ≥ 19% indicates a keto-acid. In the methane CI mass spectra, a base peak at $(M-89)^+$ and a low intensity (≤1%) $(M+H)^+$ ion strongly suggests a carbonyl with a tertiary –OH group. The identification of a carbonyl with a tertiary –OH group is strengthened by a base peak at $(M-15)^+$ or $(M-89)^+$ and low intensity (≤ 16%) $(M+H)^+$ and $(M+181)^+$ ions in the PFBOH CI ion trap mass spectra.

The EI mass spectrum for the PFBHA-BSTFA derivative from the MBO + ·OH reaction (Figure 3.3, compound **IIIA**) provides evidence that this compound is a C_4-hydroxycarbonyl,

rather than a C_3- aldo- or keto-acid because $M^{+\cdot}$ and $(M-17)^+$ ions are absent. The methane CI and PFBOH CI mass spectra (Figure 3.4) provide substantial evidence that the -OH group is tertiary, because of the absence of an $(M+H)^+$ ion in both spectra and the low intensity of the $(M+181)^+$ ion in the PFBOH CI mass spectrum. The only possible C_4-hydroxycarbonyl containing a tertiary -OH group is 2-hydroxy-2-methylpropanal.

C. Gas chromatographic separation of the PFBHA-BSTFA derivatives of glycolaldehyde, 2-hydroxy-2-methylpropanal, and 3-hydroxy-2-butanone.

Extracts of air sampled at the Blodgett Forest were first analyzed by using a low-polarity GC column [DB-XLB; liquid phase equivalent to (12%-phenylmethyl) polysiloxane]. The electron ionization mass spectrum of a peak from these extracts with the same relative retention time as the peak **III** in Figure 3.2 is presented in Figure 3.6. As determined previously, this peak can be composed of two co-eluting compounds, glycolaldehyde and 2-hydroxy-2-methylpropanal, both of which are expected to be present in Blodgett Forest air. The m/z 312 ion is likely the $(M-15)^+$ ion for PFBHA-BSTFA derivatized glycolaldehyde, and the m/z 340 ion is likely the $(M-15)^+$ ion for PFBHA-BSTFA derivatized 2-hydroxy-2-methylpropanal. However, it is possible that this peak could also contain 3-hydroxy-2-butanone, which we identified at a similar relative retention time in work described in Chapter 1. In this complex mixture, quantification of glycolaldehyde is possible by using the $(M+H)^+$ ion at m/z 328 in the methane CI mass spectra. However, quantifying 2-hydroxy-2-methylpropanal in the presence of 3-hydroxy-2-butanone poses a problem because the two compounds are structural isomers, whose mass spectra would exhibit ions at the same mass to charge ratios. Additionally, in order to confirm the identification of 2-hydroxy-2-methylpropanal with an authentic standard, chromatographic resolution is desired. We thus pursued separation of these compounds on a GC column with a more polar phase, [(50%-phenylmethyl) polysiloxane; DB-17ms].

We demonstrate resolution of three co-eluting compounds on a DB-17ms GC column in Figure 3.6B. The mass spectrum and relative retention time of compound **IIIA** corresponds to the mass spectrum and relative retention time of the PFBHA-BSTFA derivative that was obtained from the analysis of the reaction products of hydroxyl radical reaction with MBO (see Figure 3.3B

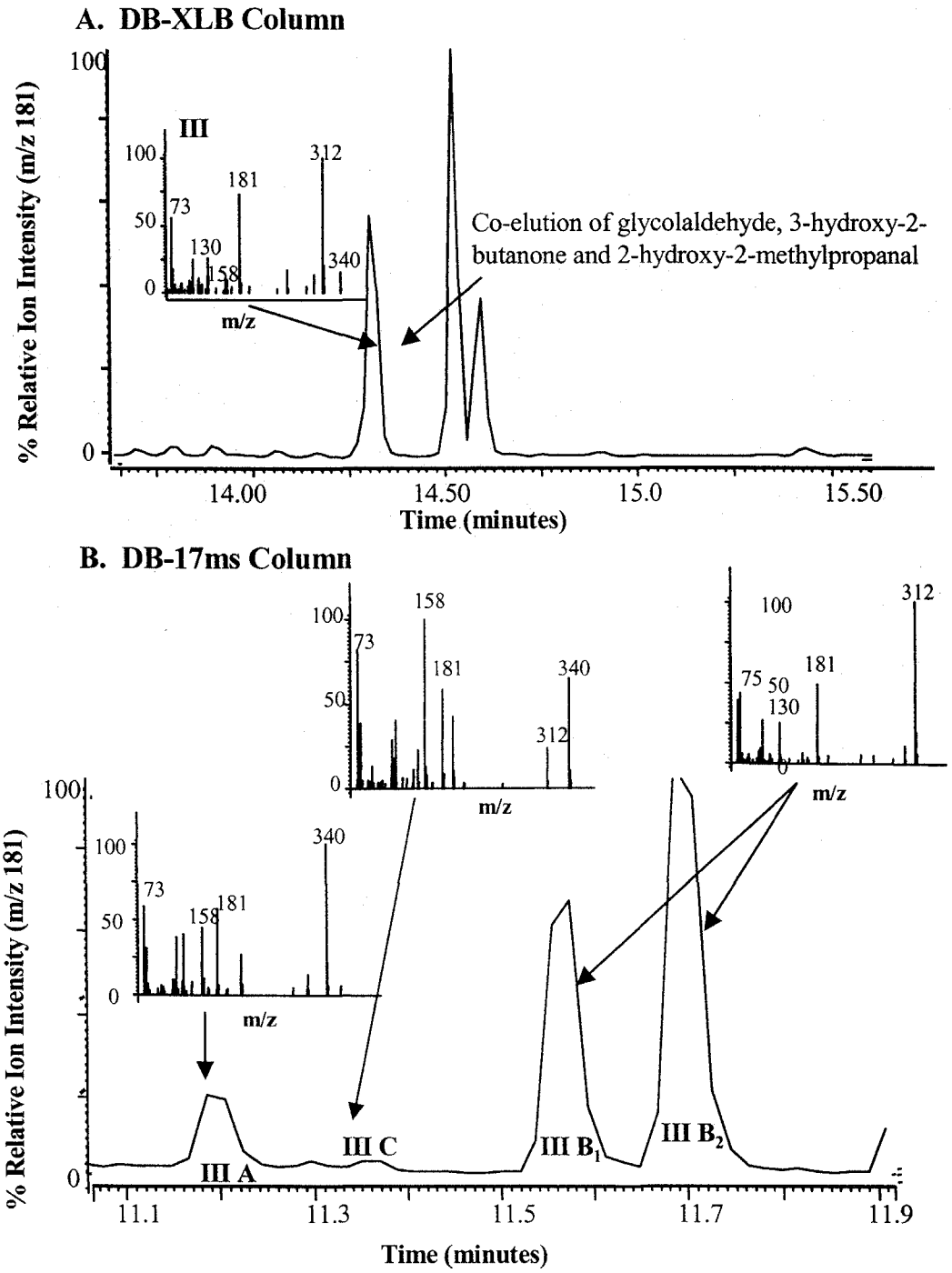


Figure 3.6. Chromatographic separation of PFBHA-BSTFA dervivatives in an extract of Blodgett Forest air on a DB-XLB GC column (A), and a DB-17ms GC column (B).

compound **IIIA**). The compounds in peaks **IIIB$_1$** and **IIIB$_2$** correspond to the mass spectra of glycolaldehyde (see Figure 3.3B, compound **IIIB**). The compound in peak **IIIC** was tentatively identified as 3-hydroxy-2-butanone. The identification of the PFBHA-BSTFA derivatives of glycolaldehyde and 3-hydroxy-2-butanone were confirmed by comparing the relative retention times and mass spectra in the sample extract to those of the PFBHA-BSTFA derivatives of authentic standards (peaks **IIIB$_1$** and **IIIB$_2$** are the *E*- and *Z*- isomers of the PFBHA-BSTFA derivative of glycolaldehyde; the *E*- and *Z*-isomers of 3-hydroxybutanone are not resolved).

In the methane CI ion chromatograms comprised of m/z 340 and 266, the $(M-15)^+$ and $(M-89)^+$ ions of the PFBHA-BSTFA derivative of 2-hydroxy-2-methypropanal, we observed two peaks, corresponding to 3-hydroxy-2-butanone (**IIIC**) and the compound tentatively identified as 2-hydroxy-2-methylpropanal (**IIIA**) in some sample extracts (see Figure 3.7A). However, in other extracts, we observed three peaks (**IIIA$_1$**, **IIIA$_2$**, and **IIIC**), as presented in Figure 3.7B. Moreover, the relationship between peaks **IIIA$_1$** and **IIIA$_2$** was not constant. In some cases, peak **IIIA$_1$** was larger than peak **IIIA$_2$**, and in other cases, the peaks were approximately the same size, or peak **IIIA$_2$** was absent. To further investigate this phenomenon, we re-analyzed extracts of air collected from the reaction of MBO with ·OH in the chamber experiment, using the DB-17ms column. We observed the same phenomenon in these extracts. Thus, the compounds comprising peaks **IIIA$_1$** and **IIIA$_2$** must be products arising from the reaction of MBO with ·OH.

The base peak in the methane chemical ionization mass spectra of peaks **IIIA$_1$** and **IIIA$_2$** is the m/z 266 ion. Initially, we thought that the two peaks were the *E*- and *Z*-isomers of PFBHA-BSTFA derivatives of 2-hydroxy-2-methylpropanal. However, the absence of an $(M-15)^+$ ion at m/z 340 in peak **IIIA$_1$** raised doubt about this identification. The ion at m/z 266 in peak **IIIA$_1$** could be the $(M-89)^+$ ion of the PFBHA-BSTFA derivative of 2-hydroxy-2-methylpropanal, or it could be the $(M+H)^+$ ion or a fragment ion from a different compound. We examined the EI and PFBOH CI mass spectra to obtain further information.

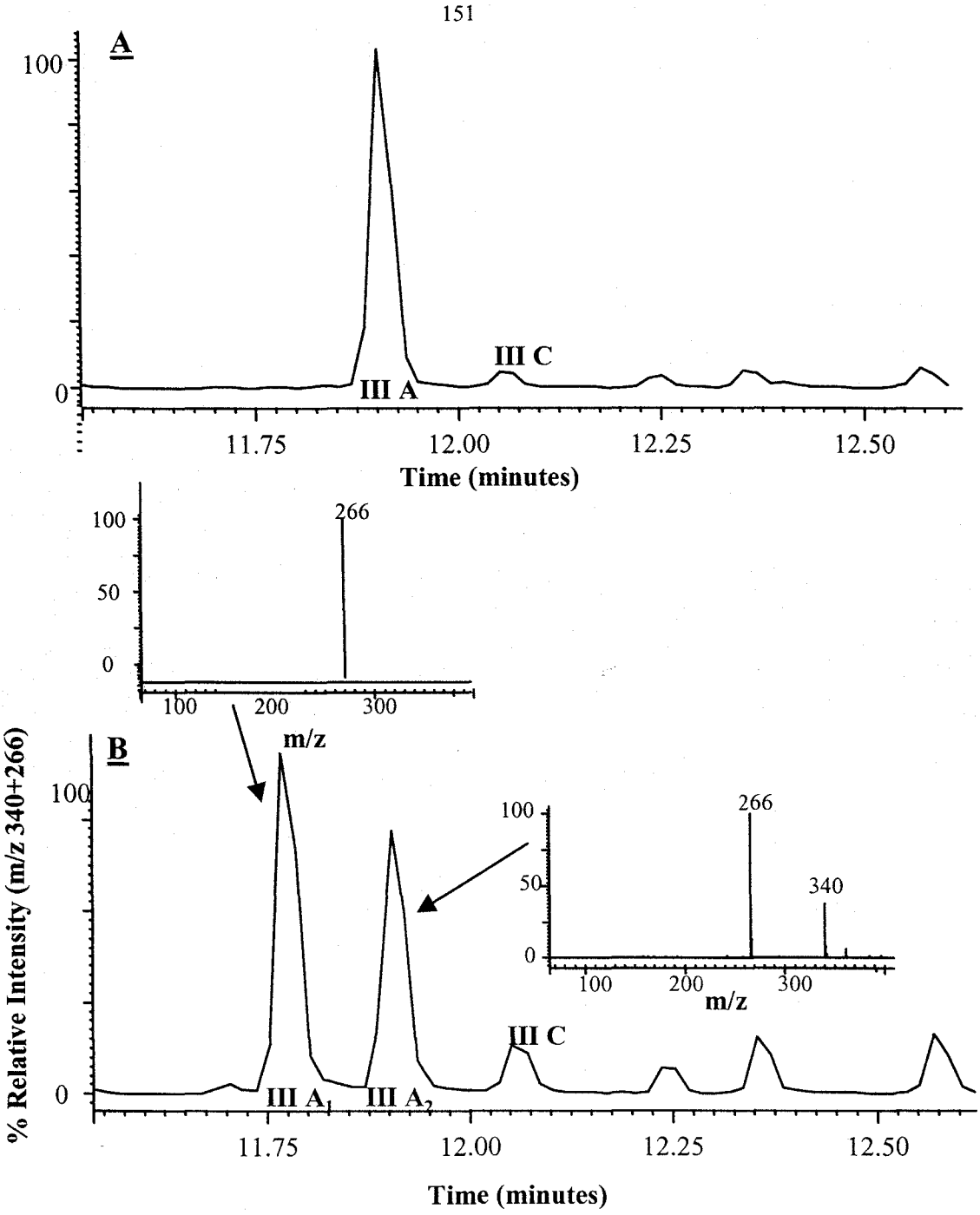


Figure 3.7. Ion chromatogram (m/z 266 + m/z 340) in the methane chemical ionization mass spectra of PFBHA-BSTFA derivatives in an extract of Blodgett Forest air.

The EI and PFBOH CI mass spectra from peak **IIIA$_1$** are presented in Figure 3.8. The EI mass spectrum (Figure 3.8A) is characterized by the expected pentafluorobenzyl cation at m/z 181, which confirms that this compound is a PFBHA derivative of a carbonyl. However, the absence of ions at m/z 73 and 75 indicates that the compound is not the PFBHA-BSTFA derivative of a hydroxycarbonyl. The absence of an ion at m/z 340 further indicates that it is not the PFBHA-BSTFA derivative of 2-hydroxy-2-methylpropanal. The PFBOH CI ion trap mass spectrum is characterized by ions at m/z 266 and 464 (Figure 3.8B). The absence of $(M-15)^+$ and $(M+181)^+$ ions at m/z 340 and 536 provides further evidence that the mass spectrum is not of the PFBHA-BSTFA derivative of 2-hydroxy-2-methylpropanal. If the m/z 464 ion is the $(M+181)^+$ ion of a PFBHA-derivative, then the molecular weight of the derivative would be 283 Da, which is the molecular weight of the PFBHA derivative of 2-hydroxy-2-methylpropanal. Together, the data indicate that this compound is the PFBHA derivative of 2-hydroxy-2-methylpropanal. Thus, the ion at m/z 266 in both the methane and PFBOH CI mass spectra is likely an $(M-OH)^+$ ion. The m/z 266 ion is likely common to both the PFBHA derivative (**IIIA$_1$**) and the PFBHA-BSTFA derivative (**IIIA$_2$**) of 2-hydroxy-2-methylpropanal because it is a stable tertiary carbocation, formed by loss of OH from the PFBHA derivative and by loss of $Si(CH_3)_3O$ from the PFBHA-BSTFA derivative.

These data indicate incomplete BSTFA derivatization of 2-hydroxy-2-methylpropanal in certain sample extracts, and thus the observation of the PFBHA and the PFBHA-BSTFA derivatives. The fact that both peaks are observed, and that the peak shape for the PFBHA-derivative is good, invokes the question "why derivatize with BSTFA?" In previous work, we demonstrate that derivatization with BSTFA improves the chromatography and sensitivity for a many hydroxy carbonyls and aldo- and keto-acids on a DB-5ms column (Spaulding et al., 1999). However, because the chromatography for PFBHA derivatives of hydroxy carbonyls and aldo- and keto-acids could be different on a DB-17ms column, we compared the signal to noise ratio for PFBHA and PFBHA-BSTFA derivatives of hydroxy carbonyls and a keto-acid on a DB-17ms column. These data are presented in Table 3.3 for the $(M+H)^+$ and $(M-OH)^+$ ions from the PFBHA derivatives and the $(M+H)^+$, $(M-15)^+$, and $(M-89)^+$ ions from the PFBHA-BSTFA derivatives. When the *E*- and *Z*- isomers were resolved, two values are reported. The data demonstrate that BSTFA derivatization improves the signal to noise ratio for glycolaldehyde,

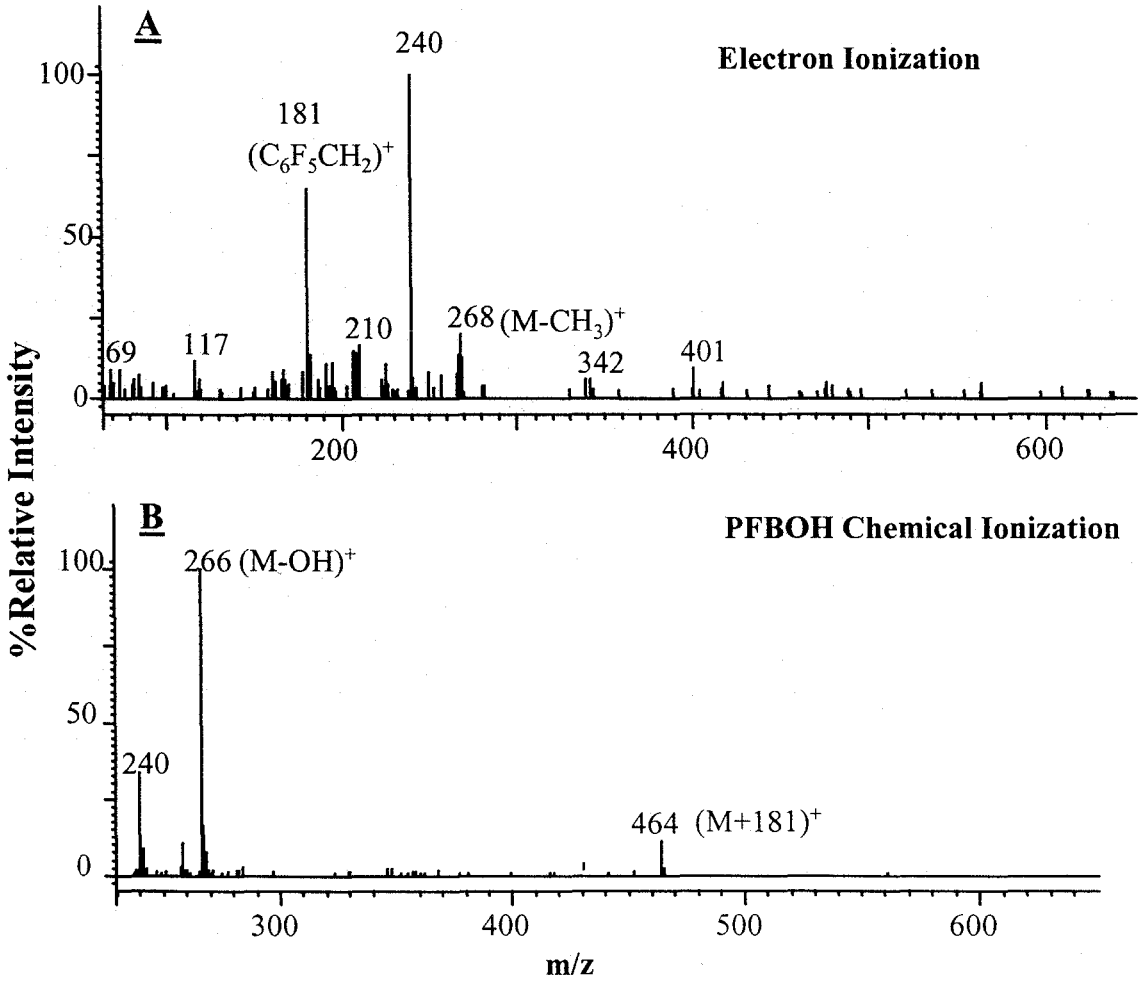


Figure 3.8. Electron ionization (A) and PFBOH chemical ionization (B) mass spectra of peak **IIIA$_1$** in Figure 3.7.

hydroxyacetone, 1-hydroxy-2-butanone, 4-hydroxy-3-methyl-2-butanone, and pyruvic acid, but the signal to noise ratio is the same with or without BSTFA derivatization for 3-hydroxy-3-methyl-2-butanone. The tertiary -OH group on 3-hydroxy-3-methyl-2-butanone is probably protected from interaction with the column, and thus the chromatography and sensitivity are good without BSTFA derivatization. In our work, BSTFA derivatization is required because glycolaldehyde, hydroxyacetone, and pyruvic acid are also photooxidation products of biogenic and anthropogenic hydrocarbons.

Table 3.3. Comparison of signal:noise ratio for PFBHA- and PFBHA-BSTFA derivatives of hydroxy carbonyls and keto-acids.

Analyte	Concentration (pg/μL)	Signal:Noise Ratio				
		PFBHA-derivative		PFBHA-BSTFA-derivative		
		$(M+H)^+$	$(M-OH)^+$	$(M+H)^+$	$(M-CH_3)^+$	$(M-89)^+$
Glycolaldehyde	24	2, 1	3, 2	28, 29	29, 40	19, 13
Hydroxyacetone	24	3, 3	6, 2	23	13	13
1-hydroxy-2-butanone	24	1, 1	2, 1	1, 8	1, 10	1, 8
4-hydroxy-3-methyl-2-butanone	26	2	1	8	7	7
3-hydroxy-3-methyl-2-butanone	23	1	21	1	1	23
Pyruvic Acid	50	1	1	71	12	18

D. Confirmation of the identity of 2-hydroxy-2-methylpropanal.

In order to confirm the identification of the C_4-hydroxycarbonyl that is produced from the reaction of MBO with ·OH, we synthesized 2-hydroxy-2-methylpropanal. Chamber experiments and analysis of ambient air samples were concluded prior to the availability of an authentic standard 2-hydroxy-2-methylpropanal. We were unable to retroactively analyze the sample

extracts due to concerns about possible degradation of the analyte in the extract. In Figure 3.9, we present the EI and methane CI ion trap mass spectra of the PFBHA derivative of 2-hydroxy-2-methylpropanal. The relative retention time of the gas chromatographic peak is the same as that for peak **IIIA$_1$** in Figure 3.7, and the ions and the relative intensity of the ions in the mass spectra are nearly identical to the spectra for peak **IIIA$_1$**, as presented in Figures 3.7B (methane CI) and 8A (EI). The EI mass spectra area characterized by the presence of ions at m/z 268, 240 and 181. The ions at m/z 268, and 240 are the $(M\text{-}CH_3)^+$ and $(M\text{-}CH_3\text{-}(CH_2)_2)^+$ ion of the

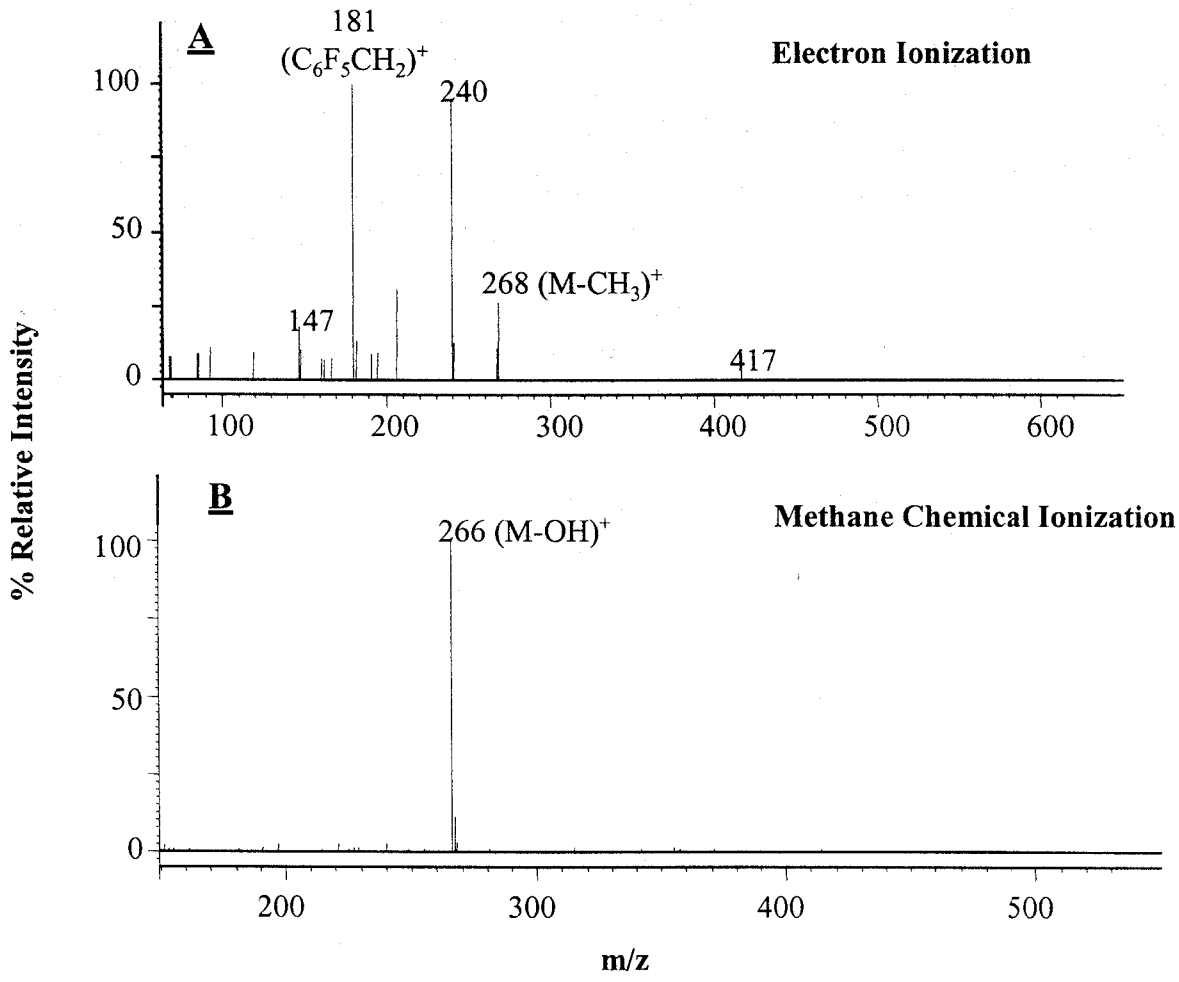


Figure 3.9. Electron ionization (A) and methane chemical ionization (B) mass spectra of the PFBHA derivative of 2-hydroxy-2-methylpropanal.

PFBHA derivative of 2-hydroxy-2-methyl propanal, respectively. The only ion, and hence the base peak in the methane CI mass spectra is the ion at m/z 266 due to the loss of a hydroxyl group from the PFBHA derivative of 2-hydroxy-2-methylpropanal. In Figure 3.10, we present the EI and methane CI ion trap mass spectra for the PFBHA-BSTFA derivative of 2-hydroxy-2-methylpropanal. The relative retention time of the gas chromatographic peak is the same as that for peak **IIIA$_2$** in Figure 3.7, and again the ions and the relative intensity of the ions in the mass spectra are nearly the same as the spectra for peak **IIIA**, as shown in Figures 3.4A (methane CI) and 6B (EI). In addition to the presence of characteristic ions at m/z 73 and m/z 181 ions, ions at m/z 158 $(M\text{-}C_6F_5CH_2O)^+$ and 340 $(M\text{-}CH_3)^+$ are observed. The methane CI mass spectra exhibit ions at m/z 340 and m/z 266. In the mass spectra of the authentic standard, we observe ions at m/z 158 and 361 which are not present in the methane CI mass spectra of the sample extract. The ion at m/z 158 is presumably due to the loss of $C_6F_5CH_2O$, and the ion at m/z 361 is due to a co-eluting interferant. Thus, the presence of ions at similar ion intensities in PFBHA and PFBHA-BSTFA derivative in the EI and methane CI mass spectra of the authentic standard, as compared to derivatives in the sample extract confirm the presence of 2-hydroxy-2-methylpropanal.

E. Semi-quantification of 2-hydroxy-2-methylpropanal in air samples collected at the Blodgett Forest.

Since an authentic standard of 2-hydroxy-2-methylpropanal was not available at the time that Blodgett Forest samples were quantified, we evaluated the use of 3-hydroxy-3-methyl-2-butanone, and 4-hydroxy-4-methyl-2-pentanone, two ketones with tertiary –OH groups as surrogates. These compounds were chosen because we were unable to locate a commercial source of an aldehyde with a tertiary -OH group, which would be more structurally similar to 2-hydroxy-2-methylpropanal than a ketone. We evaluated whether a ketone is a reasonable surrogate for a structurally similar aldehyde by comparing the relative response factors between methacrolein and methyl vinyl ketone. Since the total concentration of the analyte derivative will be the concentration of the PFBHA derivative and the concentration of the PFBHA/BSTFA due to the inconsistent BSTFA derivation, and the response factor of a ketone with a tertiary -OH

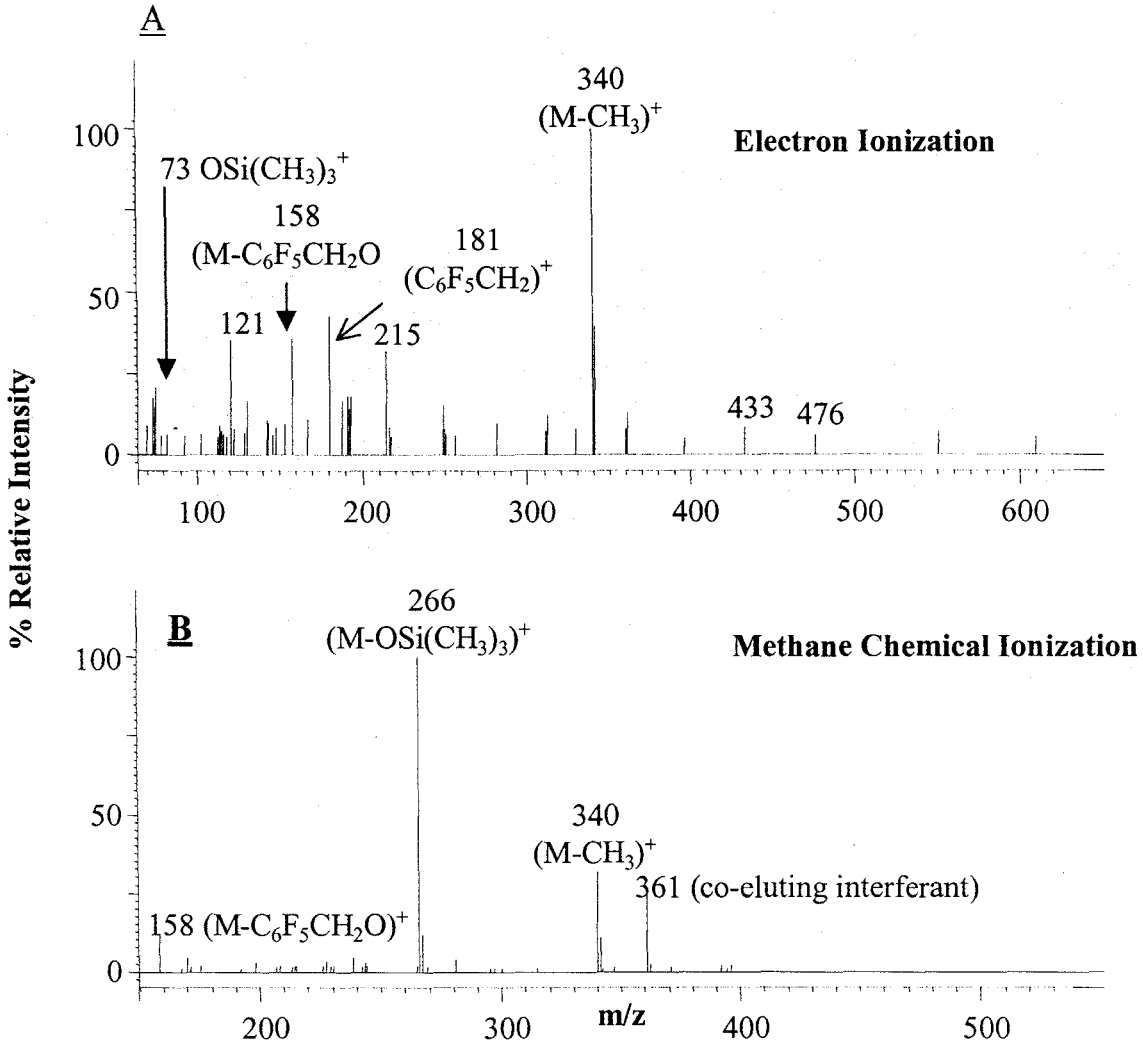


Figure 3.10. Electron ionization (A) and methane chemical ionization (B) mass spectra of the PFBHA derivative of 2-hydroxy-2-methylpropanal.

group to the internal standard may be compound dependent, we also compared the difference between the relative response factors of the two ketones with tertiary –OH by using a predominant ion in the mass spectra of the PFBHA derivative, or the PFBHA/BSTFA derivative as a single quantifying ion, or by using a sum of the ions. We obtained a 6% difference and a 9% relative standard deviation between relative response factors obtained by analyzing standards of methacrolein and methyl vinyl ketone ranging from 241 to 1024 pg/μL. The small difference between the relative response factors of the two compounds suggests similar responses between a structurally similar aldehyde and a ketone. We compared the relative response factor obtained by using the $(M-17)^+$ ion of the PFBHA derivative, and the $(M-15)^+$ or $(M-89)^+$ ions of the PFBHA/BSTFA derivatives of 3-hydroxy-3-methyl-2-butanone and 4-hydroxy-4-ethyl-pentanone, each separately as the quantifying ions, and as the sum of these ions to quantify 2-hydroxy-2-methyl-propanal. For concentrations ranging from 115 to 864 pg/μL, the % difference between the relative response factor for the $(M-17)^+$, $(M-15)^+$ and the $(M-89)^+$ ions differed by 49%, 125%, and 120%, respectively. This difference between the compounds was reduced to 16% by using the sum of the three ions. We thus chose to quantify by using the sum of the ions to reduce differences that may exist among structurally similar molecules, and to account for inconsistent BSTFA derivatization. We constructed standard curves using the sum of the areas of the $(M-15)^+$ and $(M-89)^+$ ions from PFBHA-BSTFA derivative and the $(M-OH)^+$ ion from the PFBHA derivative of 3-hydroxy-3-methyl-2-butanone. The response factor for the sum of the equivalent ions from the PFBHA and PFBHA-BSTFA derivatives of 2-hydroxy-2-methylpropanal was substituted into the regression equation to "semi-quantify" 2-hydroxy-2-methylpropanal.

We provide evidence that the method of semi-quantification is reasonable by comparing the values obtained by our method to values obtained by using FT-IR for the concentration of 2-hydroxy-2-methylpropanal produced from the reaction of ·OH with MBO in an environmental chamber. The concentration obtained by using FT-IR was estimated from calibration data obtained in a previous experiment, and a yield of 29±3%. By using the PFBHA_BSTFA method we measured mean (n=2) concentrations of 266, 396, and 483 ppbv for 3 samples, compared to 380 ppbv, 570 ppbv, and 820 ppbv by using the FT-IR method. Thus, assuming a yield of 29% from MBO, the PFBHA/BSTFA method estimates a 2-hydroxy-2-methylpropanal concentration

that is 30-41% lower than the concentration estimated by FT-IR. However, Alvarodo et al., 1999, using silylation and GC-FID, estimated that the 2-hydroxy-2-methylpropanal yield was only 19 ± 9. If a yield of 19% is assumed the values reported by the FT-IR method would then be lower (249, 373 and 537 ppbv in the three sample extracts). In this case, the % relative difference would range from 6 to 10% between the two methods. The values reported by the FT-IR method would then be higher (249, 373 and 537 ppbv in the 3 sample extracts), if a 19% yield is assumed. In this case, the % relative differences would be 42%, 43% and 70% for the three samples analyzed. The concentration of 2-hydroxy-2-methylpropanal semi-quantified by the PFBHA-BSTFA compared to the FT-IR method varies from 6% to 41%, depending on the assumed yield of hydroxy-2-methyopropanal.

We present the mixing ratios of MBO (Gunnar Schade, personal communication) and 2-hydroxy-2-methylpropanal (2-HMPR) as a function of time in Figure 3.11. Overall, the average ratio of [2-hydroxy-2-methylpropanal] / [MBO] was 0.33 ± 0.26, providing further support that the semi-quantification of 2-hydroxy-2-methylpropanal is reasonable, since the expected yield of 2-hydroxy-2-methylpropanal from the reaction of MBO with ·OH is 0.19 - 0.35 (Ferronato et al., 1998m Fantechi et al., 1998, Alvarado et al., 1999).

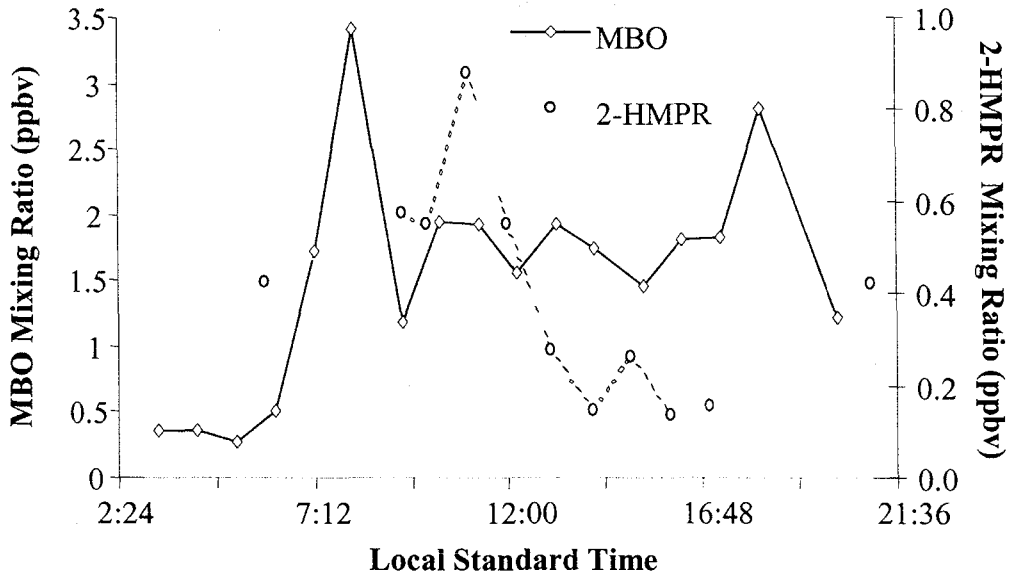


Figure 3.11. Mixing ratios of 2-methyl-3-buten-2-ol (MBO) and its photooxidation product, 2-hydroxy-2-methylpropanal (2-HMPR), in Blodgett Forest air.

The mixing ratio of 2-hydroxy-2-methylpropanal increase or decrease approximately 2 to 2.5 hours after increases and decreases in MBO, which is consistent with a local source of MBO and *in situ* photochemical production of 2-hydroxy-2-methylpropanal. Additionally, the ratio of [2-hydroxy-2-methylpropanal] / [MBO] was higher (0.5 – 0.9) during early morning and nighttime compared to mid-day and early evening (≤ 0.2). This is expected, because during daytime MBO is continuously emitted by trees [10], 2-hydroxy-2-methylpropanal is produced from the reaction of MBO with ·OH, and the build-up of both is limited by reactions with ·OH (Ferronato et al., 1998, Fantechi et al., 1998, Alvarado et al., 1999). However, after sunset, emissions of MBO cease, MBO is depleted by reactions with O_3 and NO_3, and small amounts of 2-hydroxy-2-methylpropanal may be produced by reaction of MBO with O_3 (Fantechi et al., 1998, Alvarado et al., 1999, Grosjean and Grosjean, 1994, Grosjean and Grosjean, 1995). Additionally, changing wind direction at night could bring in air with higher 2-hydroxy-2-methylpropanal mixing ratios from surrounding forests (Lamanna and Goldstein, 1999). Therefore, at night MBO will be depleted more rapidly than 2-hydroxy-2-methylpropanal, and small amounts of 2-hydroxy-2-methylpropanal may be formed or carried in by wind, creating higher [2-hydroxy-2-methylpropanal] / [MBO] ratios. When the sun rises, MBO and ·OH mixing ratios will increase, 2-hydroxy-2-methylpropanal will still be formed by MBO reactions, but will also be depleted by reaction with ·OH and possibly by photolysis, and by afternoon, the [2-hydroxy-2-methylpropanal] / [MBO] ratio will be significantly smaller.

IV. Conclusions

Interpretation of EI, methane CI, and PFBOH CI ion trap mass spectra of PFBHA and PFBHA-BSTFA derivatives was critical for: 1) identifying the structure of the C_4-hydroxycarbonyl produced by the reaction of ·OH with MBO; 2) solving co-elution problems on a DB-XLB GC column; and 3) developing a method to semi-quantify 2-hydroxy-2-methylpropanal in air. Ion-molecule reactions which occur only in an ion trap mass spectrometer were facilitated by bleeding PFBOH directly in to the ion trap. The resulting $(M+181)^+$ ions aided in determining the structure of the C_4-hydroxycarbonyl and were essential for differentiating the PFBHA derivative of 2-hydroxy-2-methylpropanal from the PFBHA-BSTFA derivative in the absence of an authentic standard. Semi-quantification of 2-hydroxy-2-methylpropanal by FT-IR and by the

method developed here compared favorably. We thus used the method to obtain the first diurnal measurements of 2-hydroxy-2-methylpropanal in ambient air, and to gain insight into the relationship between 2-hydroxy-2-methylpropanal and its precursor, MBO, in the ambient atmospheric environment.

V. References Cited

1. Alvarado, A., Tuazon, E.C., Aschmann, S.M., Arey, J., Atkinson, R., *Atmos. Environ.*, 1999, *33*, 2893-2905.
2. Andreae, M.O., Crutzen, P.J., *Science*, 1997, *276*, 1052-1058
3. Atkinson, R., *J. Phys. Chem. Ref. Data*, 1997, *26*, 215-290.
4. Atkinson, R., Carter, W.P.L., Winer, A.M., Pitts, J.N., Jr., *APCA Notebook*, 1981, *31*, 1090-1092.
5. Baeckstrom, P., Li, L., *Tetrahdron*, 1991, 47, 6533.
6. Cancilla, D.A., Chou, C.-C., Barthel, R., Que Hee, S.S., *J. AOAC Int.*, 1992, *75*, 842-854.
7. Chameides, W.L., Lindsay, R.W., Richardson, J., Kiang, C.S., *Science*, 1988, *241*, 1473-1475.
8. Chien, C.-J., Charles, M.J., Sexton, K.G., Jeffries, H.E., *Environ. Sci. Technol.*, 1998, *32*, 299-309.
9. Cofer, W.R.I., Collins, V.G., Talbot, R.W., *Environ. Sci. Technol.*, 1985, *19*, 557-560.
10. Fantechi, G., Jensen, N.R., Hjorth, J., Peeters, J., *Int. J. Chem. Kinet.*, 1998, *30*, 589-594.
11. Feedman, H. H., Dubois, R. A., Tetrahedron Lett. *1976*, 17, 3535.
12. Ferronato, C., Orlando, J.J., Tyndall, G.S., *J. Geophys. Res.*, 1998, *103*, 25579-25586.
13. Fessner, W. D., Gobe, C., Jaeschke, G., Eyrisch, O. Eur, *J. Org. Chem.*, 2000, 125.
14. Frazey, P., Rao, X., Spaulding, R., Beld, B., Charles, M.J., *Int. J. Mass Spectrom.*, 1999, *191*, 343-357.
15. Goldan, P.D., Kuster, W.C., Fehsenfeld, F.C., *Geophys. Res. Let.*, 1993, *20*, 1039-1042.
16. Grosjean, E., Grosjean, D., *J. Geophys. Res.*, 1995, *100*, 22815-22820.
17. Grosjean, E., Grosjean, D., *Int. J. Chem. Kinet.*, 1994, *26*, 1185-1191.
18. Harley, P., Fridd-Stroud, V., Greenberg, J., Guenther, A., Vasconcellos, P., *J. Geophys. Res.*, 1998, *103*, 25479-25486.
19. Jenkin, M.E., Clemitshaw, K.C., *Atmos. Environ.*, 2000, *34*, 2499-2527.
20. Klemm, O., Talbot, R.W., *J. Atmos. Chem.*, 1991, *13*, 325-342.
21. Lamanna, M.S., Goldstein, A.H., *J. Geophys. Res.*, 1999, *104*, 21247-21262.
22. LeLacheur, R.M., Sonnenberg, L.B., Singer, P.C., Christman, R.F., Charles, M.J., *Environ. Sci. Technol.*, 1993, *27*, 2745-2753.

23. Pierce, T., Geron, C., Bender, L., Dennis, R., Tonnesen, G., Guenther, A., *J. Geophys. Res.*, 1998, *103*, 25611-25629.

24. Rao, X., Kobayashi, R., White, R., Spaulding, R., Frazey, P., Charles, M.J., *J. AOAC Int.*, 2001, *84*, 699-705.

25. Saxena, P., Hildemann, L.M., *J. Atmos. Chem.*, 1996, *24*, 57-109.

26. Schade, G.W., Goldstein, A.H., Gray, D.W., Lerdau, M.T., *Atmos. Environ.*, 2000, *34*, 3535-3544.

27. Spaulding, R.S., Talbot, R.W., Charles, M.J., *Environ. Sci. Technol.*, 2002, *in press.*

28. Spaulding, R.S., Frazey, P.A., Rao, X., Charles, M.J., *Anal. Chem.*, 1999, *71*, 3420-3427.

29. Trainer, M., Williams, E.J., Parrish, D.D., Buhr, M.P., Allwine, E.J., Westberg, H.H., Fehsenfeld, F.C., Liu, S.C., *Letters to Nature*, 1987, *329*, 705-707.

30. Willard, H.H., Merritt, J., L. L., Dean, J.A., Settle, J., F. A., Instrumental Methods of Analysis, Wadsworth, Inc., Belmont, CA, 1988.

31. Yu, J., Flagan, R.C., Seinfeld, J.H., *Environ. Sci. Tech.*, 1998, *32*, 2357-2370.

32. Yu, J., Jeffries, H.E., Sexton, K.G., *Atmos. Environ.*, 1997, *31*, 2261-2280.

33. Yu, J., Jeffries, H.E., LeLacheur, R.M., *Environ. Sci. Technol.*, 1995, *29*, 1923-1932.

Chapter 4

Measurement of Carbonyls and Multifunctional Carbonyls in $PM_{2.5}$ Particles Emitted from Motor Vehicles.

Table of Contents

List of Tables

Abstract

A method was developed and tested to identify and quantify carbonyls and multifunctional carbonyls in fine particulate matter ($PM_{2.5}$; <2.5μm aerodynamic diameter). The method relies on ultrasonic extraction of particulate matter on filters a –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 using gas chromatography/ion trap mass spectrometry. Ultrasonic extraction of model compounds from enriched particles was affected by solvent polarity (water > methylene chloride > toluene/isopropanol (v/v, 2:1)). 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°C 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 quantification of carbonyls and multi-functional carbonyls in sample extracts of fine particulate matter ($PM_{2.5}$) collected in the Caldecott tunnel. 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 to an authentic standard. Quantification 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-hydroxybenzaldheyde in $PM_{2.5}$ particles sampled in a roadway tunnel. It is also the first report of a C_{10} carbonyl with the molecular formula of $C_{10}H_{16}O_2$, a hydroxy carbonyl with the molecular formula of $C_{17}H_{21}NO_2$, and a hydroxy or di-hydroxy carbonyl with the molecular formula of $C_{16}H_{14}O_2$ or $C_9H_{10}O_3$. The high-molecular weight hydroxy carbonyls, which were found only in the heavy- duty (diesel) bore, may be tracers of diesel emissions in air.

I. Introduction

Motor vehicle emissions are primary sources of particulate matter, volatile organic compounds (VOC's) and NO_x. There is a growing interest and need for molecular speciation of motor vehicle emissions (Siegl et al., 1999, Miguel et al., 1998, Weingartner et al., 1988, Zielinska et al., 1966, Pierson et al., 1996) due to the impact of motor vehicle emissions 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 U.S., approximately 50% of the total non-methane hydrocarbon (NMHC) emissions from heavy-duty diesel engines in the Fort McHenry Tunnel in Baltimore, Maryland, and the Tuscarora Mountain Tunnel, Pennsylvania were comprised of high molecular weight C_{10}-C_{20} hydrocarbons (Zielinska et al., 1996, Pierson et al, 1996). These high molecular weight compounds accounted for only 10-25% of the total NMHC diesel emission rates (Zielinska et al., 1966). Aromatic compounds, including naphthalene and substituted naphthalenes were identified as the reactive constituents with respect to ozone-forming potential. Carbonyls were reported to comprise a minor contribution to the ozone forming potential, although formaldehyde was the only carbonyl quantified (Zielinska, et al., 1996, Pierson et al., 1996, Sagiebel et al., 1996). In contrast, other studies conducted in the Caldecott Tunnel, CA., the Van Nuys Tunnel in Los Angeles and the Gubrist Tunnel, Switzerland, demonstrate that carbonyls are important reactive components of diesel and gasoline vehicle exhaust (Fraser et al., 1998, Staehelin et al., 1998, Schauer et al., 1999). Most notably, increased use of oxygenated and reformulated gasoline in the San Francisco Bay Area 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. (Kirchstetter et al., 1996). 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 (Fraser et al., 1998).

Limitations of previous studies are the lack of data on high-molecular weight ($>C_{10}$) species, and particle phase carbonyls. A recent study addressed this limitation by measuring C_1 through C_{30} organic compounds emitted from medium duty diesel trucks (Schauer et al., 1999). The results indicated the importance of C_1-C_{13} carbonyls as gas phase constituents and the significance of C_{14}-C_{20} alkanoic and C_8-C_9 alkanedioic acids in the particle phase. Although hypothesized to exist in the water-soluble fraction of particles, the significance of particle- phase carbonyls and multi-functional carbonyls (e.g., hydroxy carbonyls and oxo-acids) is unknown (Aumnot et al., 2000, Pun et al., 2000, Saxena et al., 1996).

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 utilized to measure carbonyls that relies on 2,4-dinitrophenylhydrazine derivatization (DNPH) of the carbonyl moiety. In contrast to the DNPH method, the employment of PFBHA and PFBHA/BSTFA provides excellent chromatographic separation and detection of multifunctional carbonyls, including hydroxy carbonyls (Spaulding et al., 999, Yu et al., 1995, Le Lacheur et al., 1993). 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 (Spaulding et al., 1999, Frazey et al., 1999).

II. Experimental

A. Materials

Methyl *tert*-butyl ether (MTBE; HPLC grade) and water (HPLC grade) were purchased from Fisher Scientific, Inc., Fairlawn, N.J. 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.

B. Sample Collection

Fine particulate matter ($PM_{2.5}$) was sampled inside the Caldecott Tunnel, a traffic tunnel on U.S. Highway 24 between Oakland and Orinda, California. Samples were collected with a single IMPROVE (Interagency Monitoring of Protected Visual Environments) Module Aerosol during a four 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 two 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 500^0C for 4 hours 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).

C. 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 Davis, CA. air. The particulates on the quartz fiber filters were enriched with tolualdehyde, methacrolein, methyl vinyl ketone, 2,3-butanedione, hydroxy acetone and pyruvic acid (1μg of each compound). The concentration of these compounds in the particulates did not affect the recovery because the filters were enriched with μg quantities, at least 100x 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 of water, methylene chloride or toluene/isopropanol. The compounds on the filter were then ultrasonically extracted for 2 minutes (550 Sonic Dismembrator, Fisher Scientific). The carbonyls and multifunctional carbonyls were derivatized with PFBHA, and PFBHA/BSTFA, respectively, as described in previous research (Spaulding et al., 1999, Frazey et al., 1999). 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

temperature on the per cent 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). Background levels of carbonyls did not affect the overall recoveries since the filters were enriched with microgram quantities, at least 100x background levels observed in the laboratory.

D. 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 x 0.32 mm i.d. and 0.25 μm film thickness; Restek Corp., Bellefonte, PA.) was employed for GC separation of the derivatives. The injector temperature was increased from 280°C to 320 °C at 180 °C/min and held at 320 °C for 33 minutes. The GC oven temperature was initially held at 69 °C for 1 min., ramped from 69 °C to 100 °C at 5 °C/min., then from 100 °C to 320 °C at 10 °C/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 (Spaulding et al., 1999, Frazey et al., 1999). 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.

E. Identification and Quantification

Identification of the compounds was accomplished by interpreting the electron-ionization, methane chemical ionization and pentafluorobenzyl alcohol (PFBOH) chemical ionization mass spectra as described by Spaulding et al., 1999 and Frazey et al., 1999). 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 to the derivative of an authentic standard. Quantification 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 pg/μL to 500 pg/μL prior to and after the analysis of sample extracts. The peak area (m/z $181_{analyte}$)/
peak area (m/z181 ion $_{internal\ standard}$) versus 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.

II. Results and Discussion

A. Recovery Studies.

The mean (n=2) recoveries of water, methylene chloride and toluene/isopropanol to extract 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 4.1. The polarity index (P'), which is a measure of the relative polarity of the solvents are 10.2 for water, 3.1 for methylene chloride, 2.4 for toluene and 3.9 for isopropanol (Snyder, 1978). The P' for the mixture of toluene and isopropanol was calculated to be 2.08 according to protocol outlined by Snyder, 1974. Overall, as expected, the recovery is affected by the solvent polarity and water solubility of the compound. Methylene chloride which is less polar than water and more polar than toluene/isopropanol (v/v, 2:1) is a better solvent for the less water soluble

Table 4.1. Recovery of Model Carbonyls and Multi- Functional Carbonyls In Enriched Particles.

Compound	Vapor Pressure (mm Hg)[1]	Water Solubility (mg/L)[1]	Solvent		
			Water	Methylene Chloride	Toluene/Isopropanol (2:1 v/v)
			% Mean Recovery (S.D. of n=2)		
Methacrolein	1.55×10^{2} (@25°C)	5.00×10^{4} (@20°C)	14 (± 4)	64 (±3)	2 (±1)
2,3-Butanedione	5.68×10^{1} (@15°C)	2.00×10^{5} (@25°C)	27 (± 6)	39 (±3)	2 (±1)
Dihydroxy Acetone	2.08×10^{-2} (@25°C)	5.03×10^{5} (@25°C)	144 (±34)	89 (±8)	28 (±8)
Tolualdehyde	2.5×10^{-1} (@25°C)	2.27×10^{3} (@25°C)	55 (±46)	63 (±13)	39 (±5)
Pyruvic Acid	1.29 (@20°C)	1.00×10^{6} (@25°C)	129 (±36)	70 (±11)	7 (±1)
Hydroxy Acetone	2.95 (@20°C)	1.00×10^{6} (@25°C)	110 (±30)	64 (±11)	2 (±1)

[1] Howard, P. H. and Meylan, W. M. 1997. Handbook of Physical Properties of Organic Chemicals. Lewis Publishers, New York, New York.

compounds (e.g., tolualdehyde, methacrolein and 2,3-butanedione). Water which is more polar than methylene chloride or toluene/isopropanol (v/v, 2:1) 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 -8^0C. The results are presented in Table 4.2. Improvements of 3-67% in the recovery were observed for the first six compounds listed in Table 4.2. 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 $-8\,^{\circ}$C.

B. Identification of Carbonyls and Multifunctional Carbonyls in Motor Vehicle Exhaust.

We tentatively identified 11 carbonyls and 7 multifunctional by interpreting the methane chemical ionization and pentafluorobenzyl alcohol chemical ionization mass spectra. The molecular formulas of the tentatively identified and confirmed compound are presented in Tables 4.3 and 4.4. 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 to 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.

Table 4.2. The Effect of Temperature on the Recovery of Model Carbonyls and Multi-Functional Carbonyls On Enriched Particles.

Compound	Temperature		
	0°C	-8°C	
	% Recovery (S.D. of n=2)		% Difference
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

Crotonaldehyde and glyoxal have previously been identified as gas phase emissions from gasoline- and diesel- vehicles (Fraser et al., 1998, Kirchstetter et al., 1996, Schauer et al., 1999, Graedel et al., 1986), and 2,3-butanedione was identified in the gas phase in emissions from a diesel- vehicle (Schaeur et al., 1999). 9H-fluoren-9-one was also previously identified in gasoline- and diesel- particulate emissions, and also as a product of combustion reactions (Rogge et al., 1993, Graedel et al., 1986, Behymer et al., 1985)

Although oxo acids, such as glyoxylic acid have been reported in arctic aerosol samples (Kawamura and Kaplan, 1987), characterization of acids emitted from motor vehicles has mostly been limited to carboxylic and dicarboxylic acids (Kawamura , 1985, Kawamura and Kaplan, 1987). The identification of glyoxylic and levulinic acid in motor vehicle fine particulate matter

Table 4.3. Tentatively Identified and Confirmed[1] Carbonyls in PFBHA Derivatized Extracts of Fine Particulate Matter ($PM_{2.5}$).

		Sample					
		Heavy-Duty Bore			Light-Duty Bore		
Molecular formula (molecular weight of the derivative)	**Molecule**	**1**	**3**	**5**	**6**	**7**	**8**
C_4H_6O (265)	crotonaldehyde	x	x	x	x	x	x
C_4H_6O (265)		x	x		x		x
$C_4H_6O_2$ (281)	2,3-butanedione	x	x	x	x	x	x
C_5H_4O (275)		x	x	x	x	x	x
C_6H_8O (291)		x	x	x	x	x	x
C_9H_8O (327) or $C_7H_4N_2O$				x			
$C_{13}H_8O$ (375)	9H-fluoren-9-one	x	x	x	x	x	x
$C_2H_2O_2$ (448)[2]	glyoxal	x	x	x	x	x	x
$C_{17}H_{19}NO$ (448)		x	x		x	x	x
$C_7H_{12}O_2$ (518)		x	x		x	x	
$C_{10}H_{16}O_2$ (558)		x	x	x	x	x	x

[1] Compounds were confirmed by comparing the retention time and the mass spectra of the PFBHA derivative of the analyte to the PFBHA derivative of an authentic standard. [2]The compound at m/z 448 is the molecule formed by the derivatization of both carbonyl moieties.

Table 4.4. Tentatively Identified and Confirmed[1] Multi-functional Carbonyls in PFBHA/BSTFA Derivatized Extracts of Fine Particulate Matter ($PM_{2.5}$).

		Sample					
		Heavy-Duty Bore			Light-Duty Bore		
Molecular Formula (molecular weight of derivative)	**Molecule**	**1**	**3**	**5**	**6**	**7**	**8**
			x		x		x
$C_2H_4O_2$ (327)	glycolaldehyde		x		x		x
$C_2H_2O_3$ (341)	glyoxylic acid	x	x	x	x	x	x
C_4H_9NO (354) or $C_3H_5NO_2$						x	
$C_5H_8O_3$ (383)	levulinic acid	x	x	x	x	x	x
$C_7H_6O_2$ (389)	hydroxybenzaldehyde		x	x			
$C_{16}H_{14}O_2$ (505) or $C_9H_{10}O_3$		x	x				
$C_{17}H_{21}NO_2$ (538)			x				

[1] Compounds were confirmed by comparing the retention time and the mass spectra of the PFBHA derivative of the analyte to the PFBHA derivative of an authentic standard

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 $>C_{10}$ compounds which have not been previously identified – a carbonyl with a molecular formula of $C_{10}H_{16}O_2$, and hydroxy carbonyls with a molecular formula of $C_{17}H_{21}NO_2$, and a molecular formula of either $C_{16}H_{14}O_2$ or $C_9H_{10}O_3$. The $C_{16}H_{14}O_2$ molecule would have one –OH group and the $C_9H_{10}O_3$ compound would have two -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 $>C_{10}$ hydroxy carbonyls were only present in samples collected in the heavy-duty bore. These data suggest that $>C_{10}$ 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 (1994) demonstrated that quartz fiber filters adsorb organic matter and that the particulate loading does not impact the extent of adsorption since the surface area of the particles is small compared to the surface area of the filter. In contrast, Saxena and Hildemann (1996) predict 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 (Wenclawiak et al., 1993). To shed further light on this controversy, further work is needed which utilizes the sample preparation and analysis protocol described herein in concert with another sampling technique, which is capable of separating gas- and particulate- phase species.

C. Quantification of Carbonyls and Multifunctional Carbonyls in Motor Vehicle Exhaust.

The levels of crotonaldehyde, 2, 3-butanedione, glyoxal, glyoxylic acid and levulinic acid were quantified (See Table 4.5). In fine particulate matter sampled from the heavy- duty bore, the concentration of crotonaldehyde ranged from ND to 67 ng/mg; the concentration of glyoxal

Table 4.5. Concentration of select carbonyls and multi-functional carbonyls in fine particulate matter ($PM_{2.5}$) sample extracts.

Compound	**Concentration (ng/mg)**			
	Heavy-Duty Bore		**Light-Duty Bore**	
	1	3	5	6
Crotonaldehyde	67	ND	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

ranged from 93 to 216 ng/mg; the concentration of 2,3-butandione ranged from ND to 90 ng/mg; and the concentration of levulinic acid ranged from 192-220 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 avid 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 (Staehlin et al., 32). 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 vs. 24 ng/m^3 in the heavy-duty bore and light-duty bore, respectively).

D. 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 HPLC- grade water, and the laboratory air. We investigated the effect of redistillation of MTBE, recrystalization of PFBHA, sample preparation in a N_2 atmosphere and permanganate oxidation of the organics in the water on the levels of acetaldehyde, acetone, propionaldehyde and 2-butanone and four unidentified compounds recovered from a filter that was processed through the analytical protocol. The results are presented in Table 4.6. Removal of 80-100% of the compound was evident after redistillation of MTBE, recrystalization of PFBHA, sample preparation under N_2 and oxidation of the organics in the water with potassium permanganate. Oxidation of the water with potassium permanganate appears to be the most effective removal step. Sample preparation under nitrogen provided was also effective for reducing impurities of acetaldehyde, acetone, propionaldehyde and 2-butanone, as was recrystillazation of the PFBHA two times for all the compounds. From these data, it is difficult to suggest which of the treatments might be eliminated since we did not quantify 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 the sensitivity of the method.

IV. Conclusions

Carbonyls and multi-functional 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 quantified by using gas chromatography/chemical ionization ion trap mass spectrometry. The recovery of model carbonyls (tolualdehyde, methacrolein, and 2,3-butanedione) and multi-functional 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°C 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 quantification of carbonyls and multifunctional carbonyls. The identities of crotonaldehyde, 2,3-butanedione, glyoxal, 9H-fluoren-9-one, glyoxylic acid, and levulinic were confirmed. The identification of glyoxylic acid and levulinc 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 moelcular 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 quantified. 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 recrystalization of the solvent, recrystalization 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 is developed and tested capable of identifying high-molecular weight (>C_{10}) carbonyl s and multi-functional carbonyls for which no data exist, and which may be significant combustion products in fine particulate matter. Since stationary sources emit compounds into the atmosphere by combustion processes, the method may also be useful for the identification of compounds in stationary sources.

V. References

Aumont, B.; Madronich, S.; Bey, I.; Tyndall, G. S. (2000) *Journal of Atmospheric Chemistry*, **35**, 59-75.

Behymer, T. D., Hites, R. A. (1985) *Environ. Sci. Technol.* **19**, 1004-1006.

Fraser, M. P., Cass, G. R., Simoneit, B. R. T. (1998) *Environ. Sci. Technol.* **32**, 2051-2060.

Frazey, P.; Rao, X.; Spaulding, R.; Beld, B.; Charles, M. J. (1999) *International Journal of Mass Spectrometry.* **190/191**, 343-357.

Graedel, T. E.; Hawkins, D. T.; Claxton, L. D. (1986) *Atmospheric chemical compounds-wsources, occurrence, and bioassy*; Academic Press: Orlando, FLA.

Kawamura, K.; Gagosian, R. B. (1987) *Nature,* **325**, 330-332.

Kawamura, K. (1985) *Environ. Sci. Technol.* **19**, 1082-1086.

Kawamura, K.; Kaplan, I. R. (1987) *Environ. Sci. Technol.* **21**, 105-110.

Kirchstetter, T. W.; Singer, B. C.; Harley, R. A.; Kendall, G. R.; Chan, W. (1996) *Environ. Sci. Technol.* **30,** 661-670.

Le Lacheur, R. M.; Sonnenberg, L. B.; Singer, P. C.; Christman, R. F.; Charles, M. J. (1993) *Environ. Sci. Technol.,* **27,** 2745-2753.

Miguel, A. H.; Kirchstetter, T. W.; Harley, R. A.; Hering, S. V. (1998). *Environ. Sci. Technol.* **32**, 450-455.

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.

Pun, B. K.; Seigneur, C.; Grosjean, D.; Saxena, P. (2000) *Journal of Atmospheric Chemistry,* **35**, 1999-223.

Rogge, W. F.; Hildemann, L. M.; Mazurek, M.; Cass, G. R. (1993) *Environ. Sci. Technol.* **27**, 636-651.

Sagiebiel, J. C.; Zielinska, B.; Pierson, W. R.; Gertler, A. W. (1996) *Atmos. Environ.* **30**, 2287-2296.

Saxena, P.; Hildemann, L. M. *J.* (1996*) Atmos. Chem.,* **24**, 57-109.

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

Siegl, W. O.; Hammerle, R. H.; Herrmann, H. M.; Wenclawiak, B. W.; Luers-Jongen, B. (1999) *Atmos. Environ.*, **33,** 797-805.

Snyder, L. R. (1978) *J. Chromatogr. Sci.* **16**, 223-234.

Snyder, L. R. (1974) *J. Chromatogr.* **92**, 223-230.

Spaulding, R. S.; Frazey, P.; Rao, X.; Charles, M. J. (1999) *Anal. Chem*, **71**, 3420-3427.

Staehelin, J.; Keller, C.; Staehl, W.; Schlapfer, K.; Wunderlis, S. (1998) *Atmos. Environ.* **32**, 999-1009.

Turpin, B. J.; Huntzicker, J. J. (1995) *Atmos. Environ.* **29**, 3527-3544.

Weingartner, E.; Keller, C.; Stahel, W. A.; Burtscher, H.; Baltensperger, U. (1977). *Atmos. Environ.* **31,** 451-462.

Wenclawiak, B. W.; Jensen, T. E.; Richert, J. F. O. (1993) *Fresenius J. Anal. Chem.*, **346,** 808-812

Yu, J.; Jeffries, H. E.; Le Lacheur, R. M. (1995) *Environ. Sci. Technol.* **29,** 1923-1932.

Zielinska, B.; Sagebiel, J. C.; Harshfield, G.; Gertler, A. W.; Pierson, W. R. (1966) *Atmos. Environ.* **30,** 2269-2286.

Chapter 5.

Summary and Conclusions and Recommendations

Table of Contents

I. Summary and Conclusions

In spite of the enormous effort to reduce levels of ozone and particulate matter in the environment, millions of people reside in counties that exceed state and federal regulatory standards. Two significant gaps that affect the reduction of levels of these pollutants are: 1) an understanding of chemical processes affecting the formation of ozone and fine particulate matter, that includes knowledge of the generation and fate of first-, second- and third- generation oxidation products of anthropogenic and biogenic emissions, and 2) a complete understanding of sources of fine particulate matter, and photooxidation reactions occurring on the particles as they are transported from source to receptor. Herein, we address these gaps by developing and applying methods to measure oxygenated organics (*e.g*, carbonyls and multi-functional carbonyls) in aerosols and fine particulate matter.

The methods developed rely on derivatization of carbonyl moieties with *O*- (2,3,4,5,6-pentalfuorobenzyl)-hydroxylamine (PFBHA); silylation of the hydroxyl and carboxyl groups on the PFBHA derivatives of hydroxy carbonyls, and oxo-acids using Bis (trimethylsilyl) trifluoroacetamide (BSTFA) and detection of the PFBHA and PFBHA/BSTFA derivatives by using gas chromatography/ion trap mass spectrometry (GC/ITMS). The typical method to measure carbonyls uses 2,4-dinitrophenyl hydrazine (DNPH) as a derivatization reagent. The DNPH derivatives are analyzed by using high-performance liquid chromatography (HPLC)/UV Vis spectrometry. Limitations of the DNPH/UV Vis method are that: 1) it has not afforded the measurement of hydroxylated carbonyls identified as photooxidation products of anthropogenic and biogenic hydrocarbons in chamber studies, 2) it suffers form poor chromatographic resolution of similar carbonyls, 3) DNPH derivatives of α-dicarbonyls and hydroxycarbonyls cannot be differentiated, and thus glycolaldehyde cannot be distinguished from glyoxal, and methyl glyoxal cannot be distinguished from hydroxyacetone, 4) DNPH derivatives of unsaturated carbonyls, such as acrolein are unstable, and 5) the method is not suitable for the identification of carbonyls for which authentic standards do not exist.

A unique feature of the PFBHA/GC ITMS method is the presence of a $(M+181)^+$ ion that arises from the reaction of neutral analyte molecules with the pentafluorobenzyl cation. The presence of this ion, along with the $(M+H)^+$ ion facilitates molecular weight determinations of the derivatives. By using pentafluorobenzyl alcohol (PFBOH) as a chemical ionization reagent, the intensity of the $(M+H)^+$ and $(M+181)^+$ ions can be increased to simplify molecular weight determinations. In contrast to the DNPH method, advantages of the PFBHA/GC ITMS method are: 1) excellent chromatographic resolution of carbonyls, 2) the ability to accurately measure α-dicarbonyls and hydroxycarbonyls, 3) unambiguous identification of carbonyls for which authentic standards by interpreting the electron-ionization, methane chemical ionization and pentaflurobenzyl chemical ionization mass spectra, 4) stable derivatives of unsaturated carbonyls, and 5) interpretation of the methane chemical ionization and pentafluorobenzyl chemical ionization mass spectra enables identification of trace levels (part-per-trillion) of carbonyls in the presence of co-eluting interferences.

In initial work, described in Chapter 1 entitled "The Measurement of Hydroxy Carbonyls and other Carbonyls in Ambient Air Using Pentafluorobenzyl Alcohol as a Chemical Ionization Reagent", we first demonstrate the power of the method. We sampled air in Azusa, CA. and Davis, CA. by using impingers. Molecular weight determinations of part-per-trillion levels of carbonyls in the presence of co-eluting interferences were possible by using pentafluorobenzyl alcohol as a derivativzation reagent. Methyl vinyl ketone, methacrolein, methyl glyoxal, glycolaldehyde and hydroxy acetone were identified in air collected in Azusa, CA. Methyl vinyl ketone, methacrolein, methyl glyocal, hydroxy acetone, glyoxal and 3-hydroxy-2-butanone were identified in samples collected in Davis, CA. To our knowledge, this was the first report of hydroxy acetone and 3-hydroxy-2-butanone in the ambient atmospheric environment. The work was significant because: 1) it demonstrated the power of the method to measure water soluble carbonyls for which no or little ambient air data exists, 2) it was the first study that applied pentafluorobenzyl derivatization along with ion trap mass spectrometry to measure carbonyls in the ambient atmospheric environment, and 3) it was the first

study to apply pentaflurobenzyl alcohol chemical ionization to identify carbonyls in aerosols.

A limitation of the previous method was the use of impingers that operate at low flow rates (0.5-1.0 L/minute). To detect, part-per-trillion levels of the hydroxycarbonyls, long (4 hour) sampling times are needed. The mist chamber is an attractive device because it operates at flow rates of 20 to 70 L/minute, and thus can afford short (10 minute) sampling times. Although, the mist chamber was previously used to sample formaldehyde, pyruvic acid, glyoxal and methylglyoxal, all in separate studies, no data existed on the collection efficiency of the device for carbonyls and multi-functional carbonyls, or parameters that might affect the collection efficiency. In Chapter 2, entitled " Optimization of a Mist Chamber (Cofer Scrubber) for Sampling Water-Soluble Organics in Aerosols", we present the results of research in which we investigated the effect of pH of the PFBHA solution, the addition of salts, and temperature on the collection efficiency, and apply the mist chamber to measure photooxidation products of isoprene in the Blodgett Forest, CA. The results establish a relationship between the Henry's law constant (K_H) and the collection efficiency, and demonstrate the suitability of the method to measure analytes with $K_H \geq 10^3$ M atm^{-1}. Adjusting the pH, adding quaternary ammonium salts, or decreasing the temperature of the solution in the mist chamber did not significantly affect the collection efficiency. We tested the method by sampling photooxidation products of isoprene (glyoxal, methylglyoxal, hydroxyacetone, and glycolaldehyde) in the Blodgett Forest, CA. This is the first report of a study that employs the mist chamber to sample hydroxy carbonyls. The accuracy and the reproducibility of the method were evaluated by the analysis of duplicate samples and field spikes. The mean recovery of field spikes was $\geq 80\%$, and the relative standard deviation was $\leq 22\%$ between duplicate measurements. The detection limits were 48, 15, 7.7 and 2.7 part-per-trillion for glycolaldehyde, hydroxyacetone, methylglyoxal, and glyoxal, respectively. The method provides detection limits that are an order of magnitude more sensitive than other methods for the measurement of glyoxal and hydroxyacetone, and similar detection limits for glycolaldehyde and glyoxal. This work demonstrates the utility of the mist chamber in concert with the PFBHA/GC ITMS

method to measure part-per-trillion concentrations of water-soluble organics with a sampling time of 10 minutes.

While isoprene is the dominant biogenic hydrocarbon worldwide, in the western United States, oxidation of 2-methyl-3-buten-2-ol (MBO) can affect the oxidative capacity of the atmosphere. Hydroxyl radical oxidation of MBO can play an important role in forming tropospheric ozone and secondary organic aerosols. The products of this reaction are formaldehyde, 2-hydroxy-2-propanal, glycolaldehyde and acetone. The compound 2-hydroxy-2-propanal was tentatively identified as a product due to the lack of an authentic standard. Due to the absence of data on 2-hydroxy-2-propanal in the ambient environment, we applied the mist chamber method to gain insight into the generation and fate of this product at the Blodgett Forest, CA. The results of this investigation are described in Chapter 3, entitled "Advances in the Analytical and Atmospheric Chemistry of 2-Hydroxy-2-Methylpropanal, a Proposed Photooxidation Product of 2-methyl-3-buten-2-ol". Herein, we provide further evidence that 2-hydroxy-2-methylpropanal is generated by ·OH reaction with MBO by identifying 2-hydroxy-2-methylpropanal in an indoor chamber experiment and in ambient air sampled in the Blodgett Forest, where MBO emissions are high. Tentative identification of 2-hydroxy-2-methylpropanal was possible by using knowledge gained in this study regarding the mass spectrometry of PFBHA-BSTFA derivatives of carbonyls with primary, secondary, and tertiary -OH groups, and aldo- and keto-acids. The identification was confirmed by comparing the methane CI mass spectra and relative gas chromatographic retention time obtained by analyzing 2-hydroxy-2-methylpropanal in a sample extract and a synthesized authentic standard. Since the standard became available at the end of this study (after all samples were analyzed), we also developed a method for semi-quantification of 2-hydroxy-2-methylpropanal, with a detection limit of 27 pptv in air. We used the method to provide the first ambient air measurements of 2-hydroxy-2-methylpropanal. The analyte is not commercially available, and hence other researchers who have not synthesized an authentic standard can employ the method.

In the final chapter, Chapter 4, entitled "Measurement of Carbonyls and Multifunctional Carbonyls in $PM_{2.5}$ Emitted for Motor Vehicles, we developed and tested to identify and quantify carbonyls and multifunctional carbonyls in fine particulate matter ($PM_{2.5}$; <2.5μm aerodynamic diameter). An investigation of ultrasonic extraction of model compounds from enriched particles demonstrated that the % extracted was affected by solvent polarity (water > methylene chloride > toluene/isopropanol (v/v, 2:1)). 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°C 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 quantification of carbonyls and multi-functional carbonyls in sample extracts of fine particulate matter ($PM_{2.5}$) collected in the Caldecott tunnel. 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 to an authentic standard. Quantification 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-hydroxybenzaldheyde in $PM_{2.5}$ particles sampled in a roadway tunnel. It is also the first report of a C_{10} carbonyl with the molecular formula of $C_{10}H_{16}O_2$, a hydroxy carbonyl with the molecular formula of $C_{17}H_{21}NO_2$, and a hydroxy or di-hydroxy carbonyl with the molecular formula of $C_{16}H_{14}O_2$ or $C_9H_{10}O_3$. The high-molecular weight hydroxy carbonyls, which were found only in the heavy- duty (diesel) bore, may be tracers of diesel emissions in air.

II. Recommendations

Following is a list of suggested research to improve the methods developed herein, and to use the methods to gain insight into the generation and fate of first-, second-, and third generation photooxidation products; to speciate the organics on fine particulate matter; and to sample aerosols in the environment to understand the formation of secondary organic aerosols.

1) The mist chamber method should be improved to measure a broad range of carbonyls, and to increase the limits of detection to provide measurement of carbonyls at the part-per-quadrillion level using sampling times of 10 minutes or less. The improved method can be utilized to gain insight into the generation and fate of photooxidation products of anthropogenic and biogenic emissions; to evaluate exposures to carbonyls; and to understand transformation reactions that affect the toxicity of aerosols as they are transported from source to receptor.

2) Proton transfer mass spectrometry is emerging as a powerful tool to measure a parent hydrocarbons and their photooxidation products. A limitation of the method however is the lack of the ability to identify isomers. Further work is needed to explore mass spectrometry/mass spectrometry as a means to identify species. The method should also be validated to compared to conventional methods, and applied to understand the impact of anthropogenic and biogenic emissions on tropospheric ozone and fine particle formation.

3) We recommend that the Air Resources Board utilize PFBHA derivatization to measure carbonyls since many of the difficulties posed by DNPH derivatization can be addressed by using PFBHA instead of DNPH.

4) Further work is needed to speciate the organic fraction of fine particulate matter for source apportionment; to gain insight into the health effects of fine particulate matter and transformation reactions that occur as particles are transported from source to receptor.

5) We recommend that other samplers than the IMPROVE sampler be investigated to differentiate between gas- and particle- phase species as utilization of the IMPROVE sampler likely resulted in adsorption of gas- phase species on the particles. Such a sampler should be utilized to gain insight into gas- and particle phase photooxidation

projects of anthropogenic and biogenic species that effect the formation of secondary organic aerosols. Specifically, work is needed to understand OH radical oxidation of pinenes in the ambient atmospheric environment.