

Final Report

The Identities and Behavior of Multi-Functional Carbonyls in Simulated and Ambient
Atmospheric Environments

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Abstract

We developed and tested a field method to measure carbonyls and multifunctional carbonyls in air. The method involves sampling air using impingers filled with an aqueous solution of *O*-(2,3,4,5,6-pentafluorobenzyl)-hydroxylamine (PFBHA) to derivatize carbonyls *in situ*. After extraction of the derivatives from water, an aliquot of the extract is reacted with *bis* (trimethylsilyl) trifluoroacetamide (BSTFA) to silylate the hydroxyl group on hydroxy carbonyls and oxo acids. The PFBHA derivatives of aldehydes, ketones, and dicarbonyls and the PFBHA/BSTFA of hydroxy carbonyls and oxo acids were detected by using gas chromatography along with electron-impact ionization (EI), methane chemical ionization (CI) and pentafluorobenzyl alcohol chemical ionization (PFBOH CI) ion trap mass spectrometry. We identified methyl vinyl ketone, methacrolein, methyl glyoxal, glycolaldehyde and hydroxy acetone in Azusa, CA, and methacrolein, methyl vinyl ketone, 3-hydroxy-2-butanone, and hydroxy acetone in Davis, CA air. We also identified 2,3-butanedione and glyoxal in Davis air. However, since the concentration of these compounds was greater in samples collected without removing ozone from the airstream, they may be artifacts generated from the oxidation of other species. We report concentration ranges of 245 to 348 pptv for methyl vinyl ketone, 113 to 232 pptv for methacrolein, ND (non-detectable) to 182 pptv for methyl glyoxal, ND to 840 pptv for glycolaldehyde and ND to 534 pptv for hydroxy acetone in Azusa air. To our knowledge, this is the first report of 3-hydroxy-2-butanone and hydroxy acetone in the ambient atmospheric environment. PFBOH chemical ionization was critical to identify glycolaldehyde and hydroxy acetone in the presence of co-eluting interferences, and to confirm the identity of glyoxal. By extrapolation, the method detection limit at a S:N of 3:1 is 1 pptv for methyl vinyl ketone, 3 pptv for methacrolein, 12 pptv for methyl glyoxal, 11 pptv for glycolaldehyde, and 49 pptv for hydroxy acetone. Although, herein we only report the measurement of select carbonyls, an advantage of the method as demonstrated in chamber studies, is that the method is suitable for the measurement of a broad range of carbonyls, including aldehydes, ketones, hydroxy carbonyls, epoxy carbonyls and oxo acids. In addition, the method enables the determination of molecular weights of carbonyls for which authentic standards do not exist.

Executive Summary

Background: Multifunctional and polar organics are first- and second-generation photooxidation products comprised of oxo acids, carbonyls, dicarbonyls, hydroxy carbonyls and epoxy carbonyls. In the ambient environment, such products can be further oxidized or partition to particles. They play a critical role in ozone generation by influencing the creation and depletion of radical oxidizing species, and as constituents of particulate matter, they may affect the hygroscopicity and light scattering properties of particles. Multifunctional and polar compounds commonly found in gas and particulate phases are also mutagenic, carcinogenic, and cause adverse effects on human cardiovascular and respiratory systems. Thus, to protect the environment and human health, it is essential that we gain insight into the generation and fate of these compounds in the ambient environment.

Existing knowledge on multifunctional carbonyl photooxidation products is primarily derived from product identification studies conducted in chambers to elucidate photochemical reaction mechanisms. To gain insight into the interplay among meteorological conditions (*e.g.*, solar intensity, temperature, humidity) and tropospheric ozone formation, ambient air data is needed. The sources and distribution of carboxylic acids and carbonyls in the gas and particle phases, as well as wet precipitation have received widespread attention. A paucity of data exists on the generation and distribution of dicarbonyls, oxo acids, and hydroxy carbonyls. The common method employed to measure carbonyls in air employs 2,4-dinitrophenylhydrazine (DNPH) derivatization and high performance liquid chromatography (HPLC)/UV detection. Limitations of the method are poor resolution of similar carbonyls, difficulties differentiating α -hydroxy carbonyls from dicarbonyls, the absence of authentic standards, the formation of artifacts, and retention of glycolaldehyde and hydroxy acetone on DNPH cartridges. New approaches to unambiguously identify and quantify multifunctional carbonyls are thus needed.

Methods: Field measurement of carbonyls and multifunctional carbonyls was accomplished by sampling air with impingers filled with an aqueous solution of *O*-(2,3,4,5,6-pentafluorobenzyl)-hydroxylamine (PFBHA), a derivatizing reagent selective to carbonyls. After derivatization of the carbonyls *in situ*, the PFBHA derivatives were isolated and enriched by solvent extraction with methyl-*tert* butyl ether or C₈ solid phase extraction cartridges. An aliquot was removed and reacted with *bis* (trimethylsilyl) trifluoroacetamide (BSTFA) to form oxime - trimethyl silyl ether derivatives. The PFBHA derivatives of aldehydes, ketones and dicarbonyls, and the PFBHA/BSTFA derivatives of hydroxy carbonyls and oxo acids were measured by using gas chromatography/ion trap mass spectrometry.

Results: We identified the carbonyls and multifunctional carbonyls in the sample extracts by interpreting the electron-impact ionization (EI), methane chemical ionization (CI) and pentafluorobenzyl chemical ionization (PFBOH CI) mass spectra. We identified methyl vinyl ketone, methacrolein, methyl glyoxal, glycolaldehyde and hydroxy acetone in Azusa, CA. air, and methacrolein, methyl vinyl ketone, 3-hydroxy-2-butanone, and hydroxy acetone in Davis, CA air.

We also identified 2,3-butanedione and glyoxal in Davis air. However, since the concentration of these compounds was greater in samples collected without removing ozone from the airstream, they may be artifacts generated from the oxidation of other species. We report concentration ranges of 245 to 348 pptv for methyl vinyl ketone, 113 to 232 pptv for methacrolein, ND (non-detectable) to 182 pptv for methyl glyoxal, ND to 840 pptv for glycolaldehyde and ND to 534 pptv for hydroxy acetone in Azusa air. To our knowledge, this is the first measurement of 3-hydroxy-2-butanone and hydroxy acetone in the ambient atmospheric environment. Employment of KI traps to remove ozone appears necessary to deter oxidation of certain compounds and the generation of others.

We also established the complementary nature of the EI, methane CI, and PFBOH CI ion trap mass spectra. The EI mass spectra provides functional group information, and the methane and PFBOH chemical ionization mass spectra provide molecular weight information. The enhancement of the relative intensity of molecular and *pseudo*-molecular ions when PFBOH was employed as a CI reagent gas instead of methane afforded the identification of glycolaldehyde and hydroxy acetone in the presence of co-eluting interferences.

Quantification was accomplished by internal standardization. In certain cases the elimination of values that were outliers at a 95% confidence interval improved the linearity of the linear regression equation employed to quantify the analytes. By extrapolation, the method detection limit at a S:N of 3:1 is 1 pptv for methyl vinyl ketone, 3 pptv for methacrolein, 12 pptv for methyl glyoxal, 11 pptv for glycolaldehyde, and 49 pptv for hydroxy acetone.

Conclusions: We established that pptv levels of carbonyls, dicarbonyls and hydroxy carbonyls can be unambiguously identified and quantified by a method developed and evaluated in this study. The method involves sampling with impingers filled with PFBHA, and measuring the PFBHA derivatives of aldehydes, ketones and dicarbonyls, and the PFBHA/BSTFA derivatives of hydroxy carbonyls and oxo acids by using gas chromatography/ion trap mass spectrometry. We also establish the power of PFBOH chemical ionization to identify analytes at trace levels in the presence of co-eluting interferences. Although, herein we only report the measurement of select carbonyls, an advantages of the method, as demonstrated in chamber studies is that it is suitable for the measurement of a broad range of carbonyls, including aldehydes, ketones, hydroxy carbonyls, epoxy carbonyls and oxo acids. In addition, the method enables the determination of molecular weights of carbonyls for which authentic standards do not exist. Hence, elemental formulas for such carbonyls can be obtained and possible structures can be postulated. Further work is needed to improve the sampling method. Evaluation of a mist sampler that affords collection of 35L/minute of air is underway. The improved method can be utilized to gain insight into anthropogenic and biogenic sources of multifunctional carbonyls and the role that these compounds play in the generation of tropospheric ozone. Modification of the sampling method for the collection of size-segregated particles is necessary to improve an understanding of secondary organic aerosol formation.

I. Introduction

Hydroxy carbonyls are photooxidation products of alkoxy radical reactions with biogenic and anthropogenic hydrocarbons (1, 2). Atmospheric pressure chemical ionization mass spectrometry (APCI/MS), and *O*-(2,3,4,5,6-pentafluorobenzyl)-hydroxylamine (PFBHA) derivatization/chemical ionization ion trap mass spectrometry (CI/ITMS) were critical to the identification of hydroxy carbonyls generated from OH radical initiated reactions in chambers. These studies establish that hydroxy carbonyls are photooxidation products of C₄-C₈ alkanes (3), C₄-C₈ alkenes (4), linalool (5), isoprene (6-8), 4-dimethyl-2-pentanone, 3,5-dimethyl-3-hexanol, *cis*-3-hexen-1-ol, and the alkylbenzenes, toluene, *p*-xylene, *m*-xylene, *o*-xylene, 1,3,5-trimethyl benzene and 1,2,4-trimethyl benzene (9). (See Table I). Oxidation of alkanes yields hydroxy carbonyl products with the same number of carbon atoms, with an increase in formation yields with increasing carbon number. For example, 4-hydroxy butanal is generated from *n*-butane and 5-hydroxy-2-pentanone arises from oxidation of *n*-pentane. Hydroxy carbonyls with fewer carbon atoms are also formed from *n*-heptane and *n*-octane. Oxidation of *n*-heptane yields C₃, C₅ and C₇ hydroxy carbonyls, and C₄₋₆ and C₈ hydroxy carbonyls are products of *n*-octane photooxidation reactions (3). OH radical oxidation of C₄₋₈ alkenes yields dihydroxy carbonyls. 4-hydroxy-4-methyl-5-hexan-1-al is a photooxidation product of the alkene, linalool. Glycolaldehyde and hydroxy acetone were identified as isoprene photooxidation products in early studies (10-12). In later work, these and other products were identified, including C₃-C₅ hydroxy saturated dicarbonyls (8). Photooxidation of alkyl benzenes (*e.g.*, toluene, *p*-xylene, *m*-xylene, *o*-xylene, 1,3,5-trimethyl benzene and 1,2,4-trimethyl benzene) yields glycolaldehyde, C₃₋₄ hydroxy carbonyls, and C₄ hydroxy dicarbonyls.

A paucity of ambient air data exists for dicarbonyls, oxo acids, hydroxy carbonyls and dicarbonyls. Most of the studies report measurements of pyruvic acid, glyoxal and methyl glyoxal (13-23, 24, 25-28). Hydroxy carbonyls in ambient air have been reported by several investigators (23, 27-31). Nondek *et al.*, 1992 (29) utilized dansylhydrazine (DNSH) impregnated cartridges and HPLC/fluorescence detection to identify *p*-hydroxybenzaldehyde

Table I. Select Gas Phase Multifunctional Carbonyls Generated From OH Radical Initiated Reactions in Chamber Studies.		
Precursor	Multifunctional Carbonyls	Reference
C₄-C₈ <i>n</i>-Alkanes		
<i>n</i> -butane	4-hydroxy butanal	(1,2,3)
<i>n</i> -pentane	5-hydroxy-2-pentanone, 4-hydroxypentanal, 5-hydroxyhexan-2-one	
<i>n</i> -hexane	C ₆ hydroxy carbonyl, 4-hydroxy butanal, hexan-2,5-dione (secondary product) 6-hydroxyhexan-3-one (tentatively identified)	
<i>n</i> -heptane	C ₄ , C ₅ , C ₇ hydroxy carbonyls	
<i>n</i> -octane	C _{4-6, 8} hydroxy carbonyls	
Alkenes		
1-butene	C ₄ -dihydroxy carbonyl	(4)
1-pentene	C ₅ -dihydroxy carbonyl	
1-hexene	C ₆ -dihydroxy carbonyl	
1-heptene	C ₇ -dihydroxy carbonyl	
1-octene	C ₈ -dihydroxy carbonyl	
linalool	4-hydroxy-4-methyl-5-hexan-1-al	(5)
isoprene	glycolaldehyde, hydroxy acetone, pyruvic acid, C ₃ hydroxy saturated dicarbonyls, C ₄ hydroxy unsaturated dicarbonyls, C ₅ hydroxy unsaturated carbonyls, methyl glyoxal, glyoxal, dicarbonyls	(6,7,8,9)

Table I. Select Gas Phase Multifunctional Carbonyls Generated From OH Radical Initiated Reactions in Chamber Studies (continued).		
Alkyl benzenes		
toluene	glycolaldehyde, hydroxy acetone, benzaldehyde, C ₆ unsaturated hydroxy epoxy cyclic carbonyl, glyoxal, methyl glyoxal, C ₇ unsaturated epoxy dicarbonyl, propanedial, butenedial, 4-oxo-2-pentenal, C ₄ hydroxy dicarbonyls, C _{3,5} saturated dicarbonyls or C _{3,5} trione, C _{3,4} hydroxy carbonyls, C ₆ unsaturated hydroxy carbonyls	(10,11)
<i>p</i> -xylene	2-methyl butenedial, 4-oxo-2-pentenal, 3-hexene-2,5-dione, C ₄ hydroxy dicarbonyls, C _{6,8} hydroxy unsaturated epoxy cyclic carbonyls	
<i>m</i> -xylene	2-methyl-butenedial, 4-oxo-2-pentenal, <i>cis</i> -2-methyl-4-oxo-2-pentenal, C ₄ hydroxy dicarbonyls, C ₄ hydroxy dicarbonyls, C _{6,8} hydroxy unsaturated hydroxy carbonyls	
<i>o</i> -xylene	butenedial, 4-oxo-2-pentenal, C ₄ hydroxy dicarbonyls, C _{6,8} hydroxy unsaturated epoxy cyclic compounds	
1,3,5-trimethylbenzene	<i>cis</i> -2-methyl-4-oxo-2-pentenal, <i>trans</i> -2-methyl-4-oxo-2-pentenal, C ₄ hydroxy dicarbonyls, C _{6,8} hydroxy unsaturated epoxy cyclic carbonyls	
1,2,4-trimethyl benzene	2-methyl-butendial, 3-hexene-2,5-dione, <i>trans</i> -2-methyl-4-oxo-pentenal, C ₄ hydroxy dicarbonyls, C _{6,8} unsaturated epoxy cyclic carbonyls	
Alcohols		
2,4-dimethyl-2-pentanol	4-hydroxy-4-methyl-2-pentanone	(2)
3,5-dimethyl-3-hexanol	4-hydroxy-4-methyl-2-pentanone 4-hydroxy-4-methyl-2-pentanone	
<i>cis</i> -3-hexen-1-ol	1,3-dihydroxy-4-hexanone	(12)
2-methyl-3-buten-2-ol	2-hydroxy-2-methylpropanal, glycolaldehyde	(13)

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and C₃, C₄ and C₆ hydroxy carbonyls in ambient air. In 1993, Lee and Zhou (30) first reported the measurement of soluble carbonyls, including glycolaldehyde in air by using 2,4-dinitrophenylhydrazine (DNPH) derivatization and high performance liquid chromatography with UV/Vis detection. In subsequent studies they employed the method to measure glycolaldehyde, and other carbonyls including glyoxal, methyl glyoxal and formaldehyde in air (23, 27, 28, 30, 31). The DNPH method however cannot differentiate between α -hydroxycarbonyls and dicarbonyls. The absence of authentic standards for many hydroxy carbonyls also makes it impossible to identify compounds by using UV/Vis detection. Moreover, the method has not provided the measurement of most of the hydroxylated carbonyls identified by Yu *et al.* and Atkinson and co-workers in chamber studies.

The primary objective of this work was to establish that methods utilized by Yu *et al.*, 1995 (8, 9) and Chien *et al.*, 1998 (32) to measure pentafluorobenzyl derivatives of carbonyls and carboxylic acids in chamber studies are suitable for field measurements. The power of the method lies in the generation of unique ions that facilitate molecular weight determinations. By observing the juxtaposition of $(M+H)^+$ and $(M+181)^+$ ions in the methane chemical ionization (CI) ion trap mass spectra, Yu *et al.*, 1995, 1997 (8,9) identified novel carbonyl, dicarbonyl, oxo acid, hydroxy carbonyl and epoxy carbonyl photooxidation products of biogenic and anthropogenic hydrocarbons in chamber studies. In previous work, we utilized a combination of pentafluorobenzyl alcohol (PFBOH) and methane as chemical ionization reagents to effect the formation of the $(M+181)^+$ ion. PFBOH/methane CI was critical to the identification of novel carboxylic acid intermediates of isoprene and toluene. Herein, we utilize PFBOH by itself as a chemical ionization reagent.

We employed PFBHA filled impingers to sample air, and identified carbonyls and dicarbonyls in sample extracts by interpreting the electron-impact ionization (EI), methane CI and PFBOH CI ion trap mass spectra of PFBHA derivatives. In a similar fashion, we identified PFBHA-trimethyl silyl derivatives of hydroxy carbonyls generated by reacting the PFBHA derivatives with *bis* (trimethylsilyl) trifluoroacetamide (BSTFA). To our knowledge, this is the first study that applies pentafluorobenzyl derivatization along with ion trap mass spectrometry to field measurement of carbonyls, dicarbonyls, and hydroxy carbonyls. It is also the first report of 3-

hydroxy-2-butanone and hydroxy acetone in ambient air. PFBOH CI was essential for unambiguous identification of hydroxy carbonyls and other carbonyls at the pptv level in the presence of co-eluting interferences, and methyl vinyl ketone, methacrolein, methyl glyoxal, glycolaldehyde and hydroxy acetone were quantified in Azusa, CA air.

II. Materials and Methods

Chemicals. We employed *O*-(2,3,4,5,6-pentafluorobenzyl)-hydroxylamine hydrochloride (PFBHA) to derivatize the carbonyls, *bis* (trimethylsilyl) trifluoroacetamide (BSTFA), and *N tert*-butyl(dimethylsilyl)-*N*-methyltrifluoroacetamide (MTBSTFA) as silylation reagents. We obtained pentafluorobenzyl alcohol and authentic standards from Aldrich Chemical Co., Inc., Milwaukee, WI. We utilized HPLC- grade water, methyl- *tert*-butyl ether (MTBE) and concentrated sulfuric acid (Fisher Scientific, Fairlawn, NJ). Prior to sampling air in Azusa, CA, HPLC water was further purified by passing the water through a Norganic cartridge (Millipore Corporation, Bedford, MA) to remove organic contaminants. For the sampling that was conducted in Davis, CA, HPLC grade water was purified by distillation with KMnO_4 .

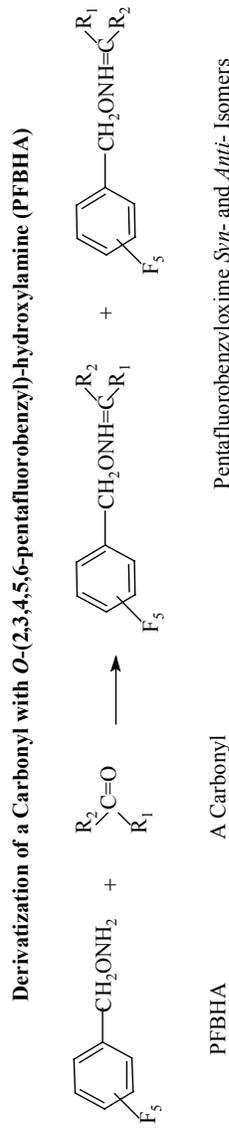
Sample Collection. We sampled air in Azusa, CA, an urban site located in the Pomona Valley, on September 23 and 24, 1997. On September 23, air was sampled from 1:00-4:00 p.m., and from 5:00-8:00 p.m. On September 24, we sampled from 1:00 p.m. to 5:00 p.m. We utilized four impingers in series to sample the air. This was necessary since we were unable to conduct experiments to determine breakthrough volumes prior to field sampling. Since few ambient measurements of hydroxy carbonyls exist, we were also uncertain about concentrations in ambient air, and thus the amount of air we needed to collect.

We sampled air in Davis, CA on the roof of Meyer Hall on May 14, 1998 from 1:20-2:50 p.m and then from 3:10-6:15 p.m. We operated two sampling trains in parallel, each comprised of four impingers in series. Each impinger contained 0.10 mM of an aqueous solution of PFBHA prepared in purified HPLC grade water. We employed 400 mL impingers when sampling in Azusa, CA, and 10 mL impingers when sampling in Davis, CA. Potassium iodide (KI) scrubbers were placed in the airstream before the impingers to remove ozone. When sampling in Davis, CA,

we collected two samples in the absence of KI traps. The volume of air sampled in Azusa, CA was measured with the dry gas meter and corrected to standard 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 carbonyls, and covered with aluminum foil to prevent photolysis reactions from occurring in solution.

Potassium Iodide (KI) Scrubbers. We prepared KI traps by coating 1 m lengths of stainless steel tubing (1/4" o.d., 3/8" i.d.) with three volumes of a saturated KI solution. We dried the tubing with a stream of nitrogen and sealed the traps until used in the field. We established that the traps were capable of removing 99.5% of the ozone from a 1 ppm air standard sampled at a flow rate of 2 L/min prior to field sampling.

Preparation of Samples and Field Blank. The field blank was a 0.01 mM aqueous solution of PFBHA kept in an ice bath with the impingers during sampling. We added 1 Φ g of 4-fluorobenzaldehyde, the internal standard to each sample, and the PFBHA was allowed to react with the analytes for 24 hours at room temperature. We acidified the solution with 5 mL 18 N H_2SO_4 . For the 400 mL samples, we extracted the derivatives from solution by using C_8 solid phase cartridge (6 mL, 500 mg; Varian Associates, Sugarland, TX), and eluting the derivatives from the cartridges with 12 mL of methyl *tert*-butyl ether (MTBE). We extracted the PFBHA derivatives from 10 mL water by liquid-liquid extraction into MTBE. In both cases, we passed the extract through a Na_2SO_4 chromatographic column (6 mm i.d. x 6.5 cm) to remove water, and reduced the volume to 475 Φ L by passing a gentle stream of nitrogen through the extract. We transferred a 200 Φ L aliquot to another vial, evaporated the solvent with nitrogen, and redissolved the extract in 200 Φ L of BSTFA. We evacuated air from the vial, sealed and heated to 42°C, and the BSTFA was allowed to react with the PFBHA derivative at this temperature for 12 hours. (The chemical reactions that derivatize carbonyls and hydroxy carbonyls are presented in Figure I).



Derivatization of a Hydroxy Carbonyl with *O*-(2,3,4,5,6-pentafluorobenzyl)-hydroxylamine (PFBHA) and bis (trimethylsilyl) trifluoroacetamide (BSTFA)



Figure I. Chemical Reactions Elucidating PFBHA Derivatization of Carbonyls and PFBHA/BSTFA Derivatization of Hydroxy Carbonyls. (Note: PFBHA derivatization forms *syn*- and *anti*- oxime isomers).

Gas Chromatography/Ion Trap Mass Spectrometry (GC/ITMS). We identified and quantified the carbonyls and hydroxy carbonyls by using a Varian Star 3400 CX gas chromatograph with a programmable injector interfaced to a Saturn 2000 ion trap mass spectrometer. We employed a RTX-5MS chromatographic column (60m, 0.32 mm i.d., 0.25 μ m film thickness). The oven of the gas chromatograph was held at 69°C for 1 minute. The temperature was then increased to 100°C at a rate of 5 °C/min., and then 320°C at a rate of 10°C/min., and held at 320°C for 4 minutes. We set the injector temperature to increase from 280°C to 320°C at 180°C/min.

Electron-impact ionization experiments were conducted at an ion trap temperature of 200°C, a filament current of 10 μ amps, and a target value that ranged from 19,000-44,000 with an ionization time of 25 ms. The mass spectra was obtained over a mass range of 50 to 650 amu. For methane chemical ionization, the methane pressure was set so that the ratio of m/z 17:29 was about 1:1. We employed a filament current of 10 μ amps and an ion source temperature of 150°C. The target value was optimized to 10^5 gain prior to the onset of analysis and varied from 10,000 to 28,000. The pentafluorobenzyl alcohol (PFBOH) chemical ionization was introduced into the mass spectrometer by a method similar to that of Chien *et al.*, 1998 (32).

III. Results and Discussion

Comparison of Sensitivity and Chromatography for PFBHA and PFBHA/BSTFA derivatives. We observed poor chromatography, and hence sensitivity 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 (33) proved unsatisfactory due to poor derivatization yields. We began utilizing *bis* (trimethylsilyl) trifluoroacetamide (BSTFA) as a silylating reagent after learning that Yu *et al.*, 1998 (34) were developing a similar approach to identify multifunctional carbonyls.

We demonstrate the improvements in chromatography and sensitivity that is achieved by silylating PFBHA derivatives of hydroxy carbonyls and oxo acids with BSTFA in Figure II. The

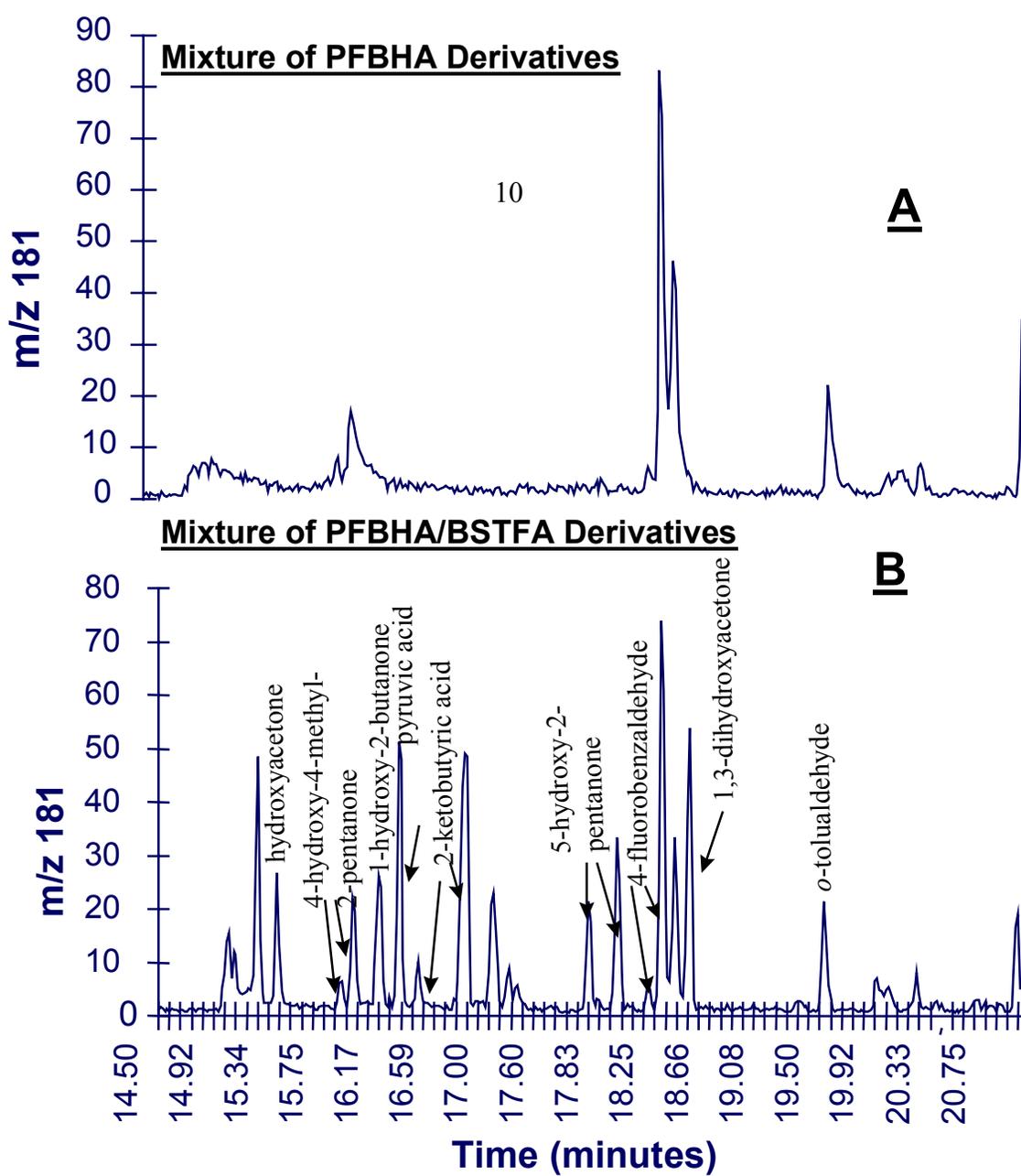


Figure II. A Comparison of the Chromatography for a Mixture of PFBHA and PFBHA/BSTFA Derivatives.

top (A) chromatogram was obtained from the analysis of 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 were reacted with BSTFA. For certain compounds, the *syn*- and *anti*- pentafluorobenzoyloxime isomers are resolved as evident by two gas chromatographic peaks. For other compounds, we assume co-elution of the isomers due to the presence of only one gas chromatographic peak.

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 derivatives were reacted with BSTFA. We also discovered that the intensity of $(M+H)^+$ and $(M+181)^+$ ions critical for molecular weight for PFBHA/BSTFA derivatives is greater than for pentafluorobenzyl derivatives of oxo acids. In past work, we derivatized the hydroxyl group of oxo acids with pentafluorobenzyl bromide (PFB), but identification of unknown compounds may be difficult as indicated by the low intensity (<10%) of the $(M+H)^+$ and $(M+181)^+$ ions in the methane CI mass spectra of PFB derivatives of glyoxylic acid, pyruvic acid and keto butyric acid. We enhanced the intensity of the molecular and *pseudo*- molecular ions by using PFBHA/BSTFA derivatization and methane or PFBOH CI ion trap mass spectrometry. This enhancement is exemplified in Figure III which presents a comparison of PFBOH CI ion trap mass spectra for pentafluorobenzyl and PFBHA/BSTFA derivatives of pyruvic acid. 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. We therefore suggest derivatization of hydroxy carbonyls and oxo acids with PFBHA and BSTFA due to the excellent chromatography, and improved sensitivity that is achieved, 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.

Effect of Ionization Mode on Generation of Molecular and *Pseudo*- Molecular Ions. We explored PFBOH as a reagent to effect the formation of molecular and *pseudo*- molecular ions by comparing the EI, methane CI and PFBOH CI mass spectra of model compounds (See Table II). As expected from previous work (8, 33, 35), the m/z 181 fragment ion $(C_6F_5CH_2)^+$ is the base

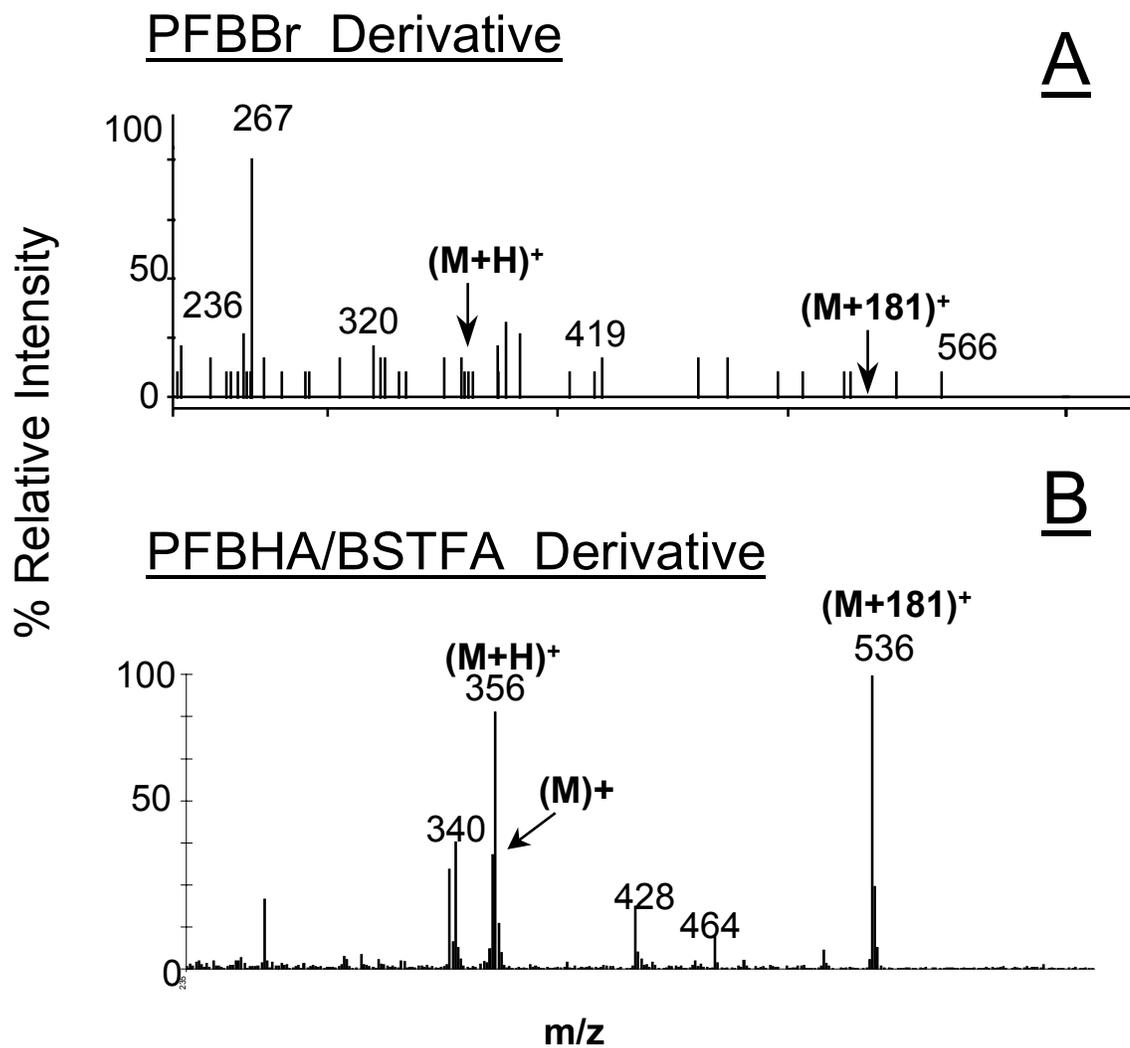


Figure III. A Comparison of PFBOH Chemical Ionization Ion Trap Mass Spectra of PFBBR (A) and PFBHA/BSTFA (B) Derivatives of Pyruvic Acid.

peak in the EI mass spectra of the PFBHA derivatives, and little structural information is evident in the mass spectra. Functional group information can be gleaned from the EI mass spectra of PFBHA/BSTFA derivatives. The base peak in the EI mass spectra of the PFBHA/BSTFA derivatives can either be a $(M-CH_3)^+$ fragment ion, the m/z 181 pentafluorobenzyl ion or a fragment ion at m/z 73 $[Si(CH_3)_3]^+$. The $(M-CH_3)^+$ ion or the ion at m/z 73 is typically 40-100% relative intensity. Hence, the m/z 181 establishes the presence of a carbonyl moiety; the ion at m/z 73 indicates the presence of a hydroxyl or carboxyl group; and the $(M-CH_3)^+$ fragment ion can indicate the molecular weight of the derivative.

Also as expected from previous work, methane chemical ionization promotes the generation of $(M+H)^+$ ions. These ions are often the base peak, but if not, they are present at high relative intensities as indicated by relative intensities of 16-92% for glyoxal, methyl glyoxal and hydroxy acetone. Low intensity (<10%) $(M-H)^+$, $(M)^+$ and $(M+181)^+$ ions are also present in the methane chemical ionization mass spectra. Molecular weight determinations of PFBHA and PFBHA/BSTFA derivatives can be made by observing the juxtaposition of these molecular and *pseudo*-molecular ions.

PFBOH enhances the relative intensity of the $(M-H)^+$, $(M)^+$, $(M+H)^+$ and $(M+181)^+$ ions compared to the methane CI ion trap mass spectra for the PFBHA and PFBHA/BSTFA derivatives. For glyoxylic acid, the relative intensities intensity in the methane CI spectra $(M)^+$, $(M+H)^+$ and $(M+181)^+$ ions are 2, 11, and 0.2% compared to 38, 89 and 96%, respectively in the PFBOH chemical ionization mass spectra.

In summary, the EI, methane CI and PFBOH CI complement each other. 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 and *pseudo*-molecular ions are present in the methane chemical ionization mass spectra which are enhanced when PFBOH is employed as a chemical ionization reagent. 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

Table II. The 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				
		<u>(M-H)⁺</u>	<u>(M)⁺</u>	<u>(M+H)⁺</u>	<u>(M+181)⁺</u>	<u>Other</u>
<u>PFBHA Derivative</u>						
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 II. The Effect of Ionization Mode on Production of Molecular and <i>Pseudo</i> - Molecular Ions for PFBHA and PFBHA/BSTFA Derivatives of Carbonyls (continued).						
Compound (molecular weight of the derivative)	Mode of Ionization	% Relative Intensity of Ions				
		<u>(M-H)⁺</u>	<u>(M)⁺</u>	<u>(M+H)⁺</u>	<u>(M+181)⁺</u>	<u>Other</u>
PFBHA/BSTFA Derivatives						
Hydroxy acetone (345)	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	66.0	7.0	
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-Keto butyric 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	

derivative. As in the mass spectra of the PFBHA derivatives, molecular and *pseudo*- molecular ions are present in the methane chemical ionization mass spectra which 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 is substantial, PFBOH chemical ionization may be preferred over methane chemical ionization.

Identification of Carbonyls. We identified methyl vinyl ketone, methacrolein, methyl glyoxal, glycolaldehyde and hydroxy acetone in sample extracts collected in Azusa, CA. In sample extracts collected in Davis, CA, we identified methacrolein, methyl vinyl ketone, 3-hydroxy-2-butanone, and hydroxy acetone. Although 2,3-butanedione and glyoxal were also identified in Davis air, the higher concentration of these compounds in samples collected in the absence of KI scrubbers compared to those collected in the presence of KI scrubbers indicate that these compounds may be formed by the oxidation of other species.

Methyl vinyl ketone, methacrolein, methyl glyoxal, glycolaldehyde, and hydroxy acetone are photooxidation products of isoprene, and methyl glyoxal, glycolaldehyde and hydroxy acetone are photooxidation products of alkyl benzenes (6, 8-12, 36). Few ambient measurements exist of methacrolein and methyl vinyl ketone (15, 19, 37-41), and fewer measurements exist of glyoxal, methylglyoxal and glycolaldehyde (23, 25, 27, 28, 30, 31). To our knowledge, no measurement of 3-hydroxy-2-butanone or hydroxy acetone has been reported in the scientific literature.

We identified the compounds by establishing reasonable 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. Although this approach is acceptable, we also confirmed the identity of the compounds by interpreting the methane CI and PFBOH CI mass spectra. Here, we present three case studies that establish the power of PFBOH to identify compounds in the ambient environment. In case I, PFBOH CI was critical to identify glycolaldehyde. In case II, PFBOH CI was essential to identify hydroxy acetone, and in case III, we discuss the merits of PFBOH CI to confirm the presence of glyoxal.

Case I: *Identification of glycolaldehyde in a sample extract of Azusa, CA air in the presence*

of a co-eluting interferant. In Figure IV, we present the EI, methane CI and PFBOH CI mass spectra of a PFBHA/BSTFA derivative in a sample extract. In the EI mass spectra (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 carbonyl. In this case, the $(M-CH_3)^+$ ion characteristic of the BSTFA derivatives could either be the ion at m/z 312 or the m/z 387 ion. We attempted to determine which ion was a fragment ion from the PFBHA/BSTFA derivative by conducting a methane CI experiment (B). Although the juxtaposition of the m/z 328 and m/z 312 ions indicate that these ions are the $(M+H)^+$ and $(M-CH_3)^+$ ions, respectively, the ion at m/z 418 confuses their identification. The juxtaposition of the m/z 328 and 508 ions in the PFBOH CI mass spectra suggest that they are the $(M+H)^+$ and $(M+181)^+$ ions, respectively arising from the same derivative. Similarly, the juxtaposition of the ions at m/z 418 and 598 indicate that these ions are the $(M+H)^+$ and $(M+181)^+$ ions from the same derivative. We thus conclude that the mass spectra is of two co-eluting compounds. One which has a molecular weight of 327 and the other which has a molecular weight of 417. The compound with the molecular weight of 327 was tentatively identified as the PFBHA/BSTFA derivative of glycolaldehyde, 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 interpretation of the PFBOH CI mass spectra.

Case II. Identification of hydroxy acetone in a sample extract Davis, CA air in the presence of a co-eluting interferant. We present the EI and PFBOH CI mass spectra of a chromatographic peak in an extract of Davis, CA air in Figure V. We tentatively identified the compound as the PFBHA/BSTFA derivative of hydroxy acetone by observing an ion at m/z 326 in the EI mass spectra (A) that corresponds to the $(M-CH_3)^+$ ion, and matching the retention time of the gas

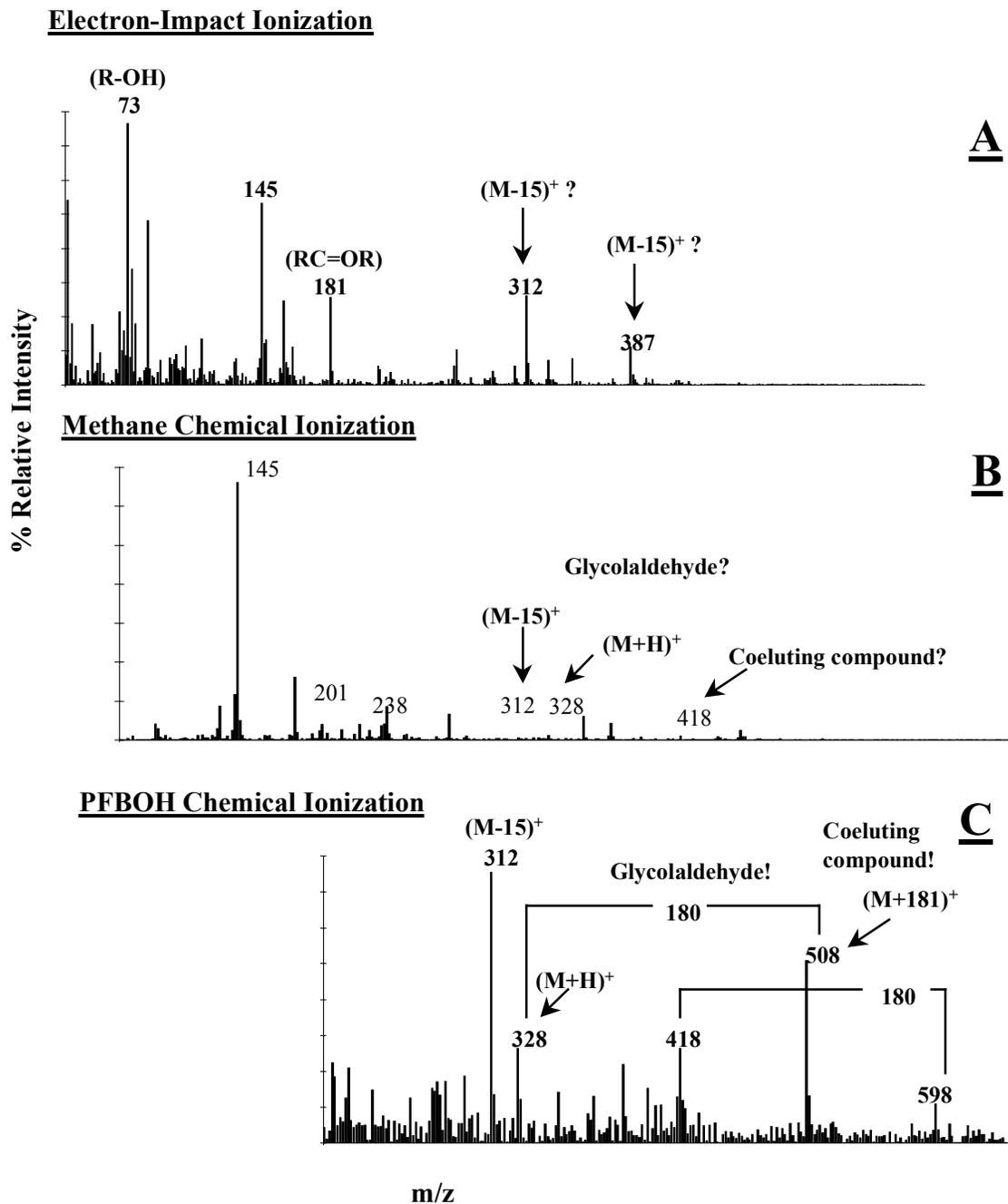


Figure IV. Electron-Impact Ionization (A), Methane Chemical Ionization (B) and PFBOH Chemical Ionization (C) Mass Spectra of a Gas Chromatographic Peak in a PFBHA/BSTFA Derivatized Sample Extract of Azusa, CA Air.

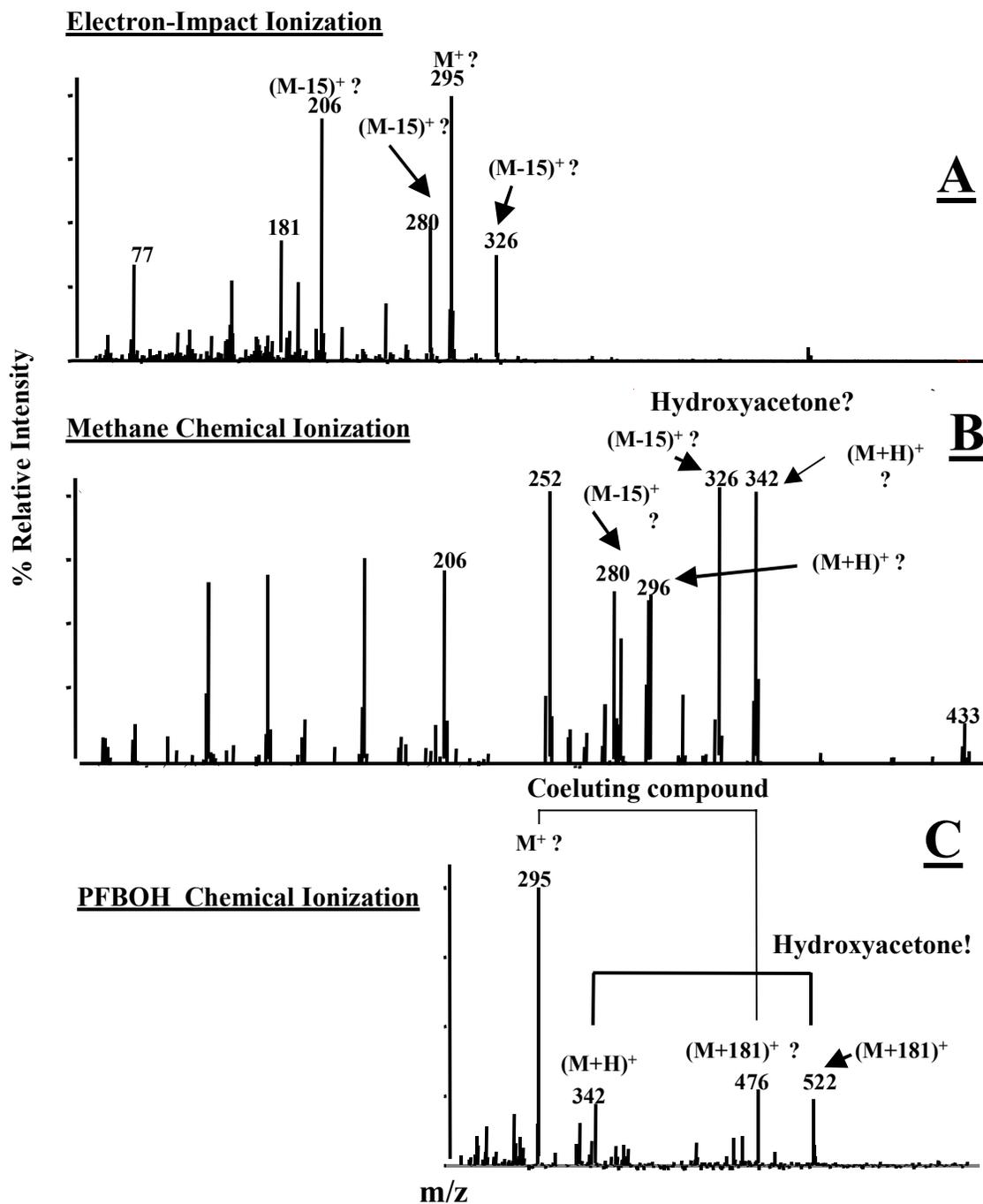


Figure V. Electron-Impact Ionization (A), Methane Chemical Ionization (B) and PFBOH Chemical Ionization (CI) Mass Spectra of a Gas Chromatographic Peak in a PFBHA/BSTFA Derivatized Sample Extract of Davis, CA Air.

chromatographic peak to that of an authentic standard of the hydroxy acetone derivative. We were not entirely comfortable with basing the identification on the retention time and the EI mass spectra in this case because of the presence of high intensity ions at m/z 206, 280 and 295. These ions co-elute with the ion at m/z 326 but are not present in the EI mass spectra of an authentic standard. We hypothesized that these ions were generated from two other derivatives. One derivative with a molecular weight of 221 (*i.e.*, the m/z 206 ion is an $(M-CH_3)^+$ ion), and one derivative with a molecular weight of 295 (*i.e.*, the m/z 280 ion is a $(M-CH_3)^+$ ion of the molecule yielding an $(M)^+$ in at m/z 295).

We confirmed the identity of hydroxy acetone by observing ions at m/z 326, 342 and 522 in the PFBOH CI mass spectra that correspond to the $(M-CH_3)^+$, $(M+H)^+$, and $(M+181)^+$ of the PFBHA/BSTFA derivative of hydroxy acetone, respectively. We could not confirm the presence of derivatives with a molecular weight of 221 or m/z 295. We expect ions at m/z 280, 296 and 477 that correspond to the $(M-CH_3)^+$, $(M+H)^+$ and $(M+181)^+$, respectively if a derivative with a molecular weight of 221 were present.

Case III. Confirmation of glyoxal in Davis, CA air by using PFBOH chemical ionization.

We present the EI, methane CI, and PFBOH CI mass spectra of glyoxal from an extract of an air sample in Figure VI. In the EI mass spectra (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 spectra 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 spectra (C).

Summary. It is possible to identify carbonyls for which authentic standards exist by matching retention times and the EI mass spectra of the analyte in the sample to an authentic standard. In cases, where molecular weight information is not apparent, or in which the compound is present

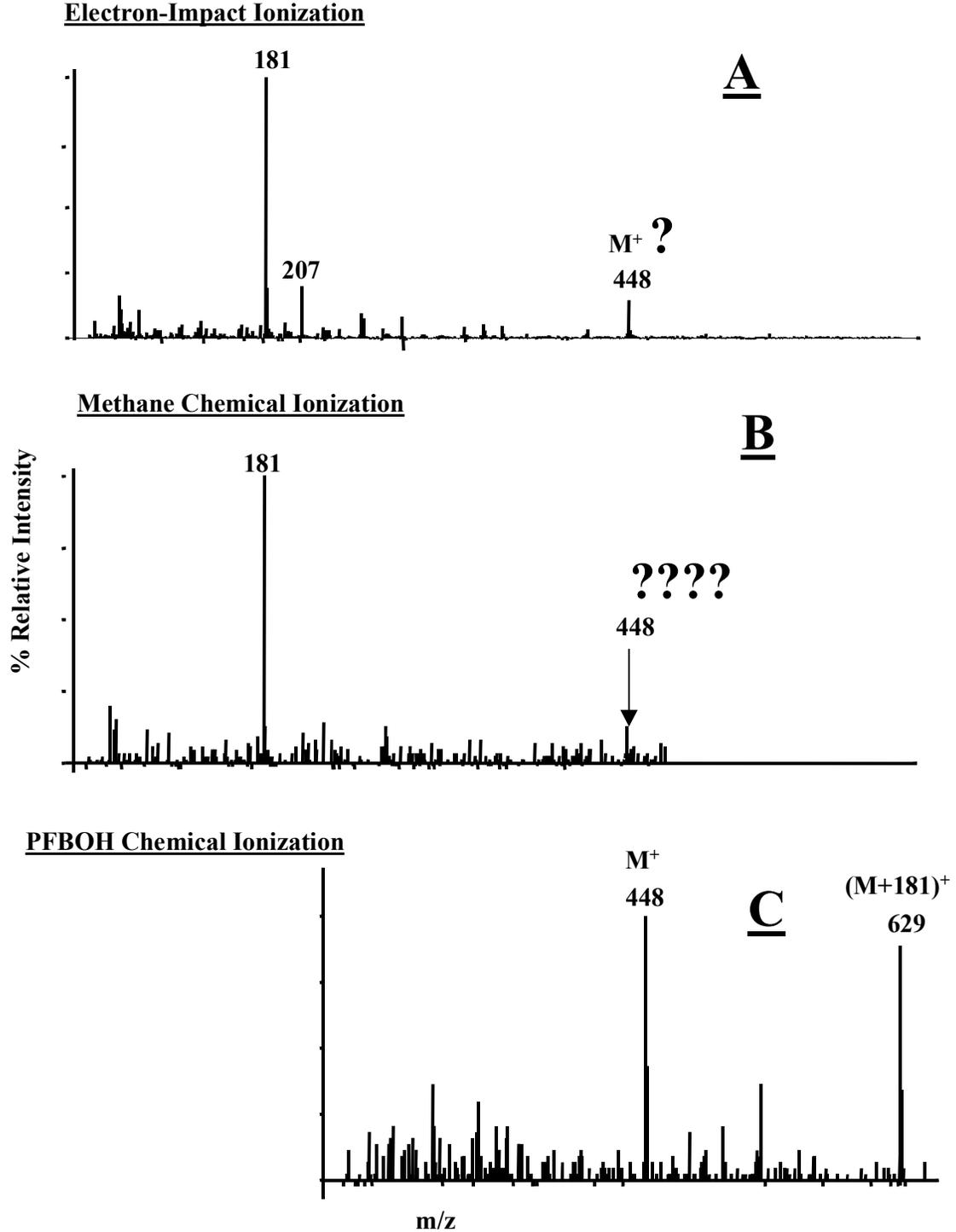


Figure VI. Electron-Impact Ionization (A), Methane Chemical Ionization (B) and PFBOH Chemical Ionization (CI) Mass Spectra of a Gas Chromatographic Peak in a Sample Extract of Davis, CA Air Derivatized with PFBHA.

near the detection limit, the identification can be strengthened by the presence of molecular ions in the methane CI mass spectra. Novel carbonyl intermediates have and can be identified by this approach (8, 9). In the ambient environment, the mixture of compounds is more complex and the concentration of the analyte may be lower than in chamber studies. By using PFBOH CI, we can identify or confirm the identity of carbonyls, dicarbonyls, hydroxy carbonyls and oxo acids that exist at trace levels in complex mixtures. The mass spectra are easy and straight forward to interpret since one need only search for ions whose mass differs by 180. Moreover, the PFBOH CI mass spectra may yield sufficient information to obviate the need for methane CI for samples collected in the ambient atmospheric environment.

Quantification. We establish the ability of the method to provide quantitative data by exploring the recoveries of the analytes in the impingers; evaluating the linear dynamic range of the calibration curves, and quantifying methyl vinyl ketone, methacrolein, and methyl glyoxal, glycolaldehyde and hydroxy acetone in sample extracts of Azusa, CA air. We were unable to quantify the analytes in sample extracts of Davis, CA air because the presence of compounds in the fourth impinger raises uncertainty with respect to losses from this impinger.

Collection of Analytes in Impingers. In Table IIIA, IIIB and IIIC, we present the data for the percent of the total concentration collected in each impinger for replicate samples. On September 23rd and 24th (Table IIIA and IIIB), the analytes were present in the first two impingers. For the samples collected on September 24th (Table IIIC), methacrolein and glycolaldehyde were measured in the fourth impinger for sample 1 and 2, respectively. The difference between replicate impinger samples could be due to variability in either the flow-rate or the temperature. However, we checked these variables throughout the sampling period and did not witness any obvious differences. Thus, at this time we cannot explain the discrepancies between replicate measurements.

Linear dynamic range of calibration curves. The linear dynamic range of the calibration curve was investigated by examining the r^2 of the linear regression equation derived from a plot of the

response of the analyte to the internal standard, by examining the agreement among the relative response factors (RRF), and by conducting a Q test, a statistical outlier test (42) to determine which RRF values could be eliminated at a 95% confidence level. Instrument optimization of the detection method may correct the significant differences among the RRF.

The outlying values, those in which a 5% probability exists that the value is not an outlier were not used in constructing the standard calibration curve. (The response factor (RF) = A_a/A_{is} where A_a and A_{is} are the peak area of the analyte and internal standard, respectively. The relative response factor (RRF) = $(A_a)(C_{is})/(A_{is})(C_a)$, where A_a and C_a are the area and concentration of the analyte, and A_{is} and C_{is} are the concentration and area of the internal standard, respectively). For environmental analyses, a percent relative standard deviation (% RSD) of 20-30% among the RRF is generally acceptable. (The data employed to calculate the response factor and relative response factor is presented in the Appendix).

The RRF for the PFBHA derivatives and PFBHA/BSTFA derivatives are presented in Tables IVA, IVB, And IV C and Tables VA and VB. The values determined to be outliers are bolded and italicized. The % RSD, the linear regression equation and the r^2 of the linear regression equation are presented before and after elimination of the outliers. In all cases, the % RSD among the relative response factors was reduced by to about # 32% by excluding outliers. Most notably, the % RSD was decreased from 107% to 19% on one day for the PFBHA derivative of methyl vinyl ketone; from 40 to 29% RSD for data obtained on one day for the PFBHA derivative of methacrolein; from 57 to 25% on one day for the PFBHA derivative of methyl glyoxal. In addition the agreement among the RRF was decreased from 37-115% to 13-32% and from 18-63% to 18-28% for the PFBHA/BSTFA derivative of glycolaldehyde and hydroxy acetone, respectively. The r^2 of the linear regression equation also improved by exclusion of outliers, but less dramatically than the %RSD among the relative response factors. The only case in which the r^2 was significantly increased was from 0.74 to 0.95 on one day for the PFBHA/BSTFA. Since the response of the analyte to the internal standard fell within the concentration range employed, we utilized linear regression equations from the data which eliminated the outliers to quantify the analytes in the sample extracts.

Table IIIA. % Total Concentration of Methyl Vinyl Ketone, Methacrolein, Methyl Glyoxal, Glycoaldehyde and Hydroxy Acetone in Impingers Used to Sample Air in Azusa, CA			
Date and Time: 9/23/97; 1:00-4:00 p.m.		% Total Concentration	
Compound	Impinger	Sample 1	Sample 2
Methyl vinyl ketone	1	100	71
	2	ND	21
	3	ND	ND
	4	ND	ND
Methacrolein	1	71	44
	2	29	16
	3	ND	ND
	4	ND	ND
Methyl Glyoxal	1	ND	ND
	2	ND	ND
	3	ND	ND
	4	ND	ND
Glycolaldehyde	1	100	100
	2	ND	ND
	3	ND	ND
	4	ND	ND
Hydroxy Acetone	1	ND	100
	2	ND	ND
	3	ND	ND
	4	ND	ND

Table IIIB. % Total Concentration of Methyl Vinyl Ketone, Methacrolein, Methyl Glyoxal, Glycolaldehyde and Hydroxy Acetone in Impingers Used to Sample Air in Azusa, CA			
Date and Time: 9/23/97; 5:00-8:00 p.m.		% Total Concentration	
Compound	Impinger	Sample 1	Sample 2
Methyl vinyl ketone	1	100	100
	2	ND	ND
	3	ND	ND
	4	ND	ND
Methacrolein	1	92	94
	2	8	6
	3	ND	ND
	4	ND	ND
Methyl Glyoxal	1	ND	ND
	2	ND	ND
	3	ND	ND
	4	ND	ND
Glycolaldehyde	1	100	100
	2	ND	ND
	3	ND	ND
	4	ND	ND
Hydroxy Acetone	1	ND	ND
	2	ND	ND
	3	ND	ND
	4	ND	ND

Table III.C. % Total Concentration of Methyl Vinyl Ketone, Methacrolein, Methyl Glyoxal, Glycolaldehyde and Hydroxy Acetone in Impingers Used to Sample Air in Azusa, CA			
Date and Time: 9/24/97; 1:00-5:00 p.m.		% Total Concentration	
Compound	Impinger	Sample 1	Sample 2
Methyl vinyl ketone	1	100	100
	2	ND	ND
	3	ND	ND
	4	ND	ND
Methacrolein	1	33	57
	2	29	40
	3	27	3
	4	11	ND
Methyl Glyoxal	1	100	96
	2	ND	4
	3	ND	ND
	4	ND	ND
Glycolaldehyde	1	100	59
	2	ND	17
	3	ND	8
	4	ND	6
Hydroxy Acetone	1	100	100
	2	ND	ND
	3	ND	ND
	4	ND	ND

Table IVA. Relative Response Factors (RRF) ¹ for the PFBHA Derivative of Methyl Vinyl Ketone.					
Date of Analysis 1/20/98			5/5/98	6/28/98	
Conc. (pg/ Φ L)	RRF	Mean S.D %RSD	RRF	RRF	Mean S.D. %RSD
50	0.23 0.17	0.20 0.04 21	0.15	0.16	
75	0.20 0.18	0.19 0.01 7	0.92	0.06 0.04	0.05 0.01 28
100	0.18 0.16	0.17 0.01 8	0.21	ND ND	
250	0.13 0.13	0.13 0.00 0	0.16	0.16 0.15	0.16 0.01 5
500	0.15 0.13	0.14 0.01 10	0.15	0.17 0.12	0.15 0.04 24
1000	0.16 0.23	0.20 0.05 25	0.13	0.15 0.16	0.16 0.01 5
Mean S.D. %RSD	0.17 0.04 21		0.27 0.29 107	0.13 0.05 37	
Regression Equation (r²)	y=0.00019x-0.00341 (0.94)		y=0.00011x+0.01575 (0.81)	y=0.00016x-0.00308 (0.99)	
Mean** S.D. %RSD			0.16 0.03 19	0.15 0.02 10	
Regression Equation (r²)			y=0.00012x-0.00766 (0.99)	y=0.00016x-0.00097 (0.99)	

¹RRF = (Peak Area_{analyte})*(Concentration)_{internal standard}/(Peak Area_{internal standard})*(Concentration)_{analyte}

**Outlier values presented in bolded italics were not employed in calculation of average and standard deviation

ND=Not Detected

Table IVB. Relative Response Factors (RRF) ¹ for the PFBHA Derivative of Methacrolein.					
Date of Analysis 1/20/98			5/5/98	6/28/98	
Conc. (pg/ Φ L)	RRF	Mean S.D. %RSD	RRF	RRF	Mean S.D. %RSD
50	0.63 0.62	0.63 0.01 1	0.61	0.61	
75	0.63 0.50	0.57 0.09 16	0.60	0.57 0.49	0.53 0.06 11
100	0.55 0.55	0.55 0.00 0	0.63	<i>0.007</i> <i>0.005</i>	0.006 0.002 33
250	0.59 0.62	0.61 0.02 4	0.63	0.74 0.78	0.76 0.03 4
500	0.59 0.37	0.48 0.16 32	0.56	0.54 0.51	0.53 0.02 4
1000	0.69 0.86	0.78 0.12 16	0.48	0.54 0.54	0.54 0.002 0
Mean S.D. %RSD	0.60 0.12 19		0.59 0.06 10	0.53 0.21 40	
Regression Equation (r²)	y=0.00076x-0.02074 (0.94)		y=0.0047x-0.02074 (0.99)	y=0.00055x+0.00206 (0.97)	
Mean** S.D. %RSD				0.56 0.16 29	
Regression Equation (r²)				y=0.00053x+0.01062 (0.98)	

¹RRF = (Peak Area_{analyte})*(Concentration)_{internal standard}/(Peak Area_{internal standard})*(Concentration)_{analyte}

**Outlier values presented in bolded italics were not employed in calculation of average and standard deviation

ND=Not Detected

Table IVC. Relative Response Factors (RRF) ¹ for the PFBHA Derivative of Methyl glyoxal.					
Date of Analysis 1/20/98			5/5/98	6/28/98	
Conc. (pg/ Φ L)	RRF	Mean S.D. %RSD	RRF	RRF	Mean S.D. %RSD
50	0.14 0.08	0.11 0.04 39	0.09	0.04	
75	0.11 0.09	0.10 0.01 14	0.16	0.07 0.20	0.14 0.08 61
100	0.10 0.09	0.10 0.01 7	0.10	0.10 0.08	0.09 0.01 16
250	0.11 0.12	0.12 0.01 6	0.10	0.09 0.05	0.07 0.03 40
500	0.12 0.08	0.10 0.03 28	0.12	0.06 0.07	0.07 0.01 14
1000	0.08 0.13	0.11 0.04 34	0.09	0.07 0.05	0.06 0.01 24
Mean S.D. %RSD	0.10 0.02 20		0.11 0.03 24	0.08 0.04 57	
Regression Equation (r²)	y=0.00011x-0.00048 (0.93)		y=0.00010x+0.00214 (0.98)	y=0.00006x+0.00194 (0.94)	
Mean** S.D. %RSD				0.07 0.02 25	
Regression Equation (r²)				y=0.00006x+0.00080 (0.96)	

¹RRF = (Peak Area_{analyte})*(Concentration)_{internal standard}/(Peak Area_{internal standard})*(Concentration)_{analyte}

**Outlier values presented in bolded italics were not employed in calculation of average and standard deviation

ND=Not Detected

Table VA. Relative Response Factors (RRF) for the PFBHA/BSTFA Derivative of Glycolaldehyde.						
Date of Analysis 1/11/98			3/27/98		6/28/98	
Conc. (pg/ Φ L)	RRF	Mean S.D. %RSD	RRF	Mean S.D. %RSD	RRF	Mean S.D. %RSD
50	<i>3.12</i> <i>2.64</i>	2.88 0.34 12	1.85 1.25	1.55 0.42 65	1.71 1.96	1.84 0.18 10
75	<i>2.62</i> <i>2.67</i>	2.65 0.04 1	1.84 1.84	1.84 0.01 0	<i>8.80</i> <i>9.17</i>	<i>8.99</i> <i>0.26</i> 3
100	1.63 1.80	1.72 0.12 7	1.26 1.55	1.41 0.21 15	1.26 1.12	1.19 0.10 8
250	1.53, 1.41 1.54, 1.54 1.64	1.53 0.08 5	<i>0.48</i> 0.81	0.64 0.23 36	0.95 0.94	0.95 0.01 1
500	1.78 1.95	1.30 0.12 6	1.02 1.11	1.07 0.06 6	1.45 1.47	1.46 0.01 1
1000	1.35 1.24	1.35 0.08 6	0.87 0.85	0.86 0.01 2	1.12 1.21	1.17 0.06 5
Mean	1.83		1.16		2.59	
S.D.	0.69		0.46		2.99	
%R.S.D.	37		40		115	
Regression Equation (r²)	y=0.000127x+0.097 34 (0.96)		y=0.00085x+0.03072 (0.97)		y=0.00101x+0.15578 (0.74)	
Mean**	1.58		1.30		1.32	
S.D.	0.21		0.41		0.33	
%R.S.D.	13		32		25	
Regression Equation (r²)	y=0.00127x+0.1000 4 (0.96)		y=0.00085x+0.038752 (0.98)		y=0.00115x+0.03706 (0.95)	

RRF = (Peak Area_{analyte})*(Concentration)_{internal standard}/(Peak Area_{internal standard})*(Concentration)_{analyte} **Outlier values presented in bolded italics were not employed in calculation of average and standard deviation; ND=Not Detected

Table VB. Relative Response Factors (RRF) ¹ for the PFBHA/BSTFA Derivative of Hydroxy acetone.						
Date of Analysis 1/11/98			3/27/98		6/28/98	
Conc. (pg/ΦL)	RRF	Mean S.D. %R.S.D.	RRF	Mean S.D. %R.S.D.	RRF	Mean S.D. %R.S.D.
50	<i>0.35</i> <i>0.94</i>	0.65 0.42 65	0.29 0.16	0.22 0.09 42	0.22 0.30	0.26 0.06 22
75	0.47 0.29	0.38 0.13 33	0.23 0.23	0.23 0.00 0	0.28 0.33	0.31 0.04 12
100	0.25 0.19	0.22 0.04 19	0.21 0.19	0.20 0.01 7	0.21 0.22	0.22 0.01 3
250	<i>0.07</i> , 0.33 0.28, 0.25 0.14	0.11 0.05 47	0.10 0.15	0.13 0.04 31	0.20 0.23	0.22 0.02 10
500	0.36 0.27	0.32 0.06 20	0.17 0.17	0.17 0.00 0	0.24 0.25	0.25 0.01 3
1000	0.26 0.24	0.25 0.01 6	0.15 0.14	0.15 0.01 5	0.18 0.22	0.20 0.03 14
Mean	0.31		0.18		0.24	
S.D.	0.20		0.05		0.04	
%R.S.D.	63		28		18	
Regression Equation (r²)	y=0.00025x+0.00438 (0.94)		y=0.00014x+0.00882 (0.94)		y=0.0002x+0.0064 (98)	
Mean**					0.24	
S.D.					0.04	
%R.S.D.					18	
Regression Equation (r²)					y=0.0002+0.0064 (0.98)	

¹RRF = (Peak Area_{analyte})*(Concentration)_{internal standard}/(Peak Area_{internal standard})*(Concentration)_{analyte}

**Outlier values presented in bolded italics were not employed in calculation of average and standard deviation; ND=Not Detected

Methyl vinyl ketone, methacrolein, methyl glyoxal, glycolaldehyde and hydroxy acetone in Azusa,

CA. We report concentrations of methyl vinyl ketone (MVK), methacrolein (MACR), methyl glyoxal, glycolaldehyde and hydroxy acetone in sample extracts of Azusa air on September 23 and 24, 1997 which were found at in the sample extract at levels that were 3x the standard deviation of the compounds calculated in the field blanks. (Data are presented in Table VI).

These compounds are photooxidation products of are photooxidation products of anthropogenic and biogenic hydrocarbon emissions. OH radical oxidation of isoprene yields methyl vinyl ketone and methacrolein as Afirst@ generation products. In turn, methyl vinyl ketone and methacrolein are oxidized to produce glycolaldehyde and methyl glyoxal, and methyl glyoxal and hydroxy acetone, respectively (6, 8, 10, 11). A paucity of studies have addressed the sources and distribution of these compounds (19, 23, 27, 28, 30, 31, 37-40, 43). Thus, processes affecting the behavior of these compounds in the ambient environment are poorly understood.

A matrix spike comprised of methyl vinyl ketone, methacrolein and hydroxy acetone was measured and the recovery of these compounds was calculated by dividing the amount measured by the amount enriched. The average recoveries of the compounds from the three sampling periods were 92% for methyl vinyl ketone, 97% for methacrolein, and 77% for hydroxy acetone. The method detection limit, (MDL) calculated at 3x the standard deviation of the compound 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 major impediment to the analysis of these and other carbonyls, most notably acetone, acetaldehyde and pyruvic acid, was contamination of the field blank. Sources of this contamination are the derivatization reagent, the water, the extraction solvent, or exposure to the air. Preliminary studies conducted in our laboratory to determine sources of the contaminants indicate that re-distillation of the solvents, re-crystallization of the PFBHA, oxidation of organic compounds in the water with potassium permanganate followed by distillation, and derivatization under nitrogen significantly reduces the levels of these compounds in the blank.

Each of the compounds were quantified at the 10 to 840 pptv level. Such levels are expected from chamber studies and previous field measurments. Studies conducted in rural environments



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

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

report ranges in concentrations of methyl vinyl ketone, and methacrolein from 0.1 to 3 ppbv (19, 38, 39). Concentrations of glyoxal, methyl glyoxal and glycolaldehyde in rural environments were reported to range from 0.07 to 0.74 ppbv, 0.1-0.14 ppbv; and 0.1-0.78 ppbv (27,28, 44), respectively. In light of the low photochemical activity on both days (Ozone concentrations were 30-40 ppbv), the concentrations reported agree well with other studies. For comparative purposes, concentrations of formaldehyde, which is the most abundant gas phase carbonyl in rural and urban environments ranges from 0.1 to 68 ppbv (19, 45). Thus, in rural environments the multifunctional carbonyls may be present in similar concentrations as formaldehyde, while in urban environments, it is expected that levels of the multifunctional carbonyls will exist at concentrations that may be 3 orders of magnitude lower than formaldehyde.

Photochemical models which consider yields of methyl vinyl ketone (MVK) and methacrolein (MACR) from isoprene, and hydroxyl radical rate constants for the photooxidation of these products, predict that the ratio of methyl vinyl ketone to methacrolein during daytime will be in the range of 1.4 to 2.5 if isoprene is the predominant source of these compounds (24). Most measurements of methyl vinyl ketone and methacrolein in the ambient atmospheric environment agree with this prediction (15, 19, 38, 43). These studies also indicate a diurnal pattern in this ratio. The ratio is low (about 1.4-1.5) in the early morning when isoprene emissions are also low. At mid-day the ratio rises to 2.0-2.5 reflecting an increase in the isoprene emissions as well as hydroxyl radical oxidation of isoprene and its photooxidation products. The ratio then generally decreases at night time with decreases in isoprene emissions and oxidation by ozone becoming the predominant oxidation pathway. In certain cases, anthropogenic and non-photochemical sources may cause the ratio between methyl vinyl ketone and methacrolein to be at the high end of the range (2.0-2.5) and levels of the products to be poorly correlated with isoprene emissions (39, 40).

We calculated a MVK/MACR ratio of 2.8 for the extract of sample 1 collected on September 23 from 1:00-4:00 p.m., and a ratio of 1.6 and 1.2 for extracts of samples 1 and 2 collected later in the

day (5:00-8:00 p.m.). For the extract of sample 1 collected on September 24, we calculated a MVK/MACR ratio of 1.5. The decrease in the ratio from 2.8 in the extract of a sample collected from 1:00 to 4:00 p.m. to an average of 1.4 for extracts of samples collected from 5:00 to 8:00 p.m. is expected in view of lower photochemical activity during the latter time period. (On September 23, the average ozone level during 1:00 - 4:00 p.m. was 53 ppb, and the average ozone concentration was 34 ppb during the 5:00-8:00 p.m. period). A low MVK/MACR ratio on September 24 is likely due to lower photochemical activity on this day. September 23 was a bright and sunny day, whereas September 24 was an overcast day with lower average levels of ozone (24 ppb) than the previous day.

We obtained reasonable agreement between replicates of samples for methyl vinyl ketone and methacrolein in the extract of the sample collected on September 23 from 1:00-4:00, and for methyl vinyl ketone and methacrolein in the extract of samples collected later in the day. On September 24, we obtained reasonable agreement between concentrations of methyl vinyl ketone, methyl glyoxal, and hydroxy acetone. We are uncertain of the cause for discrepancies between duplicate measurements of the other compounds, and thus further work is needed to improve the precision of the measurements.

Interferences from Ozone. We compare the total concentration of the analytes measured in the four impingers in to determine if removal of ozone is necessary (See Table VII). The inlets of the

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

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. Interestingly, the opposite trend was observed for 2,3-butanedione and glyoxal. It is unlikely that they were sorbed onto the stainless steel tubing. These data also suggest that methyl vinyl ketone and methacrolein were oxidized in solution, and that other 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.

IV. Summary and Conclusions

We establish pptv levels of carbonyls, dicarbonyls and hydroxy carbonyls can be measured in air by sampling air with impingers filled with an aqueous solution of *O*-(2,3,4,5,6-pentafluorobenzyl)-

hydroxylamine (PFBHA). Reaction of the PFBHA derivatives of hydroxy carbonyls and oxo acids was necessary to detect pptv levels. We report the concentration of methyl vinyl ketone, methacrolein, methyl glyoxal, glycolaldehyde and hydroxy acetone in Azusa, CA air on September 23 and 24, 1997. Concentrations of these compounds range from 60 to 534 pptv. Such levels are expected in light of yields obtained in chamber studies, and the low photochemical on both days as evident by background concentrations of ozone (24-53 ppb). Most notably, we report the measurement of glycolaldehyde (69 to 840 pptv) and hydroxy acetone (300 to 534pptv). We also report the presence of methyl vinyl ketone, methacrolein, 3-hydroxy-2-butanone and hydroxy acetone in Davis, CA air. To our knowledge, this is the first report of hydroxy acetone and 3-hydroxy butanone.

PFBOH CI was essential to identify glycolaldehyde and hydroxy acetone in the presence of co-eluting interferences, and to confirm the identity of glyoxal. 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 needed to gain insight into reactions between PFBOH and pentafluorobenzyl derivatives and to improve quantification at low levels. Quantification may be improved by utilizing isotopically labeled carbonyls, dicarbonyls and hydroxy carbonyls, and by employing high mass ions in the methane CI or PFBOH CI to quantify the derivatives. In cases in which co-eluting carbonyls are present, quantifying compound utilizing the m/z 181 ion in the EI mass spectra may not be the best approach. An advantage of the method is that it is suitable for the measurement of a broad range of carbonyls, including aldehydes, ketones, hydroxy carbonyls, epoxy carbonyls and oxo acids.

V. Recommendations

Further work is needed to improve the sampling and quantitative aspects of the method for sampling gas and particle phase polar organics. The employment of isotopically labeled standards needs to be explored to improve quantification, and instrumental conditions should be optimized to provide a linear dynamic range from 10 pg/ Φ L to 1ng/ Φ L. The use of mist (Cofer) scrubbers to sample at a rate of 35L/min. of air is currently underway. Since the results presented indicate that

100L of air must be collected, this improvement will enable collection of gas phase samples with a time resolution of about 5 minutes. Further work is needed to modify the approach to sample polar organics on size-segregated aerosols to improve an understanding of secondary organic aerosol formation. The distribution of carbonyls and multifunctional carbonyls using these tools needs to be investigated to gain insight into the role of biogenic and anthropogenic emissions on the generation of multifunctional carbonyls and their impact on tropospheric ozone and secondary organic aerosol formation.

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VIII. Appendix