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Development and Application of a Sensitive Method to Determine Concentrations of Acrolein and Other Carbonyls in Ambient Air

Thomas M. Cahill, M. Judith Charles, and Vincent Y. Seaman

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with a Critique by the HEI Health Review Committee

Research Report 149

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ABOUT HEI

The Health Effects Institute is a nonprofit corporation chartered in 1980 as an independent research organization to provide high-quality, impartial, and relevant science on the effects of air pollution on health. To accomplish its mission, the institute

- Identifies the highest-priority areas for health effects research;
- Competitively funds and oversees research projects;
- Provides intensive independent review of HEI-supported studies and related research;
- Integrates HEI's research results with those of other institutions into broader evaluations; and
- Communicates the results of HEI research and analyses to public and private decision makers.

HEI receives half of its core funds from the U.S. Environmental Protection Agency and half from the worldwide motor vehicle industry. Frequently, other public and private organizations in the United States and around the world also support major projects or certain research programs. HEI has funded more than 280 research projects in North America, Europe, Asia, and Latin America, the results of which have informed decisions regarding carbon monoxide, air toxics, nitrogen oxides, diesel exhaust, ozone, particulate matter, and other pollutants. These results have appeared in the peer-reviewed literature and in more than 200 comprehensive reports published by HEI.

HEI's independent Board of Directors consists of leaders in science and policy who are committed to fostering the public–private partnership that is central to the organization. The Health Research Committee solicits input from HEI sponsors and other stakeholders and works with scientific staff to develop a Five-Year Strategic Plan, select research projects for funding, and oversee their conduct. The Health Review Committee, which has no role in selecting or overseeing studies, works with staff to evaluate and interpret the results of funded studies and related research.

All project results and accompanying comments by the Health Review Committee are widely disseminated through HEI's Web site (*www.healtheffects.org*), printed reports, newsletters and other publications, annual conferences, and presentations to legislative bodies and public agencies.

ABOUT THIS REPORT

Research Report 149, *Development and Application of a Sensitive Method to Determine Concentrations of Acrolein and Other Carbonyls in Ambient Air,* presents a research project funded by the Health Effects Institute and conducted by Dr. Thomas M. Cahill of the Department of Integrated Natural Sciences, Arizona State University, Phoenix, and his colleagues. This report contains three main sections.

The HEI Statement, prepared by staff at HEI, is a brief, nontechnical summary of the study and its findings; it also briefly describes the Health Review Committee's comments on the study.

The Investigators' Report, prepared by Cahill et al., describes the scientific background, aims, methods, results, and conclusions of the study.

The Critique is prepared by members of the Health Review Committee with the assistance of HEI staff; it places the study in a broader scientific context, points out its strengths and limitations, and discusses remaining uncertainties and implications of the study's findings for public health and future research.

This report has gone through HEI's rigorous review process. When an HEI-funded study is completed, the investigators submit a draft final report presenting the background and results of the study. This draft report is first examined by outside technical reviewers and a biostatistician. The report and the reviewers' comments are then evaluated by members of the Health Review Committee, an independent panel of distinguished scientists who have no involvement in selecting or overseeing HEI studies. During the review process, the investigators have an opportunity to exchange comments with the Review Committee and, as necessary, to revise their report. The Critique reflects the information provided in the final version of the report.

HEI STATEMENT

Synopsis of Research Report 149

Development and Application of a Sensitive Method for Determination of Acrolein Concentrations in Ambient Air

BACKGROUND

Acrolein is a reactive aldehyde that injures the airways in humans and other species, and the U.S. Environmental Protection Agency lists it among the mobile-source air toxics that pose the greatest health risk. Information on the acrolein concentrations to which people are exposed is an important prerequisite for assessing the risk to human health. Despite some technological improvements, it remains difficult to accurately measure acrolein at low levels because, upon collection, it rapidly forms unstable intermediates that are difficult to differentiate and quantify.

In 2001 Dr. Judith Charles of the University of California–Davis responded to HEI Request for Preliminary Applications 00-3 with a proposal to develop a new method for measuring low levels of acrolein, crotonaldehyde, and other unstable aldehydes and apply the new method to assess exposure of tollbooth attendants in the San Francisco Bay area. The Research Committee believed that the method proposed by Charles and colleagues might be useful to accurately measure low levels of acrolein and recommended the study for 2 years of funding with a focus on the development of the sampling and analytic method to determine whether the proposed approach would be successful. During the middle of the second year, Dr. Charles became ill, and Dr. Thomas Cahill replaced her as the principal investigator and completed the study.

APPROACH

The investigators proposed to evaluate a sampling method that relies on the collection of acrolein in an aqueous medium containing sodium bisulfite, with which it forms a stable chemical reaction product. The overall aim of the study was to develop and optimize a method for the collection and analysis of acrolein and to evaluate the performance of the method by three different measures. One measure was collection efficiency, calculated as the concentration of acrolein in the first of two mist chambers in series relative to that in the second chamber, expressed as a percentage. The second measure was "spike recovery" (also defined as the mass balance), a measure of the overall carbonyl recovery, from collection to analysis. It was determined by adding a known carbonyl mass to a "spiking tube" placed upstream of the mist chamber and delivering it to the chamber by blowing pure nitrogen through the tube to simulate ambient collection conditions. Recovery was calculated as the percentage of the carbonyl mass in both chambers and remaining in the spiking tube relative to the mass added initially. The third measure was retention of deuterated acrolein-d_4 that had been added directly to the bisulfite solution as an internal standard before sampling, expressed as a percentage of the initial amount.

The investigators also measured acrolein levels in two field studies and compared the results with those obtained by other sampling methods.

RESULTS AND INTERPRETATION

Methods Development and Evaluation The sampler developed by Charles and Cahill, with Dr. Vincent Seaman, consists of a custom-built glass mist chamber in which air enters at a high flow rate and carbonyls are trapped in a solution of sodium bisulfite as carbonyl-bisulfite adducts. This reaction

This Statement, prepared by the Health Effects Institute, summarizes a research project funded by HEI and conducted by Dr. Thomas M. Cahill, Department of Integrated Natural Sciences, Arizona State University, Phoenix, Arizona, and colleagues. Research Report 149 contains both the detailed Investigators' Report and a Critique of the study prepared by the Institute's Health Review Committee.

is rapid (on the order of seconds) for all the carbonyls tested, and its rate is dependent on the concentration of bisulfite. The optimal sampling time for acrolein and the other carbonyls is 10 to 30 minutes at a flow rate of approximately 20 L/min at 21°C, and the optimal setup is two mist chambers in series. Longer sampling times, lower flow rates, and different temperatures were not evaluated. After collection, hydrogen peroxide is added to free the carbonyl from the adduct, and a derivatizing agent is added to form a carbonyl derivative suitable for gas chromatography with mass spectrometry. The calculated minimum detection limit for acrolein varied between experiments and ranged from 0.012 $\mu g/m^3$ (0.005 ppb) to 0.035 $\mu g/m^3$ (0.015 ppb), values well below the detection limits of other existing methods.

The collection efficiency of the mist chamber methodology was determined to be 80% in the laboratory and 71% in the field. Assuming that the collection efficiency is the same in the two chambers, it would be approximately 91% for the whole system in the field. This is only a relative measure of collection because it does not consider the initial amount of acrolein. Using the spike-recovery approach, the investigators found that 97% of the acrolein mass was recovered. For this test acrolein was dissolved in solvent and volatilized into a nitrogen stream. Although this approach was designed to simulate sampling in the field, it may not reflect entirely the actual conditions to which acrolein is exposed when sampled in ambient air. The test using the deuterated internal standard showed that, once the acrolein was trapped, 93% was retained throughout the analytic process. Because the deuterated species was dissolved in the bisulfite solution in the mist chamber, rather than bubbled into the solution in an air stream (as it would be under ambient sampling conditions), the measure of internal standard retention does not evaluate the efficiency with which the carbonyl in the ambient air stream is trapped in the mist chamber solution. Overall, the Review Committee—in its independent evaluation of the study—thought that these analyses were useful and showed a high level of acrolein recovery under laboratory conditions. However, the dynamic processes that lead to absorption of acrolein in the field may vary.

Field Studies The first field study, conducted at the Peace Bridge in Buffalo, New York, was an opportunity to compare the mist chamber method with two methods conventionally used to measure acrolein: the dansylhydrazine-based passive sampler and Occupational Safety and Health Administration Method 52. Comparison of the methods is difficult, however, because sampling times varied widely, with the mist chamber sampling for 10 minutes (sequential measurements were averaged over 12 hours) and the other two samplers sampling continuously for 12 to 24 hours. Nevertheless, the results showed that the mist chamber methodology can detect lower concentrations of acrolein than the other two devices. The second field study, conducted using multiple mist chamber systems in three locations in California, showed that the results of the method were reproducible and detected differences in concentrations at sites that had different carbonyl sources nearby.

CONCLUSIONS

The mist chamber methodology offers greater sensitivity for measuring acrolein than other existing methods. The analytic steps allow good separation of several carbonyls. The investigators evaluated chamber performance using three different approaches; however, they did not discuss the expected relationships among them. The approach of measuring the total recovery of acrolein from collection to analysis yielded a value of 97%.

Some limitations that might prevent the use of the method in population exposure studies are that the mist chamber has to be custom-built and is quite costly and that the method is labor-intensive, requiring a number of steps in the field. Development of more practical and less expensive approaches will be important if it is to be more widely used. The method performs optimally with very short sampling periods (10 minutes). The investigators provide a good rationale for having a sampler with a short sampling time to track short-term changes in acrolein concentrations. The Review Committee thought that a sampler with a wider range of sampling times would be more useful for measuring variations in ambient levels and personal exposures, without the need to combine data from repeated measurements taken over very shorts periods. Despite its potential limitations, the Investigators' Report shows that the mist chamber methodology can provide useful information when detailed temporal characterization of acrolein concentrations is needed.

INVESTIGATORS' REPORT

Development and Application of a Sensitive Method to Determine Concentrations of Acrolein and Other Carbonyls in Ambient Air

Thomas M. Cahill, M. Judith Charles (deceased), and Vincent Y. Seaman

Department of Integrated Natural Sciences, Arizona State University at the West Campus, Phoenix (T.M.C.); Department of Environmental Toxicology, University of California–Davis (M.J.C.); and Health Investigations Branch, Division of Health Studies, Agency for Toxic Substances and Disease Registry, Centers for Disease Control and Prevention, Atlanta, Georgia (V.Y.S.)

ABSTRACT

Acrolein, an unsaturated aldehyde, has been identified as one of the most important toxic air pollutants in recent assessments of ambient air quality. Current methods for determining acrolein concentrations, however, suffer from poor sensitivity, selectivity, and reproducibility. The collection and analysis of unsaturated carbonyls, and acrolein in particular, is complicated by unstable derivatives, coelution of similar compounds, and ozone interference. The primary objective of this research was to develop an analytical method to measure acrolein and other volatile carbonyls present in low part-per-trillion concentrations in ambient air samples obtained over short sampling periods.

The method we devised uses a mist chamber in which carbonyls from air samples form water-soluble adducts with bisulfite in the chamber solution, effectively trapping the carbonyls in the solution. The mist chamber methodology proved effective, with collection efficiency for acrolein of at least 70% for each mist chamber at a flow rate of approximately 17 L/min. After the sample collection, the carbonyls are liberated from the bisulfite adducts through the addition of hydrogen peroxide, which converts the bisulfite to sulfate, reversing the bisulfite addition reaction. The free carbonyls are then derivatized by *o*-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine (PFBHA*), which stabilizes the analytes and makes them easier to detect by electron-capture negative ionization mass spectrometry (ECNI-MS). The derivatives are then extracted and analyzed by gas chromatography–mass spectrometry (GC-MS).

The mist chamber method was applied in a field test to determine the extent of acrolein in ambient air near the Peace Bridge plaza in Buffalo, New York, an area of heavy traffic near a major border crossing between the United States and Canada. In addition, XAD-2 adsorbent cartridges coated with 2-(hydroxymethyl)piperidine (2-HMP) according to Occupational Safety and Health Administration (OSHA) Method 52 and passive samplers based on the use of dansylhydrazine (DNSH) were deployed at this location at the same time, which provided the opportunity to compare methods. The mist chamber results showed that the Peace Bridge traffic was clearly a source of acrolein, with an average concentration of 0.26 μg/m^3 at a site 152.4 m downwind (northeast) of the plaza. The OSHA cartridges proved to be too insensitive to determine ambient acrolein concentrations. The DNSH passive samplers returned concentrations near the limit of detection; hence the values were a little higher and less consistent than those in the mist chamber results.

The optimized mist chamber method was then applied to determine atmospheric acrolein concentrations at three sites in northern California: a site chosen to reflect the hemispheric background, a region dominated by biogenic sources, and an urban environment. The resulting average acrolein concentrations were 0.056, 0.089, and 0.290 μg/m^3, respectively, and the limit of detection was 0.012 μg/m^3. The consistency of the replicate samples obtained in the field was good, with the relative standard deviations (RSDs)

This Investigators' Report is one part of Health Effects Institute Research Report 149 which also includes a Critique by the Health Review Committee and an HEI Statement about the research project. Correspondence concerning the Investigators' Report may be addressed to Dr. Thomas M. Cahill, Department of Integrated Natural Sciences, Arizona State University at the West Campus, P.O. Box 37100, Phoenix, AZ 85069.

Although this document was produced with partial funding by the United States Environmental Protection Agency under Assistance Award CR–83234701 to the Health Effects Institute, it has not been subjected to the Agency's peer and administrative review and therefore may not necessarily reflect the views of the Agency, and no official endorsement by it should be inferred. The contents of this document also have not been reviewed by private party institutions, including those that support the Health Effects Institute; therefore, it may not reflect the views or policies of these parties, and no endorsement by them should be inferred.

* A list of abbreviations and other terms appears at the end of the Investigators' Report.

ranging from 19% at the hemispheric background site to 3% at the urban site.

The advantage of the current mist chamber method is that it can determine ambient acrolein concentrations over short time periods with enough sensitivity to be effective even in relatively "clean" environments. This allows for the determination of temporal patterns related to acrolein concentrations, such as diurnal cycles of reaction kinetics. The main disadvantages of the method are that it is laborious and time-consuming and requires specialized equipment that makes it difficult to utilize for routine monitoring of acrolein.

INTRODUCTION

Acrolein, a highly reactive α, β-unsaturated aldehyde, is a pulmonary toxicant and a common constituent of both indoor and outdoor air (Agency for Toxic Substances and Disease Registry 1990; Concise International Chemical Assessment Document [CICAD] 2002). Acrolein is produced by the incomplete combustion of organic material as well as the oxidation of atmospheric chemicals such as 1,3-butadiene, which is a primary component of motor vehicle exhaust. Indoor sources of acrolein include heated cooking oil, cigarette smoke, incense, candles, and wood-burning fireplaces (Ghilarducci and Tjeerdema 1995; California Office of Environmental Health Hazard Assessment 2000). Although regulatory agencies consider acrolein to be one of the most dangerous components of toxic air mixtures (California Air Resources Board [ARB] 1997; U.S. Environmental Protection Agency [EPA] 2003; Tam and Neumann 2004), studies of carbonyls in the atmosphere often omit acrolein (Coutrim et al. 1993; Zhang et al. 1994; Grosjean and Grosjean 1995; Pires and Carvalho 1998; Brombacher et al. 2002; Pereira et al. 2002; Bakeas et al. 2003; Pereira et al. 2004; Sax et al. 2004; van Leeuwen et al. 2004) or report its concentration as "below the limit of detection" (Grosjean et al. 1996).

The current EPA method of determining acrolein concentrations in air (Method TO-11) is based on the well-documented reaction between carbonyls and dinitrophenylhydrazine (DNPH), which produces hydrazones that are then separated by high-pressure liquid chromatography and detected by UV spectrophotometry (Grosjean 1982; Lipari and Swarin 1982; Tejada 1986). EPA Method TO-11, though effective for many aldehydes and ketones, has not proved reliable for acrolein and other unsaturated carbonyls. Problems inherent in the methodology have been reported, including the long sampling times necessary when using cartridges (typically 4 to 12 hours at flow rates of 0.1 to 1.0 L/min), instability of the DNPH-acrolein hydrazone during collection and storage (Tejada 1986; Kieber and Mopper 1990; Goelen et al. 1997; Schulte-Ladbeck et al. 2001; Huynh and Vu-Duc 2002; Dong and Moldoveanu 2004; Weisel et al. 2005), and poor chromatographic separation of the complex carbonyl mixtures typically found in air (Coutrim et al. 1993; Otson et al. 1993; Dabek-Zlotorzynska and Lai 1999; Huynh and Vu-Duc 2002). Because these problems can bias the results both positively and negatively, acrolein concentrations reported in the literature vary widely and remain controversial. A rigorous multilaboratory study comparing several methods found the DNPH method unsuitable for acrolein (Goelen et al. 1997). Progress has been made in resolving these limitations, such as using mass spectrometry instead of UV detection, but the instability of the DNPH-acrolein hydrazone, which breaks down on the sampling cartridge during collection times longer than 1 hour (Goelen et al. 1997), has not been overcome.

Another analytical approach for acrolein determination, namely EPA Method TO-15, uses canisters to collect ambient air, and the chemicals present are then analyzed by cryofocusing followed by GC-MS. This approach, which is used by the Monitoring and Laboratory Division of the California ARB, has several advantages: it does not require derivatization; it can be used to collect samples over very short periods or daylong periods, as desired; and sample preparation and analysis are simple. The disadvantage of canister sampling is that both positive and negative artifacts can arise from ozone in the air sample. In addition, wall effects (adsorption and reactions of chemicals) may still occur despite the electropolishing designed to reduce these effects. Also, the canisters are expensive and bulky, which limits the number of samples that can be collected at any given sampling event. Finally, the canisters can only hold a limited volume of air, typically a few liters, which may limit the sensitivity of this method. The California ARB Monitoring and Laboratory Division network reports a minimum detection limit (MDL) for this method of 0.3 ppbv (0.69 μg/m^3), and almost all of its reported values for acrolein in 2005 and 2006 are between the MDL and twice the MDL, a range in which quantification is often difficult.

Other analytical methods are also available. OSHA Method 52 employs an XAD-2 adsorbent cartridge coated with 2-HMP (Rohm and Haas Co., Philadelphia, PA), but its sensitivity (3 ppb for an 8-hour sample at 0.1 L/min) is not sufficient for ambient acrolein measurements. DNSH and 4-hydrazinobenzoic acid have been used to trap carbonyls in cartridges and passive samplers, but thus far these methods have not provided reproducible values for ambient acrolein concentrations (Zhang et al. 2000; Pereira et al. 2002;

Pereira et al. 2004; Herrington et al. 2005). Methods using other carbonyl-derivatizing agents, including 2,3,4,5,6-pentafluorophenylhydrazine (PFPH), *o*-benzylhydroxylamine, *n*-benzylethanolamine, cysteamine, and *n*-methyl-4-hydrazino-7-nitrobenzofurazan, have met with limited success owing to the need for expensive equipment or reagents, inadequate sensitivity, or poor selectivity (Otson et al. 1993; Yasuhara and Shibamoto 1994; Jain and Thielen 1995; Schulte-Ladbeck et al. 2001; Ho and Yu 2004).

The objective of this research was to develop and validate an analytical procedure capable of detecting acrolein and other gaseous carbonyls at low part-per-trillion concentrations in samples collected over short periods of approximately 10 minutes. The goal of a highly sensitive method was largely dictated by the low EPA reference concentration (RfC) for acrolein, which is below the detection limits of most existing sampling methods; thus, we wanted to develop a method that could determine ambient acrolein concentrations below the RfC. A short sample collection time was given a high priority because the method could be used to determine acrolein concentrations at specific times when measuring temporally variable sources such as automobile traffic. A short sampling time also would allow the method to determine the kinetics of acrolein with greater time resolution (e.g., by determining indoor acrolein concentrations before and after cooking). In some situations, such as determining an 8-hour average concentration for regulatory purposes, a short sampling time is a disadvantage because many samples would need to be collected and the results averaged. Thus, this method is more suited to specialty applications than to routine monitoring.

The new method reported herein employs a mist chamber, also called a Cofer scrubber, containing a sodium bisulfite solution that forms stable, water-soluble sulfonates with carbonyl species (Boyce and Hoffmann 1984; Kok et al. 1986; Betterton and Hoffmann 1987; Olson and Hoffmann 1988; Kaneda 1994; Dufour et al. 1999; Lowinsohn and Bertotti 2002). After sample collection the sulfonates are dissociated, and the free carbonyls are derivatized with PFBHA and form thermally stable oxime adducts that can be analyzed by gas chromatography with visualization by ECNI-MS (Yu et al. 1995; Yu et al. 1997; Ho and Yu 2004). The potential for positive and negative artifacts arising from ozone and atmospheric precursors, such as isoprene and 1,3-butadiene, was evaluated in the analytical system. The method was then validated both in the laboratory and in the field using labeled acrolein (acrolein-d_4) to create a matrix spike before sample collection. The sensitivity and precision of the new methodology were then determined under field conditions to give the most representative estimates of method performance.

SPECIFIC AIMS

The overall objective of the project was to develop and evaluate a new method to determine concentrations of acrolein and other toxic carbonyls in air and then use the method to explore exposure of a population routinely exposed to these toxicants. The population proposed in this study was tollbooth attendants.

The first specific aim of the study was to develop and validate analytical methods to determine levels of acrolein and other small carbonyls that are found in low part-per-trillion concentrations within a sampling time of 10 minutes. To fulfill this aim, we set the following objectives: (a) investigate and optimize reaction conditions for the formation of carbonyl-bisulfite adducts to further PFBHA derivatization of the carbonyls; (b) investigate collection efficiency of the mist chamber methodology; (c) evaluate both positive and negative interferences arising from ozone; and (d) test the method by measuring acrolein and other carbonyls in the ambient environment.

The second specific aim was to develop a sampling plan, based on preliminary data, to assess the acrolein exposure of a test population. We planned to sample air inside and outside tollbooths to investigate the influence of traffic conditions, ambient air temperature, and time of day on the concentration of carbonyls in ambient air.

The third specific aim was to analyze the data to (a) evaluate whether a correlation exists between ambient and indoor air measurements; (b) assess whether higher concentrations of carbonyls, which can be produced by photooxidation reactions, are present during times of the day with higher temperatures and more intense solar radiation; (c) attempt to determine the source of the carbonyls by comparing their concentrations in tollbooths that primarily serve diesel-powered vehicles and in tollbooths that primarily serve gasoline-powered cars; and (d) assess the effects of stop-and-go traffic lanes compared with fast-track traffic lanes.

The project was discontinued after the second year, during the final experiments to validate the method. Although functional, the method was time-consuming and laborious, and it would not be easy for other research groups to replicate. Therefore, the mist chamber method did not have the widespread application of the simpler methods using cartridges and passive samplers.

Consequently, exposures to tollbooth attendants were not evaluated; however, acrolein sampling was conducted for 3 days near the Peace Bridge plaza in Buffalo, alongside sampling being conducted as part of an HEI air toxics "hot spot" study.

METHODS AND STUDY DESIGN

The core objective of this project was the development of a new analytical procedure to determine the presence of acrolein in the ambient atmosphere at trace concentrations with a high degree of time resolution. The method development consisted of five stages: namely, carbonyl trapping, carbonyl derivatization, extraction of derivatives, determination of collection efficiency, and evaluation of ozone interference.

The method was then used in two field studies. The first study was to assess the concentrations of acrolein and other small carbonyls upwind and downwind from the Peace Bridge plaza in Buffalo. This project provided an opportunity to compare sampling methods because Dr. John D. Spengler (of the Harvard School of Public Health) was also collecting samples for acrolein determination as part of an HEI air toxics hot spot study.

The second field test was designed to validate the methodology by collecting samples from three different sites in California: a clean site in the marine boundary layer along the north coast of California, chosen to represent the hemispheric background with no anthropogenic sources of air pollution; a remote forested region that has a long record of low air pollution, which was chosen to test for the influence of biogenic sources on ambient concentrations; and Roseville, an urban site northeast of Sacramento with vehicular and other anthropogenic emissions. Large numbers of replicate samples were collected in short time periods at each site to test method precision and collection efficiency under field conditions.

The method development stage of the research focused on the collection, derivatization, and extraction of several representative small, volatile carbonyls (Table 1). Four of those evaluated were unsaturated carbonyls (acrolein, methacrolein, methyl vinyl ketone, and crotonaldehyde) that have been problematic in previous research projects. Two were the small dicarbonyl species glyoxal and methylglyoxal. These six chemicals are also common products of combustion and atmospheric oxidation. At the later stages of method development, benzaldehyde was added to the tests to represent an aromatic aldehyde that may be the result of the combustion of aromatic compounds in fuels.

MIST CHAMBER METHODOLOGY

Currently, many different methods are available for the determination of carbonyls in the atmosphere. Most of these methods rely on passing air through a small cartridge and trapping the carbonyls. Unfortunately, the cartridge sampling methods require very low air flow rates (< 1 L/min), which means long sampling times are necessary to collect quantifiable amounts of the carbonyls. This presents a problem if the objective of the sampling is to determine short-term fluctuations in the concentrations of the chemicals. Longer sampling times also make the sampling method vulnerable to changing meteorologic conditions, such as shifts in the wind direction, which may complicate interpretation of the results. Long collection times may also be undesirable in terms of analyte stability. For example, the DNPH derivatives are unstable under moist conditions and may degrade in the cartridge even before sample collection is complete.

Therefore, we investigated using mist chambers as a sampling method because they can be operated at high flow rates (up to 20 L/min) and have been successfully used in the past to determine ambient carbonyl concentrations (Spaulding et al. 2002). The mist chamber is attached to a vacuum pump that pulls air through a nebulizer,

Table 1. The Seven Representative Carbonyls Used for Method Development and Validation

Common Name	IUPAC Name	CAS Registry Number	Formula
Acrolein	2-Propenal	107-02-08	C_3H_4O
Methacrolein	2-Methyl-2-propenal	78-85-3	C_4H_6O
Methyl vinyl ketone	Methyl vinyl ketone	78-98-4	C_4H_6O
Crotonaldehyde	(E)-2-butenal	123-73-9	C_4H_6O
Glyoxal	Ethanedial	107-22-2	$C_2H_2O_2$
Methylglyoxal	2-Oxopropanal	78-98-8	$C_3H_4O_2$
Benzaldehyde	Benzaldehyde	100-52-7	C_7H_6O

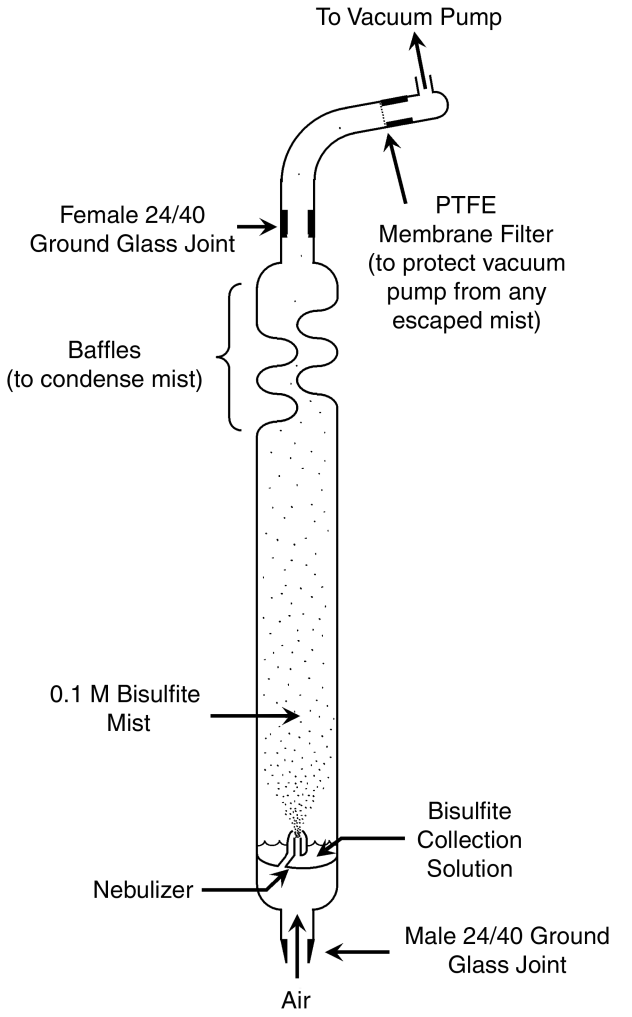

Figure 1. Diagram of the mist chamber. Air is pulled through a nebulizer that creates a fine mist from the bisulfite collection solution. The carbonyls then partition into the droplets and react with the bisulfite to form carbonyl-bisulfite adducts that are not volatile; thus, the carbonyls are trapped in the solution. The mist condenses on a series of baffles and drains down to the reservoir of bisulfite collection solution, where it is recycled.

which creates a fine mist from the aqueous collection solution in the chamber (Figure 1). The fine mist provides a large surface area for the adsorption of chemicals from the gas phase; therefore, water-soluble chemicals will partition into the water droplets. Baffles and poly(tetrafluoroethylene) (PTFE) membrane (Teflon) filters block the mist from leaving the chamber, so it drains back down into the pool of collection solution to be recycled.

Previous research indicated that a simple water solution effectively trapped chemicals with Henry law constants lower than 1.01 Pa • m^3/mol. However, acrolein has an estimated Henry law constant of 11.1 Pa • m^3/mol (Staffelbach and Kok 1993) and is not expected to be effectively trapped by water or a solution of water and PFBHA (Spaulding et al. 2002). Therefore, the mist chamber collection solution had to be modified to trap the more volatile carbonyls such as acrolein.

CARBONYL-BISULFITE ADDUCT FORMATION

Previous analytical methods that utilized the mist chamber methodology to determine carbonyl concentrations have been unable to quantify acrolein. Therefore, the first task was to identify a means to trap and retain the more volatile carbonyls such as acrolein. Carbonyls have been shown to complex with bisulfite to form stable carbonyl-bisulfite adducts (Kaneda 1994; Dufour et al. 1999; Lowinsohn and Bertotti 2002). The bisulfite attacks the carbon of the carbonyl group to form a sulfonic acid, which makes the carbonyl-bisulfite adducts highly water soluble and relatively nonvolatile. This reaction is reversible. The carbonyl-bisulfite adducts can be disassociated by removing the bisulfite from the solution, which will shift the equilibrium toward the free carbonyl species. Therefore, we investigated the use of bisulfite to trap volatile carbonyls from the air stream.

Although the formation of carbonyl-bisulfite adducts has been described previously in the literature, we wanted to verify that the adduct formation was fast enough to trap the carbonyls in the mist chamber solution and prevent revolatilization. We measured the formation constants of three carbonyl-bisulfite adducts, acrolein-bisulfite, methylglyoxal-bisulfite, and formaldehyde-bisulfite, using the *p*-rosaniline method originally developed by Dasgupta and colleagues (1980). The first step was to determine the optimal pH of the solution to ensure the greatest amount of bisulfite would be present. In aqueous (H_2O) solutions, bisulfite (HSO_3^-) can dissociate to form sulfur dioxide (SO_2) or sulfite (SO_3^{2-}) according to the following acid-base equilibria:

$$SO_2 + H_2O \leftrightarrow HSO_3^- + H^+ \quad pK_a = 1.9 \qquad (1)$$

$$HSO_3^- \leftrightarrow SO_3^{2-} + H^+ \quad pK_a = 7.17 \qquad (2)$$

where pK_a is the negative logarithm of the acid-dissociation constant. When the pH is 5.0, bisulfite is the predominant species in the solution, which should provide optimal conditions for formation of the carbonyl-bisulfite adduct. Therefore, we determined the formation constants for a bisulfite solution at pH 5.

In these experiments separate solutions containing acrolein, methacrolein, crotonaldehyde, glyoxal, methylglyoxal, and formaldehyde were prepared, and bisulfite was added to each solution in about 10-fold excess. The rate of adduct formation was monitored by the disappearance of the bisulfite as the carbonyls each react with bisulfite in a 1:1 molar ratio. Glyoxal and methylglyoxal present a problem

because they may form double adducts, in which case the loss of bisulfite may be faster. This may result in an overestimate of the second-order formation rate constant (k_f) for these carbonyls, but the maximum overestimate would be 2-fold. The experiment was allowed to proceed for 40 minutes. Equilibrium was attained for all the compounds by 20 minutes. The formation rate constants were calculated using pseudo-first-order kinetics where the bisulfite concentration is greater than the carbonyl concentration in the aqueous solution (square brackets in the following expressions indicate concentration). Therefore,

$$[\text{Carbonyl}_{\text{aqueous}}] + [\text{Bisulfite}] \rightarrow [\text{Carbonyl-bisulfite adduct}] \quad (3)$$

$$\text{Rate of loss of bisulfite} = \text{d}[\text{Bisulfite}]/\text{d}t = -k_f[\text{Bisulfite}][\text{Carbonyl}] \quad (4)$$

If bisulfite is present in vast excess, then this equation collapses to a pseudo-first-order kinetics equation:

$$\text{Rate of loss of bisulfite} = \text{d}[\text{Bisulfite}]/\text{d}t = -k_p[\text{Carbonyl}], \text{ where } k_p \text{ is the pseudo-first-order formation rate constant and } k_p = k_f[\text{Bisulfite}] \quad (5)$$

The amount of bisulfite remaining at any given time is determined by integrating the above equation from time zero (0) to any ending time (t). The resulting equation describes the first-order loss process as

$$[\text{Bisulfite}]_t = [\text{Bisulfite}]_0 \bullet e^{-kt} \quad (6)$$

Solving for k gives

$$k_p = -\{\ln([\text{Bisulfite}]_t/[\text{Bisulfite}]_0)\}/t \quad (7)$$

Once again, the loss of the bisulfite corresponds to the formation of the carbonyl-bisulfite adduct. Therefore, the rate of adduct formation can be calculated by plotting the natural logarithm of the bisulfite concentration at a given time (t) divided by the bisulfite concentration at the beginning of the experiment, against time for the experiment (Figure 2). The corresponding slope of the line is k_p, which is negative because the equations were formulated as the loss of the bisulfite, so the rate of creation of the adduct will simply have the opposite sign and thus be a positive number.

The results (Table 2) showed that carbonyls readily formed adducts, even in solutions with bisulfite concentrations that were relatively dilute (~1.5 mM) compared

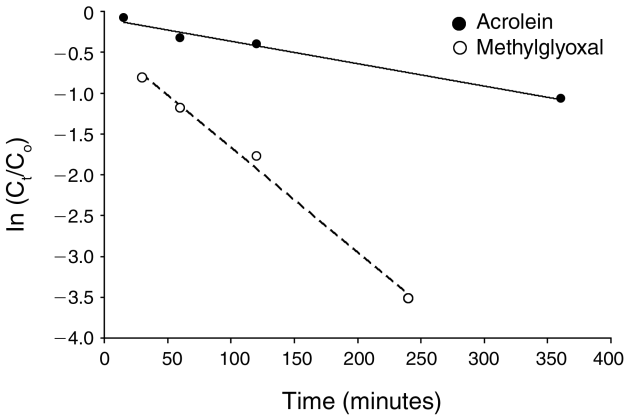

Figure 2. Decline in free bisulfite concentration over time as bisulfite binds to carbonyls. Decline is expressed as the natural logarithm of the concentration at a specific time (C_t) relative to the initial concentration (C_0). The rate constant for the formation of bisulfite adducts with single carbonyls such as acrolein is the same as the positive value of the slope of the decline curves. Dicarbonyls such as methylglyoxyal may lose bisulfite more rapidly owing to double adduct formation; in these cases the measured rate constant is expected to be a slight overestimate.

Table 2. Formation Constants of Carbonyl-Bisulfite Adducts

	Concentration (M)		Formation Constant[a]		
Carbonyl	Carbonyl	Bisulfite	k_p (sec^{-1})	k_f ($M^{-1}sec^{-1}$)	% Yield in 10 Minutes
Acrolein	1.1×10^{-4}	1.65×10^{-3}	1.2×10^{-3}	0.73 ± 0.10	96
Methacrolein	2.5×10^{-4}	1.55×10^{-3}	1.0×10^{-3}	0.65 ± 0.03	83
Crotonaldehyde	1.2×10^{-4}	1.55×10^{-3}	1.0×10^{-3}	0.65 ± 0.15	90
Glyoxal	6.2×10^{-5}	1.55×10^{-3}	3.4×10^{-3}	2.19 ± 0.28	83
Methylglyoxal	5.0×10^{-5}	1.65×10^{-3}	5.6×10^{-3}	3.39 ± 0.24	100
Formaldehyde	5.0×10^{-5}	1.65×10^{-3}	2.5×10^{-3}	1.52 ± 1.36	99

[a] The term k_p is the pseudo-first-order rate constant for formation, and k_f is the second-order formation rate constant.

Table 3. Comparison of the Second-Order Formation Constants for Carbonyl-Bisulfite Adducts in Previous Studies and the Current Study

Carbonyl	k_f ($M^{-1}sec^{-1}$)	Concentration (M)		pH	Reference
		Bisulfite	Carbonyl		
Formaldehyde	0.53	8.0×10^{-3}	8.0×10^{-4}	2.5	Boyce and Hoffmann 1984
	1.23	1.02×10^{-3}	9.65×10^{-6}	5.0	Kok et al. 1986
	1.52	1.65×10^{-3}	5.0×10^{-5}	5.0	This study
	2.26	1.25×10^{-3}	1.0×10^{-2}	3.4	Boyce and Hoffmann 1984
Glyoxal	0.72	1.5×10^{-3}	1.5×10^{-2}	3.3	Olson and Hoffmann 1988
	2.19	3.4×10^{-3}	6.2×10^{-5}	5.0	This study
Methylglyoxal	3.39	1.65×10^{-3}	5.0×10^{-5}	5.0	This study
	5.92	2.5×10^{-3}	2.5×10^{-4}	5.0	Betterton and Hoffmann 1987

with carbonyl concentrations. The rate constants for the reactions between bisulfite and formaldehyde, glyoxal, and methylglyoxal were comparable to previously reported values (Table 3) (Boyce and Hoffmann 1984; Kok et al. 1986; Betterton and Hoffmann 1987; Olson and Hoffmann 1988).

The rapid formation of adducts, ranging from 83% to 100% of the available carbonyl lost to adduct formation over a 10-minute period, indicates that bisulfite was indeed an effective trapping agent for carbonyls within the time scale chosen for sample collection. Furthermore, the concentration of bisulfite selected for the sample collection protocol (described below) was 0.1 M, which is over 100-fold higher than the concentration of bisulfite investigated in these binding experiments. Given that the formation of the bisulfite-carbonyl adduct is a second-order reaction, increasing the concentration of the reactant will further increase the rate of adduct formation. Therefore, we expect that the half-life of acrolein in the 0.1 M bisulfite solution to be approximately 9.5 seconds.

All the experiments to determine binding rates were conducted at room temperature (21°C). Field temperatures may vary widely during sample collection, which will affect the rate at which carbonyls bind to bisulfite. However, carbonyls have a very short half-life in bisulfite, which makes it unlikely they will escape, even if the binding rate in the field is slower owing to lower temperatures. Theoretically, higher temperatures would speed the binding process, and hence any effect would be to trap the carbonyls more efficiently. In practice, higher ambient temperatures result in greater evaporation and evaporative cooling of the solution, which keeps the solution temperature below the ambient temperature. Also, higher temperatures may affect the gas-solution partitioning, which may result in more chemical remaining in the gas phase.

PREPARATION OF THE 0.1 M BISULFITE SOLUTION

There are two basic approaches for preparing a bisulfite solution: either dissolving sodium bisulfite ($NaHSO_3$) directly into pure water or acidifying a sodium sulfite solution. For the research presented in this report, we used the latter approach to form the 0.1 M bisulfite solution. By this approach 12.6 g of sodium sulfite (Na_2SO_3) is dissolved in 1 L of water and then 5.5 mL of 18 M sulfuric acid is added. The solution is allowed to equilibrate for several days before use. In theory, this creates a solution of 0.1 M sodium bisulfite and 0.1 M sodium bisulfate ($NaHSO_4$). Sodium bisulfite also can be purchased and dissolved directly into water to form a 0.1 M bisulfite solution. This approach is faster and eliminates the 0.1 M sodium bisulfate component.

Therefore, we evaluated the ability of the 0.1 M bisulfite solution formed from purchased sodium bisulfite to retain carbonyls and compared it with that of the acidified sodium sulfite solutions that have been used in this research. This experiment consisted of spiking the bisulfite solutions (n = 4 samples for each type of solution, but one acidified sodium sulfate sample was lost during processing) with acrolein-d_4, benzaldehyde-d_6, and acetaldehyde-d_4. The bisulfite solutions were allowed to react with the carbonyls for 10 minutes, as called for in the standard operating procedure (Appendix A), and then the solutions were poured into mist chambers. Purified nitrogen gas was passed through the mist chambers at a rate of 19.8 L/min for 10 minutes to simulate a "normal" sample. The solutions were removed from the mist chambers and derivatized, and the amounts of the labeled carbonyls remaining were quantified. Thus, this experiment was designed to test for the loss of the adducted carbonyls from a single mist chamber by comparison with the calibration standards.

The method using acidified sodium sulfite had considerably greater retention of the labeled acrolein (92.9% ± 3.9%

retained, $n = 3$) than the approach using purchased sodium bisulfite (72% ± 7.2% retained, $n = 4$). The benzaldehyde-d_6 was less sensitive to the method of bisulfite solution formation, with both the acidified sodium sulfite approach (87.8% ± 4.9% retained, $n = 3$) and the purchased sodium bisulfite approach (90.2% ± 9.4% retained, $n = 4$) working well. In contrast, neither approach retained acetaldehyde-d_4 (< 5% retained, $n = 7$). The finding that the acidified approach was more effective for acrolein raises a question about whether the presence of additional sodium bisulfate in the solution influences the binding and retention of carbonyls. The purchased sodium bisulfite also had higher background concentrations of carbonyls.

SELECTION OF THE DERIVATIZATION AGENT

The analysis of acrolein effectively requires derivatization for two reasons. One reason is that acrolein is very reactive, and the derivatization makes the analyte more stable for transport and analysis. The other reason is that acrolein is a small hydrocarbon (molecular weight = 56 g/mol) without any readily detectable functional groups, and the derivatization results in the addition of a functional group that can be detected in minute amounts by mass spectrometry methods.

Previous research has used PFBHA to derivatize and determine concentrations of carbonyls in the atmosphere (Figure 3) (Spaulding et al. 2002). Therefore, we evaluated this reagent, as well as PFPH, which also has been used in determination of ambient carbonyl concentrations (Ho and Yu 2004). Both these compounds generate stable pentafluorophenyl derivatives of the carbonyls. These derivatives are reasonably volatile, which makes them amenable to gas chromatography (GC), and they are easily detected by ECNI-MS. We were unable to analyze the PFPH hydrazones by GC using a liquid injection (Ho and Yu 2004 used thermal desorption), and we found that the PFPH reagent remaining in the sample extract damaged the GC columns. We thus discontinued our investigation of this reagent. DNPH is another common derivatization reagent for carbonyls, but its stability is questionable (Tejada 1986; Goelen et al. 1997), and thermally unstable derivatives are unsuitable for analysis by GC. Thus, we selected PFBHA as the derivatization agent.

INSTRUMENTAL ANALYSIS AND MASS SPECTRAL CHARACTERIZATION

The pentafluorobenzyl (PFB) derivatives were analyzed by GC-MS using an Agilent 6890N gas chromatograph coupled to a 5793N quadrupole mass spectrometer. A DB-XLB capillary column was used for separating the derivatives (5% phenyl-substituted stationary phase, 30-m length, 0.25-mm I.D., 0.25-µm film thickness; J&W Scientific, Folsom, CA). The oven temperature initially was set to 50°C and held there for 2 minutes, then ramped at 5°C/min to 150°C, 20°C/min to 260°C, 30°C/min to 325°C, and held for 5 minutes. This provided good separation of

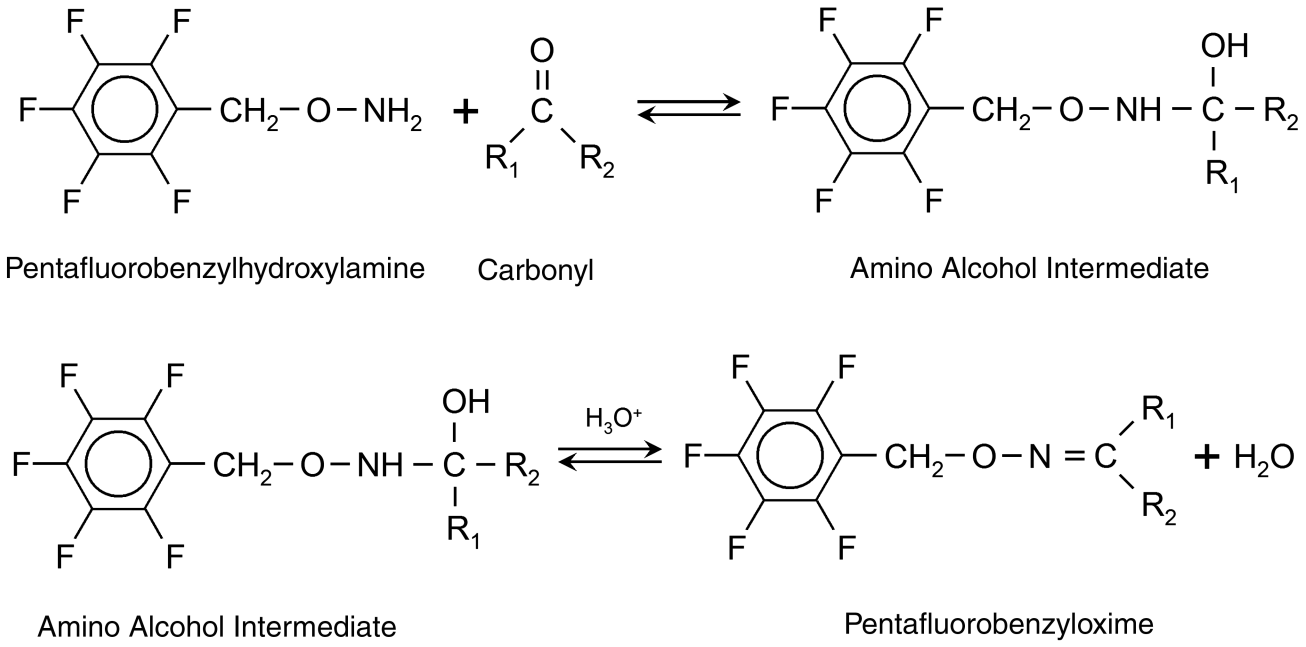

Figure 3. Derivatization reactions for the formation of a pentafluorobenzyloxime from a carbonyl.

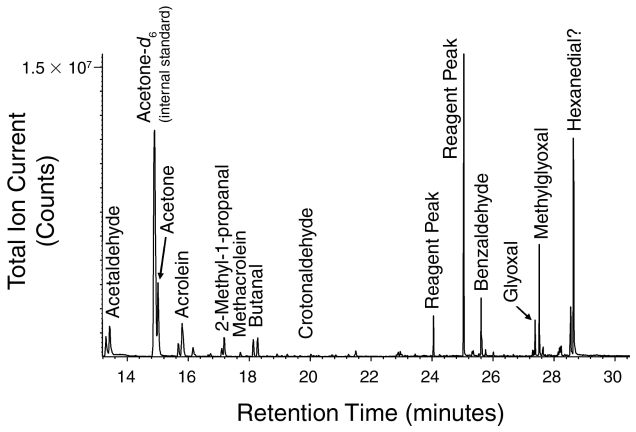

Figure 4. Chromatogram from an ambient air sample collected in Roseville. The chromatogram shows baseline resolution between analytes of interest. Many carbonyls give two peaks owing to the stereochemistry of the addition of the PFB group to the carbonyl. Hexanedial identification is uncertain owing to the lack of a standard.

the analytes both in calibration standards and in field samples (Figure 4).

The mass spectrometer was operated in the ECNI mode, with a range of *m/z* 50 to 500, which affords the highest sensitivity with fluorinated compounds. The source temperature was constant at 150°C, and the reagent gas was methane (40%). The PFBHA derivatives of the carbonyls were characterized in this ionization mode to identify the best quantification ion and the mechanism of fragmentation.

We investigated the ECNI mass spectra of acrolein, methacrolein, methyl vinyl ketone, crotonaldehyde, glyoxal, and methylglyoxal (Table 4). Few data exist on ECNI-MS analysis of PFBHA derivatives. Previous research that investigated aliphatic and unsaturated aldehydes and ketones observed low-intensity molecular anions and an $[M–HF]^-$ anion for all the compounds, but for the unsaturated aldehydes and two of the unsaturated ketones tested, the base peak (the tallest peak in a mass spectrum, which is assigned a relative intensity value of 100) was an $[M–HF]^-$ anion (Lelacheur et al. 1993). The base peak in the ECNI mass spectra of the aldehydes and ketones in the current study was an ion at *m/z* 178 $[C_6F_4CH_2O]^-$, or *m/z* 181 $[C_6F_5CH_2]^-$, or *m/z* 196 $[C_6F_5CHO]^-$. Similar to findings in previous work, dissociative resonance capture reactions appeared to dominate, as was evident by the $[M–HF]^-$ anion appearing as the base peak in the ECNI mass spectra for the unsaturated aldehydes and ketones (acrolein, methacrolein, methyl vinyl ketone, and crotonaldehyde). Figure 5 shows the spectrum for acrolein. Also similar to the previous study (Lelacheur et al. 1993), the $[M–HF]^-$ anion was absent from the ECNI mass spectra of the two dicarbonyls, glyoxal and methylglyoxal. For these compounds, the base peak was an ion that corresponds to the loss of a PFB anion, $[M–181]^-$. Therefore, $[M–HF]^-$ was selected as the quantification ion for the unsaturated carbonyls, while $[M–181]^-$ was selected as the quantification ion for the dicarbonyls.

Table 4. Major Ions of the PFBHA-Derivatized Carbonyls in Electron-Capture Negative Ionization Mass Spectrometry

Carbonyl (Molecular Weight of Derivative)	% Relative Intensities of Common Ions							
	$[M-20]^-$ $[M-HF]^-$	$[M-50]^-$ $[M-HFNO]^-$	$[M-181]^-$	$[C_6F_5CHO]^-$ (*m/z* 196)	$[C_6F_5CH_2]^-$ (*m/z* 181)	$[C_6F_4CH_2O]^-$ (*m/z* 178)	$[C_6F_5]^-$ (*m/z* 167)	Other *m/z* *m/z* (%)
Unsaturated Carbonyls								
Acrolein (251)	100	75		35	19	41	5	
Methacrolein (265)	100	44		18		21	3	
Crotonaldehyde (265)	100	54		33	9	23	1	
Methyl vinyl ketone (265)	100	17		32	24	68	5	225 (57) 210 (41) 197 (32) 192 (23)
Dicarbonyls								
Glyoxal (448)			100	43		2	8	
Methylglyoxal (462)		3	100	40		2	17	392 (7)

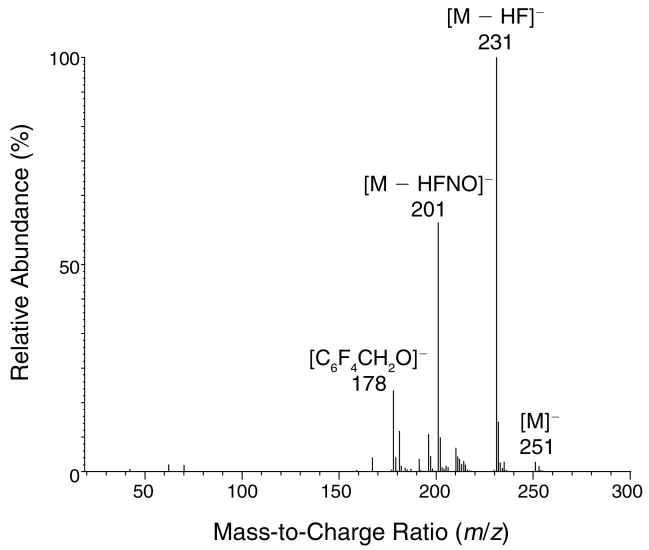

Figure 5. Mass spectrum for PFBHA-derivatized acrolein. The spectrum shows the dominance of the [M–HF]⁻ anion fragment that is typical of many PFB-derivatized carbonyls.

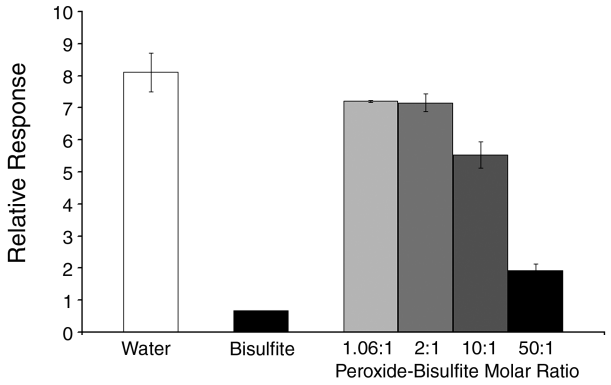

Figure 6. Influence of peroxide concentration on PFBHA derivatization of acrolein in solutions of hydrogen peroxide and bisulfite (n = 3). The first bar shows the best derivatization (in pure water), and the second bar shows typical derivatization in 0.1 M bisulfite solution without hydrogen peroxide. Error bars are ± 1 SD.

DERIVATIZATION OPTIMIZATION

The new analytical method relies on the PFBHA derivatization of the carbonyls (equations 8, 9, and 10) to stabilize the analytes and improve their detection by ECNI-MS. The first task is to break apart the carbonyl-bisulfite adducts present in the mist chamber trapping solution, to liberate the free carbonyls. The carbonyls are then derivatized to their PFB-oximes. To obtain the greatest product yield for the derivatives, we first optimized the PFBHA derivatization conditions, as follows.

- Bisulfite adduct disassociation is represented as

  Carbonyl-bisulfite adduct
  $\leftrightarrow$ Carbonyl + Bisulfite (8)

  Carbonyl + Bisulfite + H_2O_2
  $\leftrightarrow$ Carbonyl + Sulfate + H_2O (9)

- Carbonyl derivatization is represented as

  Carbonyl + PFBHA
  $\leftrightarrow$ PFB-carbonyloxime (10)

The primary conditions that need to be optimized are concentration of hydrogen peroxide (H_2O_2) to remove the bisulfite, concentration of PFBHA, derivatization time, sample storage time, and standard stability in different solvents.

Hydrogen Peroxide Concentration

The first variable to be investigated was the concentration of hydrogen peroxide necessary to remove the bisulfite. The bisulfite forms adducts with the carbonyls, and thus can compete with the PFBHA for the carbonyls. Excess peroxide is undesirable because it may degrade the analytes, but the peroxide concentration must be sufficient to completely remove the bisulfite. We tested four different molar ratios of hydrogen peroxide to bisulfite to determine which was the most effective. In addition, derivatization was conducted in both pure water, which served as a positive control, and a bisulfite solution, which served as a negative control. Three replicates were prepared for each test condition. The derivatization was conducted for 24 hours, and then the derivatized analytes were extracted and analyzed.

The results (Figure 6, Table 5) showed that a very slight excess of peroxide (1.06:1 molar ratio of hydrogen peroxide to bisulfite) was sufficient to give the maximum derivatization response in the bisulfite solution. The result with this slight excess of hydrogen peroxide in the bisulfite solution was effectively the same as the result with the pure water control (> 90% yield for acrolein), which showed that the addition of hydrogen peroxide could remove the bisulfite and allow the derivatization to proceed. The bisulfite solution without the addition of hydrogen peroxide gave the lowest response, thus showing that the derivatization cannot be conducted in the presence of bisulfite alone. Higher concentrations of peroxide (> 2:1 molar ratio of hydrogen peroxide to bisulfite) were shown to be detrimental to the analysis. Therefore, a slight excess of hydrogen peroxide was used for all future experiments.

The use of an oxidizing agent such as hydrogen peroxide in the analytical method raises questions about artifacts arising from the peroxide and either degrading the

Table 5. Effect of Hydrogen Peroxide Concentration (Normalized Response to Internal Standard, $n = 3$) on PFBHA Derivatization Yield in 0.1 M Bisulfite Solutions

	% Yield ± SD by Molar Ratio of Hydrogen Peroxide to Bisulfite				
Carbonyl	0:1[a]	1.06:1	2:1	10:1	50:1
Acrolein	1.9 ± 0.3	93.4 ± 0.4	92.8 ± 11.6	71.6 ± 17.4	25.0 ± 8.2
Methacrolein	9.1 ± 5.5	108.0 ± 3.8	102.0 ± 11.1	95.9 ± 27.2	40.1 ± 14.7
Methyl vinyl ketone	2.0 ± 1.2	15.2 ± 1.2	14.3 ± 2.5	26.2 ± 9.7	21.7 ± 4.0
Crotonaldehyde	2.4 ± 0.7	91.1 ± 2.5	106.0 ± 9.4	50.4 ± 17.2	14.9 ± 3.2
Glyoxal	7.6 ± 3.3	27.3 ± 0.4	25.5 ± 1.9	17.6 ± 9.2	2.5 ± 0.6
Methylglyoxal	33.0 ± 17.2	47.0 ± 3.9	43.9 ± 7.7	40.9 ± 12.6	8.9 ± 1.1

[a] No hydrogen peroxide is added to the solution.

analytes or forming analytes from precursor compounds. In the peroxide concentration experiment, excessive peroxide caused lower responses, and thus negative artifacts are possible. However, over 24 hours the peroxide artifacts were minimal when low ratios of hydrogen peroxide to bisulfite (1:1 or 2:1) were used. Longer periods of exposure to hydrogen peroxide may cause degradation of the analytes, so the use of internal standards such as acrolein-d_4 is recommended as a means to account for any analyte loss.

To evaluate whether or not the peroxide would create the target analytes from common atmospheric precursors, we added isoprene and 1,3-butadiene directly to our bisulfite–hydrogen peroxide–PFBHA derivatization solution ($n = 3$) at approximately 1000-fold greater concentration than would be expected in the ambient atmosphere samples. Small amounts of methacrolein and methyl vinyl ketone, which were the expected oxidation products of isoprene, were observed. However, the mass of these oxidation products was only 0.04% of the initial isoprene concentration, which is insignificant, particularly in light of the massive excess of the precursor compounds above expected environmental concentrations. No other carbonyls, including acrolein, were detected. We are thus confident that the addition of peroxide to our derivatization solution does not result in oxidation of the carbonyls or significant formation of carbonyl artifacts from expected concentrations of atmospheric precursors.

PFBHA Concentration

The second variable optimized was the concentration of PFBHA. In particular, we wanted to improve the derivatization of the dicarbonyls, which was slow because they required double derivatization. However, excessive amounts of PFBHA increase the reagent noise in the chromatograms and may contribute to column wear. Four different concentrations of PFBHA ($n = 3$ replicates per condition) were investigated to determine which gave the best response. The PFBHA concentrations investigated were 0.4 mM, 1 mM, 2 mM, and 4 mM, and the derivatization time was 24 hours.

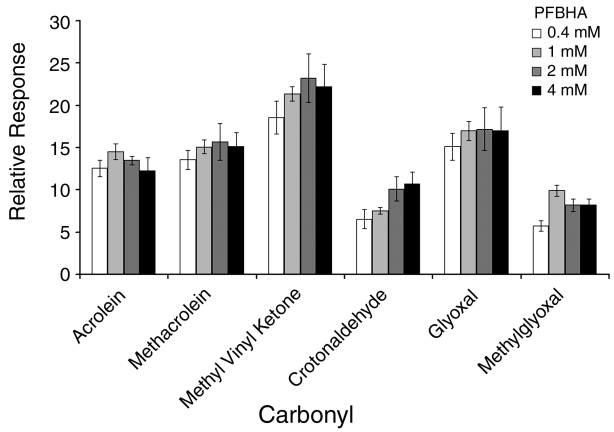

Figure 7. Effect of PFBHA concentration on carbonyl derivatization for a 24-hour reaction time ($n = 3$). Error bars are ± 1 SD.

The 0.4 mM PFBHA concentration gave lower relative responses for the two dicarbonyls, glyoxal and methylglyoxal (Figure 7), but the results with the three higher concentrations were not markedly different from each other. As the PFBHA-carbonyl reaction is a second-order reaction, increasing the concentration of the PFBHA should have increased the reaction rate. Because no increase in reaction rate was observed for most of the compounds, we concluded that the carbonyl release from the bisulfite adducts was the rate-limiting step for the derivatization. Although using a PFBHA concentration greater than 1 mM may increase the rate of derivatization for some carbonyls over 24 hours, it also increases the reagent background in the chromatogram. We therefore elected to use 1 mM PFBHA for future experiments.

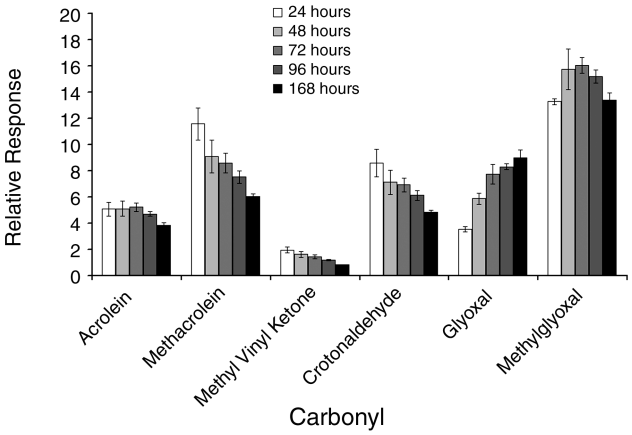

Figure 8. Recovery of derivatized carbonyls from bisulfite–PFBHA–hydrogen peroxide solution as a function of reaction time (n = 3). Error bars are ± 1 SD.

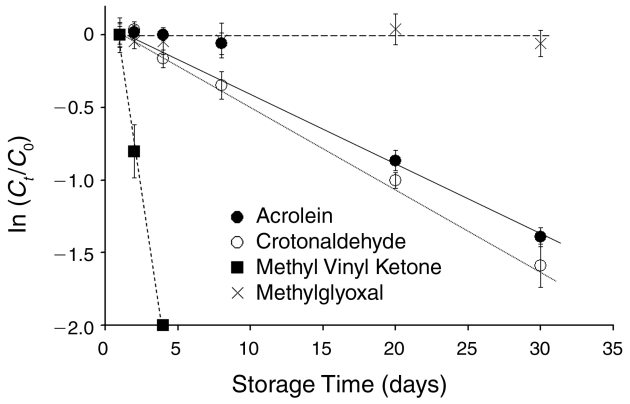

Figure 9. Loss of acrolein, crotonaldehyde, methyl vinyl ketone, and methylglyoxal as a function of storage time in a 0.1 M bisulfite solution (n = 3). Loss is expressed as the natural logarithm of the concentration at a specific time (C_t) relative to the initial concentration (C_0). Error bars are ± 1 SD.

Derivatization Time

The next variable optimized was the derivatization time. In an aqueous solution, the PFBHA-carbonyl derivatization reaction requires less than 24 hours for all carbonyls studied (Yu et al. 1995; Ho and Yu 2002; Spaulding et al. 2002). In the bisulfite solution, however, the reaction kinetics are complicated by the release of the bisulfite adduct, so the derivatization may require more time. Therefore, we compared derivatization times of 24, 48, 72, 96, and 168 hours (n = 3 replicates per condition). The responses of the derivatized analytes were analyzed relative to nonderivatized internal standards.

The results showed that the dicarbonyls required up to 168 hours for complete derivatization, while some of the unsaturated carbonyls showed declining responses after 48 hours (Figure 8). The long derivatization time for the dicarbonyls was probably caused by the release of the two bisulfite adducts and the subsequent double-derivatization of the compounds. The decline of the unsaturated carbonyls with time may be due to disulfonate formation or the longer exposure to the slight excess of hydrogen peroxide. Overall, 96 hours (4 days) appeared to be the optimal derivatization time over the range of compounds investigated.

Heating the samples may increase the derivatization reaction rate and thus shorten the reaction time, but it would most likely speed the degradation reactions of the unsaturated carbonyls. Therefore, heating would be unlikely to improve derivatization of the dicarbonyls without sacrificing the unsaturated carbonyls that are the focus of this research.

These results showed that the analyte response was very sensitive to derivatization time and that no single derivatization time was optimal for all the compounds. However, linear calibration curves were obtained for all the compounds at any time between 24 and 96 hours. Therefore, consistent calibration can be obtained by preparing the calibration curves at the same time as the samples to ensure equal derivatization times. In the case of field sampling, the calibration standards should be brought into the field and prepared when the samples are collected.

Sample Storage Time

The stability of the analytes in the bisulfite solution was another factor that required optimization to determine how long the samples could be stored before derivatization. We investigated the stability of the carbonyls in the bisulfite mist chamber solutions over a 30-day period. A 30-day sample was prepared first, followed by a 20-day sample 10 days later, and so forth, so that all the samples could be derivatized, extracted, and analyzed at the same time. The results (Figure 9) indicated that acrolein was stable in the mist chamber collection solutions for at least 7 days, but other compounds, such as methyl vinyl ketone, rapidly degraded. When the changes in concentration were plotted on a logarithmic scale, the decline in unsaturated carbonyls followed pseudo-first-order kinetics. The calculated half-lives of methyl vinyl ketone, methacrolein, crotonaldehyde, and acrolein in a 0.1 M bisulfite solution were 1.1, 12.3, 12.5, and 13.6 days, respectively. The two dicarbonyls, glyoxal and methylglyoxal, appeared to be stable in the bisulfite solution as they did not show any appreciable decline over time.

The decline of the unsaturated carbonyls in bisulfite solution appears to be related to the formation of a double bisulfite adduct as shown in Figure 10, a phenomenon that has been observed in other studies (Finch 1961; Dufour et al. 1999). The first reaction, which occurs on the order of seconds, is the addition of a bisulfite ion to the carbonyl

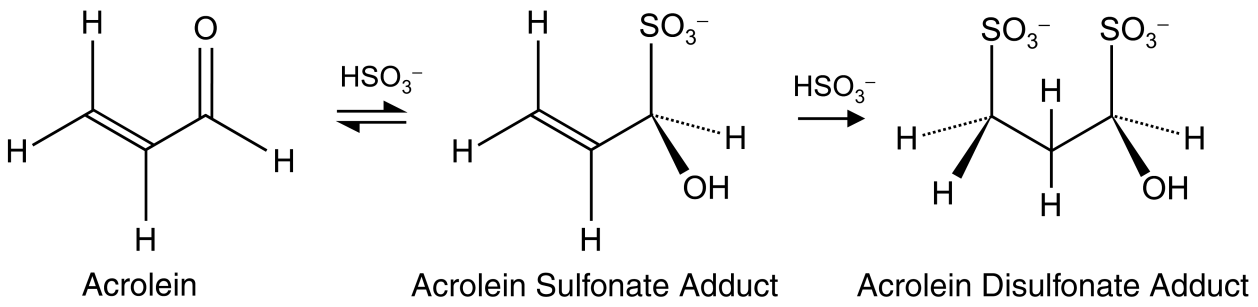

Figure 10. Formation of a double bisulfite adduct from acrolein and bisulfite.

carbon. This reaction is reversible, and it must be reversed for the analytical procedure to be effective. The second reaction, the addition of a second bisulfite group to the double bond of the unsaturated carbonyls, is much slower (on the order of days), but is irreversible. Given the relative instability of the other unsaturated compounds in the bisulfite solution, we decided to derivatize the bisulfite-carbonyl adducts immediately after collection in the mist chamber. This is easily accomplished in the field by adding the mist chamber solution directly to a tube containing the PFBHA–hydrogen peroxide mixture.

This storage experiment was conducted at room temperature to approximate a typical, nonrefrigerated temperature in the field. The storage time of the carbonyls in the bisulfite solution could probably be increased if the carbonyl-bisulfite solutions were refrigerated. However, if the rule of thumb that every 10°C decline in temperature reduces the reaction rate by 50% is correct, then refrigerated solutions could be expected to have half-lives that are four times longer. However, methyl vinyl ketone would still not be stable for more than a few days. The last option is to freeze the solutions, as the 0.1 M bisulfite solutions will freeze solid at −20°C. The analyte stability will have to be evaluated under freezing conditions before this method of sample stabilization is used. However, freezing samples is not always a viable option in the field.

Stability of Standards in Different Solvents

During the course of the research, we noticed that acrolein standards prepared in methanol and stored in the refrigerator appeared to degrade over time. Therefore, fresh standards were prepared using water, methanol, or acetonitrile as solvents to determine which of them provided the greatest stability for the acrolein standards. Although standards were typically refrigerated, this experiment was conducted at room temperature to speed the rate of chemical loss by reaction. Samples were prepared from the standards immediately after preparation, 7 days later, and 15 days later. A single sample was also prepared from the standards at 106 days to confirm the observed trends over a prolonged period of time.

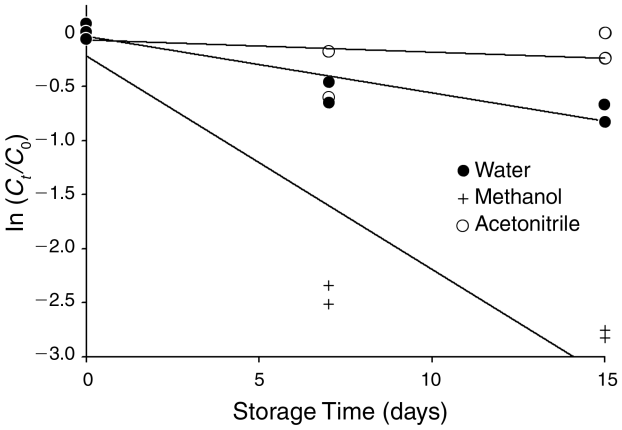

Figure 11. Decay of acrolein stored in different solvents at room temperature. Decay is expressed as the natural logarithm of the concentration at a specific time (C_t) relative to the initial concentration (C_0).

The results (Figure 11) clearly showed that acetonitrile was the best solvent for acrolein stability, water was the next best, and methanol was the worst. The samples prepared at 106 days confirmed this trend, with the change in concentration on a logarithmic scale being −3.1, −4.7, and −6.6 for acetonitrile, water, and methanol, respectively. The implication is that acetonitrile is the best solvent for use in the preparation of standards. The results also indicate that standards should be prepared on a regular basis and frozen to slow the rate of degradation of the less stable unsaturated carbonyls, such as acrolein. Furthermore, standards brought into the field for use in calibration curves should be kept cold, although standards prepared in acetonitrile are reasonably stable over 15 days at room temperature.

EXTRACTION OPTIMIZATION

The next stage of method development was the refinement of the extraction of the derivatized analytes from the aqueous

PFBHA–sulfate–hydrogen peroxide solution. Previous research using similar PFBHA approaches (Spaulding et al. 2002) extracted the derivatized analytes with methyl-*tert*-butyl ether (MTBE). However, we wanted to refine the extraction procedure to improve analyte response and reduce instrument wear. Therefore, we tested different extraction solvents, the addition of salts, and adjustments to pH, to determine which approaches could improve upon the existing methodology.

Previous research had demonstrated that MTBE was an efficient solvent for extracting PFBHA-oximes from an aqueous solution. However, the moderately polar nature of MTBE led to the extraction of a considerable amount of unreacted PFBHA and other polar species, which increased the background noise in the GC-MS chromatograms. Furthermore, injection of excess PFBHA onto the analytical column appeared to shorten the column's lifetime. Therefore, we tested both MTBE and hexane, which is less likely to remove undesirable semipolar compounds, for their ability to extract the derivatized carbonyls from the bisulfite solution (n = 3 per solvent). The results showed that essentially hexane was as effective at extracting the derivatized carbonyls as MTBE (Figure 12), but hexane resulted in a much lower background of PFBHA reagent and other contaminants in the chromatograms (Figure 13). Therefore, we selected hexane as the preferred extraction solvent.

Next, we investigated the addition of acid to the aqueous solution. Earlier methods had added acid to the aqueous PFBHA solution before extraction (Spaulding et al. 2002) to protonate the excess PFBHA and keep the ionized PFBHA in the aqueous phase and out of the sample extract. To test the effect of acid addition, three samples were prepared without acid and three more were prepared in the exact same fashion, but two drops of 18 M H_2SO_4 were added to the sample before extraction. The acid-treated samples had a cleaner extract, and in all cases the addition of acid improved extraction efficiency of the carbonyloximes (Figure 14). Therefore, we elected to continue to add acid before extraction of the derivatized analytes.

Finally, we investigated the addition of salts to the solution. This is a classic analytical tool to improve the partitioning of semipolar compounds into a nonpolar phase by making the aqueous solution more ionic (and hence more polar). Three samples were prepared in the standard fashion, and three more were prepared in the same way except that sodium sulfate was added to saturate the sample with salt before extraction. The addition of salt in an effort to "salt-out" the PFB-derivatives into hexane had negligible impacts on the amount of PFBHA-derivatized analytes extracted from the aqueous phase (Figure 15), probably because the

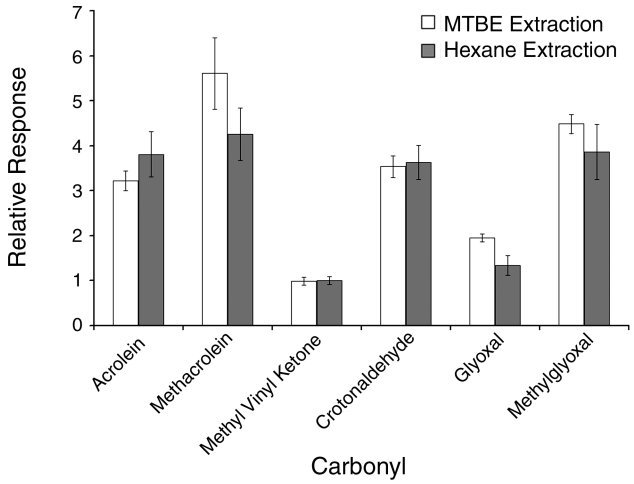

Figure 12. Comparison of PFBHA-carbonyl derivative extraction from bisulfite solutions with MTBE and hexane extraction solvents (n = 3). Error bars are ± 1 SD.

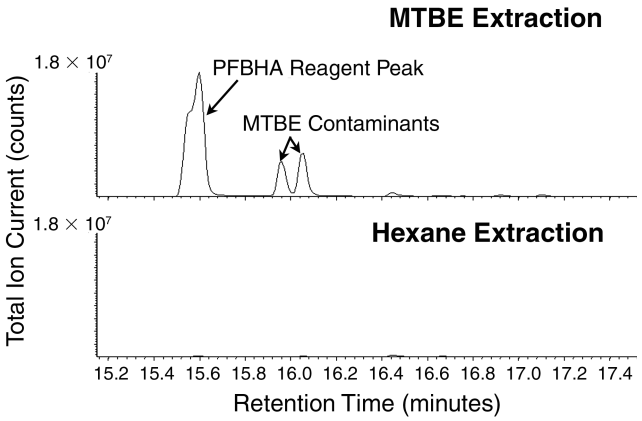

Figure 13. Comparison of contaminant peaks in a total ion current chromatogram for MTBE and hexane extraction solvents.

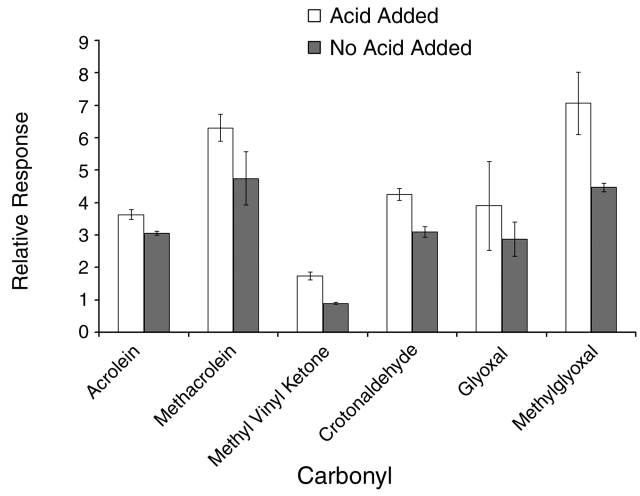

Figure 14. Effect of the addition of acid before extraction of the PFBHA-derivatized carbonyls (n = 3). Error bars are ± 1 SD.

"normal" aqueous solution already consists of 0.1 M bisulfite and sulfate, so it is already highly ionic.

Once the derivatives had been extracted and stored in anhydrous hexane, they appeared to be stable for extended periods of time. No losses were observed when derivatized and extracted acrolein (200 pg/μL) was stored at 4°C and analyzed twice monthly for 6 months (average = 200 ± 14 pg/μL, RSD = 7.0%, n = 12). Furthermore, the PFB-oximes for several common chemicals of interest, including acrolein, are sold commercially (Hayashi Pure Chemical Industries Ltd, Osaka, Japan), so the derivatives appear to be stable if they are stored properly.

SELECTION OF INTERNAL STANDARDS

In the analysis procedure we developed, two different types of standards are added to the samples, namely, the "internal standards" and the "injection standards" (Figure 16). The internal standard solution, containing acrolein-d_4 and benzaldehyde-d_6, was added to all samplers before sample collection and to all field blanks and calibration standards. Because the acrolein-d_4 will also undergo derivatization in the analysis procedure, anything that affects the volatilization, derivatization, and extraction of acrolein should also affect the acrolein-d_4 internal standard in the same fashion, thus accounting for these potential loss processes. The analytes were quantified using the isotope dilution approach in which the peak area of the analyte is divided by the peak area of the internal standard to obtain a relative response factor. The relative response factor is calculated for the calibration standards (see Appendix A for number of calibration points), and a linear "calibration curve" is fitted to the calibration standards such that the concentration of the standard is plotted against the relative response factor. This calibration curve is then used to quantify the analytes. The analyte's relative response factor is used to calculate its concentration in the solution. All analytes in this study were quantified using this isotope dilution approach.

The acrolein-d_4 was used as the internal standard to quantify the light unsaturated carbonyls (acrolein, methacrolein, methyl vinyl ketone, and crotonaldehyde). Carbonyls that lacked the reactive double bond appeared to have different chemistries with respect to stability in bisulfite, so we selected benzaldehyde-d_6 as an internal standard for all compounds other than the volatile, unsaturated carbonyls. This compound is also less volatile than the 3-carbon and 4-carbon carbonyls, so it better represents the less volatile carbonyls. In this research, acrolein-d_4 and benzaldehyde-d_6 were used to quantify the analytes. In subsequent research, acetaldehyde-d_4 was added to the internal standard mixture.

The internal standards were used in the early stages of method development to normalize the instrumental response between different test samples (for example, see Figure 6). In these cases, the relative response factor, as calculated above, was used in preference to raw instrumental response because the relative response factor removes variability associated with instrumental drift

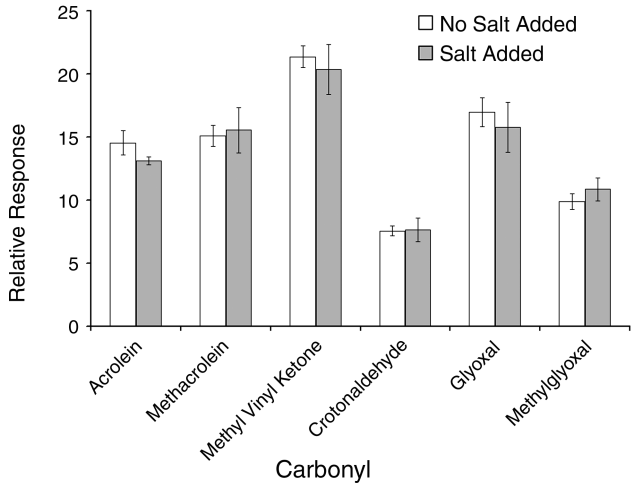

Figure 15. Effect of the addition of sodium sulfate to the aqueous phase before analyte extraction (n = 3). Error bars are ± 1 SD.

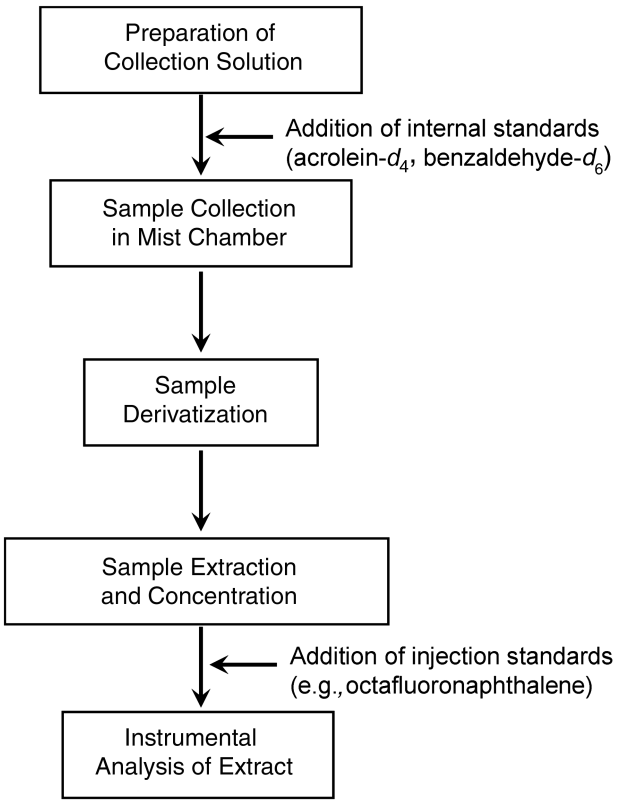

Figure 16. Timing of the addition of internal standards and injection standards to the sample.

(changes in absolute instrumental response over time due to changes in instrument conditions, such as cleanliness of the ion source, wear of the filament, etc.). However, this gives an effectively "unitless" measure of the difference in peak intensity of the analyte between two or more test conditions.

SELECTION OF INJECTION STANDARDS

The injection standard solution was added to the sample extract right before instrumental analysis. The compounds in this solution provided a backup quantification standard to use in normalizing instrumental response and sample extract volume. They were not used to quantify the analytes because they do not account for possible incomplete derivatization or "blow-off" (volatilization of analytes from the collection solution to the air stream) during sample collection, but were added as a quality control mechanism to ensure instrumental consistency between different analysis sets. Four criteria were used to select these injection standards: (1) they would not be found in ambient air samples; (2) they would give a strong ion for quantification in ECNI-MS; (3) they would have different elution times, so they would be spread throughout the chromatogram; and (4) they could be purchased commercially.

Ultimately, we selected octafluoronaphthalene, 1,2,3-tribromo-5-fluorobenzene, dibromonaphthalene, and hexabromobenzene as the injection standards, although the latter three chemicals were only added near the end of the project. The brominated compounds give strong and unique ions at *m/z* 79 and 81 for quantification. Octafluoronaphthalene also gave a strong ion at *m/z* 272 that was relatively unique in the chromatograms. Octafluoronaphthalene also eluted within 1.5 minutes of the PFB-derivatized acrolein, and thus it was representative of the instrumental conditions for the derivatized acrolein. Though the injection standards could be used for quantification, they would not account for losses of analytes during the collection, derivatization, and extraction steps of the analytical procedure. Therefore, using the injection standards for quantification would underestimate the actual concentrations of the analytes present.

To illustrate this phenomenon, we calculated the ambient acrolein concentrations determined over a 3-day study in Roseville, California, in June 2006, which was conducted after the initial HEI review of the project, using both the acrolein-d_4 internal standard and the octafluoronaphthalene injection standard. The results showed that the octafluoronaphthalene-based quantification gave concentrations that averaged 86% ± 18% (n = 70) of the concentrations determined by acrolein-d_4-based quantification. The difference between the two quantification methods was due to the loss of some acrolein-d_4 to volatilization or degradation during sample collection. These samples retained an average of 79% ± 15% (n = 70) of the initial acrolein-d_4 spike, which is fairly good given that the ambient temperatures routinely reached 38°C, with a relative humidity of 20% to 30%, during sampling. The use of the acrolein-d_4 internal standard compensates for chemical loss and volatilization, but the octafluoronaphthalene injection standard cannot.

The one application of the injection standards for quantification was to determine the amounts of the deuterated internal standards (acrolein-d_4, benzaldehyde-d_6, and acetaldehyde-d_4) that were retained in the field samples. In this case, the internal standard peak area was divided by the peak area of the injection standard to give a relative response factor. This relative response calculation can be used to normalize instrumental response and extract volume, but it would not account for any losses of the internal standards during sample collection, derivatization, or extraction. These relative response factors were then compared with the calibration standards to determine the fraction of the internal standard added to the sample that was retained during sample collection. This procedure was only applied to the deuterated internal standard as a quality control measure and was not applied to any analytes.

MIST CHAMBER COLLECTION EFFICIENCY OPTIMIZATION

The next step in the analytical method development was to determine the minimum bisulfite concentration needed to trap the carbonyls in the mist chambers. First, it was necessary to determine whether derivatization was equally effective in different bisulfite solutions, because we could not test the trapping efficiency of the different solutions without establishing that varying the bisulfite concentration does not affect the derivatization. Four bisulfite solutions were tested, ranging from 0.001 M to 0.1 M, to determine differences in derivatization. Derivatization of the carbonyls in pure water was used for comparison. For each bisulfite solution, a 1:1 molar ratio of bisulfite to hydrogen peroxide was used to degrade the bisulfite. The solutions were allowed to derivatize for 24 hours before extraction.

The results (Figure 17) showed that the initial concentration of bisulfite did not systematically affect derivatization so long as the bisulfite was converted to sulfate by hydrogen peroxide, and that derivatizations in the four different bisulfite solutions were comparable to derivatization in pure water. Therefore, we could test the effect of varying the bisulfite concentration in the mist chambers without affecting the derivatization yield.

The collection efficiency of the mist chambers was evaluated in separate experiments with different bisulfite concentrations to determine the most effective concentration for trapping the carbonyls. A Tedlar bag was filled with 200 L of zero-grade air (air that is free of total hydrocarbons) containing the carbonyls of interest. The contents of the bag were then drawn through two mist chambers in series, each containing 10 mL of the bisulfite solution being tested, at approximately 20 L/min for 10 minutes. The air flow rate was regulated by a calibrated Hastings mass flow controller. The concentrations of the analytes were determined in both mist chambers, and the collection efficiency per chamber was determined as

$$\text{Collection efficiency} = 1 - ([C_{\text{chamber 2}}] / [C_{\text{chamber 1}}]) \quad (11)$$

where $C_{\text{chamber 1}}$ and $C_{\text{chamber 2}}$ are the analyte concentrations in the first mist chamber and the second mist chamber, respectively. The value can be expressed as a fraction or percentage.

The results showed that the collection efficiencies for glyoxal and methylglyoxal were independent of the bisulfite concentration, but the collection efficiencies for the unsaturated carbonyls, acrolein and methacrolein, were directly related to the bisulfite concentration (Figure 18). Furthermore, acrolein and methacrolein were not collected to any extent in the pure water solution. This result proves that a high concentration of bisulfite was necessary to effectively trap the more volatile compounds. Therefore, we selected 0.1 M bisulfite for the mist chamber collection solution.

The collection efficiency of glyoxal and methylglyoxal reached a maximum of about 85% irrespective of the bisulfite concentration. This maximum collection efficiency is limited by loss of collection solution from chamber 1 to chamber 2 during sampling. Although the mist chambers have baffles to collect the water droplets, some solution escapes these baffles and is transported to the next mist chamber. Therefore, two mist chambers were used in series in all future experiments to achieve a total collection efficiency of 97% for the water-soluble compounds.

EVALUATION OF A WIDE RANGE OF CARBONYLS

The research reported herein focused on only seven representative carbonyls: acrolein, methacrolein, methyl vinyl ketone, crotonaldehyde, glyoxal, methylglyoxal, and benzaldehyde. The efficacy of the method for determining concentrations of these carbonyls was evaluated by three approaches: namely, analyses of collection efficiency, spike recovery, and internal standard retention. Each of these approaches has advantages and disadvantages.

To demonstrate the potential effectiveness of the method for determining the concentrations of gaseous carbonyls other than the seven listed above, we conducted a collection efficiency and mass balance test on a set of 57 common aldehydes and ketones (see Table 6). Unfortunately, this test was conducted after the field studies were completed; thus, the expanded compound list was not available for the field validation samples described later in this report.

Two mist chambers were connected in series and operated at a flow rate of 19.7 L/min (Figure 19). The mist chambers were loaded with 10 mL of 0.1 M bisulfite that had been enriched with acrolein-d_4, benzaldehyde-d_6, and acetaldehyde-d_4 according to the standard operating procedure presented in Appendix A. A glass elbow tube

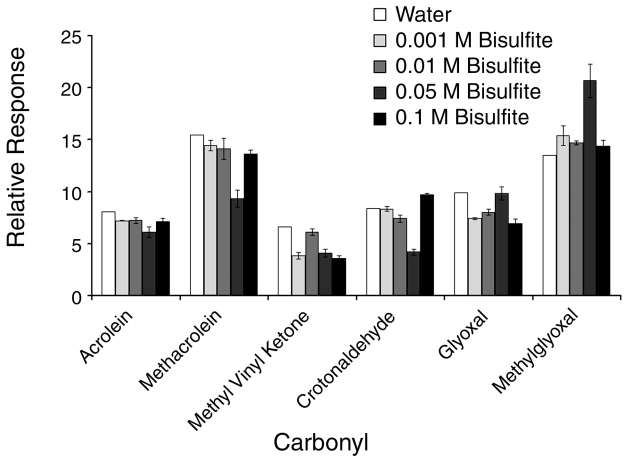

Figure 17. Influence of bisulfite concentration on derivatization of the test carbonyls when peroxide was added in amounts equimolar to the bisulfite (n = 3, except for water, which was n = 1). Error bars are ± 1 SD.

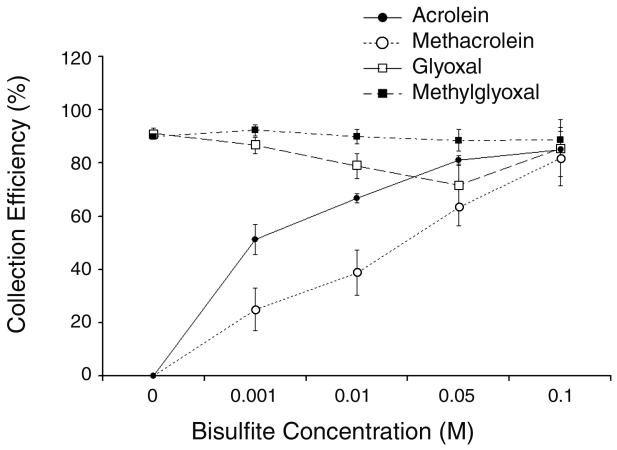

Figure 18. Influence of bisulfite concentration on collection efficiency of carbonyls from the air stream (n = 3 each). Higher bisulfite concentrations were necessary to trap the more volatile carbonyls such as acrolein, while the less volatile compounds such as glyoxal were effectively collected regardless of the bisulfite concentration. Error bars are ± 1 SD.

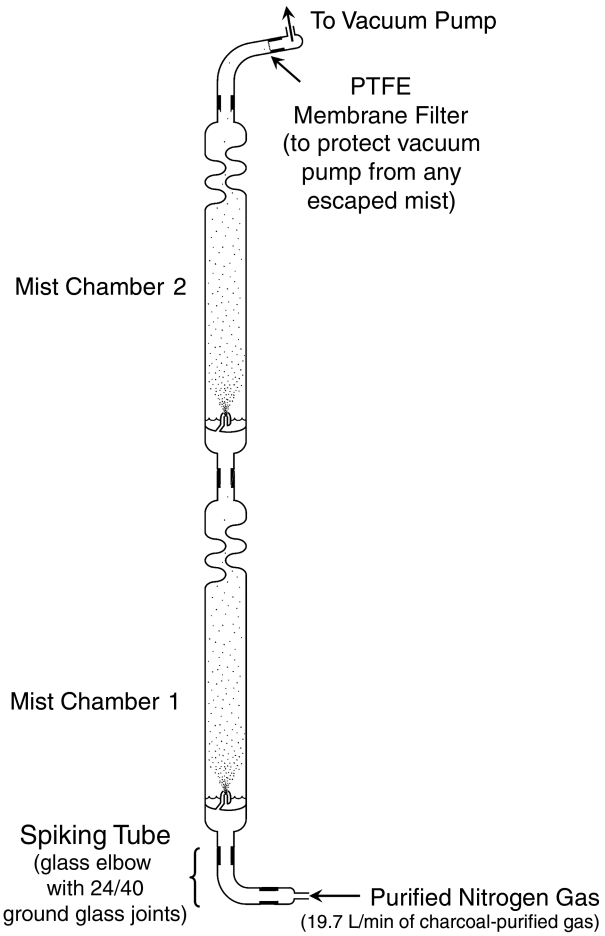

Figure 19. Diagram of the experimental apparatus for spike recovery. The test chemicals were added to the spiking tube in 10 µL of acetonitrile. The chemicals were then volatilized into the air stream by 19.7 L/min of purified nitrogen gas and carried in the gas phase into the mist chambers.

(hereafter referred to as the "spiking tube") was placed upstream of the first mist chamber where the analytes would be added to the system. The spiking tube was connected to a cylinder of 99.997% pure nitrogen that was further purified by passing through a charcoal trap. Therefore, the entire system was closed, from the nitrogen cylinder to the vacuum pump. The analyte spiking solution, prepared in acetonitrile, was added to the spiking tube, where the analytes would volatilize into the stream of nitrogen and enter the mist chambers in the gas phase, in a similar fashion as chemicals in ambient air samples. The experiments were conducted at room temperature, so heat was not added to help the analytes volatilize into the gas phase. The analyte spiking solution had a target concentration of approximately 100 ng/µL for each of the 57 analytes, and 10 µL of the solution was used for each analysis run. Therefore, the mass of each analyte added to the system was approximately 1 µg. This mass loading was higher than expected field sample values to ensure detectable concentrations of the analytes in the second mist chamber.

We used an experimental setup that was different from the earlier Tedlar bag experiments to avoid the problem of some of the "spiking" chemicals, particularly ones with low vapor pressures, sticking to the inside of the Tedlar bag and not being quantitatively recovered from the bag. Although the earlier tests only needed a chemical-enriched air sample for the calculation of the collection efficiencies, the second round of validation experiments also used a mass balance approach that required quantitative recovery of the analytes from the entire system. Adsorption of low-volatility compounds presents a problem for quantitative recovery of analytes, so the experimental setup was modified to reduce the effects of adsorption.

Two series of experiments were conducted in triplicate. The first was the standard 10-minute collection utilized in the analysis of ambient samples in this report. In this case, the spike was added to the experimental apparatus after 5 minutes, which is halfway through the sample collection. The second set of experiments utilized a 30-minute sample collection time. The spike was also added 5 minutes into the sample collection to be consistent with the first set of experiments. The longer sampling time would allow for greater loss of the chemical by volatilization; thus, these experiments were designed to demonstrate chemical loss as a function of sample collection time and to determine whether a longer sampling time would be feasible as a mechanism for improving sensitivity.

Collection Efficiency

The determination of collection efficiency is an approach that was described earlier in this report (see Mist Chamber Collection Efficiency Optimization) and was utilized in previous research (e.g., Spaulding et al. 2002). The chemical concentrations determined in the two mist chambers are used to calculate the chemical collection efficiency as a percentage or fraction. It is important to note that the collection efficiency calculation is a *relative* measure between the two mist chambers and is not related to the initial mass of chemical added to the spiking tube. One advantage of this approach is that it is not necessary to know the air concentration of the chemicals because the collection efficiency is a relative difference between the mass of chemical collected in the first and second chambers. This relative concentration approach can be applied to any sample for which the two mist chamber concentrations are determined separately, so the collection efficiency can be determined in the field under "real" sampling conditions. The disadvantage of this approach is that it is

vulnerable to systematic biases. For example, if half the chemical mass in each mist chamber is lost to wall adhesion, then the calculation will still give a high collection efficiency value because it is a relative measure between the two chambers.

Spike Recovery

The spike-recovery approach is also called mass balance or mass recovery. In this case, the mass of the analytes was determined in each mist chamber separately, as well as in a bisulfite rinse of the spiking tube to determine the mass of chemical that never volatilized into the air stream. The total mass recovered from the mist chambers and spiking tube after the sample collection was then compared with the initial mass of chemical added to the spiking tube. Therefore, the spike recovery (%) was calculated as

$$\text{Spike recovery (\%)} = [(m_{\text{chamber 1}} + m_{\text{chamber 2}} + m_{\text{spiking tube}})/m_{\text{initial}}] \times 100 \quad (12)$$

where $m_{\text{chamber 1}}$ and $m_{\text{chamber 2}}$ are the mass recovered from mist chambers 1 and 2, respectively, $m_{\text{spiking tube}}$ is the mass recovered from the spiking tube (chemical that did not volatilize), and m_{initial} is the mass of chemical initially added to the spiking tube. It should be noted that the bottom of the first mist chamber has glass surfaces where chemical could adsorb and be lost from the mass balance calculation. We anticipated this to be a minor problem except for the less volatile chemicals.

Unlike the collection efficiency calculation, the spike-recovery calculation is an *absolute* calculation that is directly related to the initial amount of chemical present. This is a more rigorous approach to determining the effectiveness of the sampler in collection of carbonyls from the gas phase because it relates the collected mass to the known initial mass of chemical added to the system. The spike-recovery approach is a common method to assess the accuracy of analytical methods because chemical lost by any mechanism (volatilization, degradation, adsorption, incomplete derivatization, sample spillage, etc.) will appear as a low recovery. The disadvantage of this approach is that it cannot be applied during field sampling because one must have a known amount of chemical to start with.

Internal Standard Retention

Another approach to assessing the efficiency of the mist chamber method is to determine the retention of internal standards added to the collection medium before sample collection starts. The internal standards used were acrolein-d_4, benzaldehyde-d_6, and acetaldehyde-d_4. Unlike the two previous approaches, the chemicals are directly added to the collection solution. This approach is not used to evaluate the ability of the mist chambers to remove chemicals from the air stream. Rather, the retention of the internal standards provides an effective measurement of any loss processes resulting from revolatilization, degradation, or sample handling.

The internal standards can be applied to every field sample, so this analysis requires no increase in the number of samples needed. The inherent assumption is that the deuterated internal standards will behave in the same fashion as the target analytes; therefore, any losses that affect the internal standard will also affect the analytes. If the majority of the internal standard is recovered, then it suggests that the majority of the analyte that enters the bisulfite solution should also be retained and that the method appears to be working well under field conditions. Conversely, if a large fraction of the internal standard is lost in a sample, then the analyte will likely be lost as well. This would indicate that there is a problem with the sample collection and analysis for a particular sample.

Because the analytes are quantified relative to these internal standards, the concentration data reported are "normalized" to these standards. Therefore, the retention of the internal standards affects the magnitude of the analyte concentration corrections necessary to account for using a relative response factor based on the internal standards. The greater the internal standard retention, the smaller the correction will be. To determine the retention of the internal standards, their peak areas are normalized to an injection standard, generally octafluoronaphthalene, to account for instrumental drift. This is the only application of the injection standards for quantification of chemicals.

EVALUATION OF POSSIBLE INTERFERENCE FROM OZONE

To address concerns about possible interference from ozone, we evaluated whether ozone could create either negative or positive artifacts in the analytical system. The question is whether ozone could degrade the carbonyls, and the unsaturated carbonyls in particular, resulting in lower concentration measurements. Conversely, ozone could create positive artifacts if it reacted with other compounds in the air being sampled to generate the carbonyls of interest. We expected the mist chamber methodology to be essentially immune to ozone effects because bisulfite is an effective ozone scrubber. The collection solution consists of 0.1 M bisulfite, so ozone is unlikely to persist in the solution for any appreciable time. Furthermore, the ozone present would be more likely to react with the high concentration of bisulfite than with the low concentrations of the analytes in the collection solution. Even though we did

not expect to observe ozone effects, we tested for both positive and negative artifacts arising from ozone.

The degradation of the collected carbonyls by ozone in the air stream was tested by adding a known concentration of carbonyls to the mist chamber solution. Either zero-grade air (control) or zero-grade air with ozone (100 ppb) was then passed through the mist chamber for 10 minutes at 20 L/min. Ozone was added to the air using an ozone generator (Jelight model 600, Jelight Co., Irvine, CA), and the ozone concentration was monitored continuously using an ozone monitor (Dasibi model 1008-AH, Dasibi Environmental Corp., Glendale, CA). In addition, a set of blanks was also prepared that simply consisted of the bisulfite solution without any carbonyls added. Three replicates were performed for each condition.

The next set of experiments determined whether the carbonyls could be generated from precursor compounds in the mist chamber. Positive artifacts can occur when ozone oxidizes precursor species present to produce carbonyls, thus creating artificially high concentrations of the carbonyls. We investigated two precursors, 1,3-butadiene and isoprene, as potential sources of carbonyls because they are considered to be the most abundant biogenic and anthropogenic substances that react in the atmosphere to produce various carbonyl species, including acrolein (from 1,3-butadiene) and methyl vinyl ketone (from isoprene).

Ambient levels of isoprene and 1,3-butadiene vary widely, so we utilized concentrations that were approximately 1000-fold higher than environmental levels to ensure that even minor carbonyl formation would be detected. The following concentrations were utilized:

1,3-Butadiene = 100 µg/200 L
= 500 µg/m^3 (ambient = 0.2 to 0.7 µg/m^3 or 0.1 to 0.3 ppbv)

Isoprene = 136 µg/200 L
= 680 µg/m^3 (ambient = 0.6 to 3.4 µg/m^3 or 0.2 to 1.2 ppbv)

The precursor compounds were added directly to the mist chamber collection solution, and then ozonated air (100 ppb) or zero-grade air was pulled through the mist chamber for 10 minutes at a flow rate of 20 L/min. This experiment has the same design as the experiment to test ozone degradation of the carbonyls, described above.

The samples were derivatized for 24 hours and extracted with hexane. The concentrations of the carbonyls in the samples treated with ozone and those treated with zero-grade air were compared. The concentrations of carbonyls in the ozone-treated precursor samples were also compared with the blank samples to determine if appreciable amounts of carbonyls were formed.

FIELD SAMPLING

Peace Bridge in Buffalo

The ultimate objective of this research was to develop a new method to determine acrolein concentrations in air and then apply it to assess the exposure of a traffic-impacted population to acrolein. The HEI Research Committee suggested that the new analytical apparatus be located next to other sampling systems to assess the consistency and sensitivity of the different available analytical methods. The HEI air toxics hot spot study was already engaged in sampling for gaseous carbonyls at the Peace Bridge in Buffalo, to assess the influence of vehicular emissions on asthma rates in the surrounding areas. Therefore, we decided to conduct acrolein sampling alongside the existing research project in the summer of 2005. The goals of this sampling were, first, to assess the influence of traffic on acrolein concentrations and, second, to compare the mist chamber method with the two other methods that were being deployed to determine acrolein concentrations at the Peace Bridge.

The other research groups were scheduled to collect samples at and around the Peace Bridge in July 2005. Although our group's new analytical methods were functional by this time, they had not been fully optimized or field tested. Some minor refinements to the sample collection procedure were made after this study.

Two sampling sites were selected to assess the impact of the Peace Bridge traffic on the local community (Figure 20). One was the "Chapel site" located at the corner of Busti Avenue and Rhode Island Street in downtown Buffalo, downwind (152.4 m to the northeast) of the Peace Bridge plaza. This was also one of the primary sampling sites for the other research groups investigating the impacts of traffic at the Peace Bridge plaza. The second site was the Great Lakes Research Center, which was chosen to represent the conditions upwind (0.8 km to the southwest) of the Peace Bridge plaza. We planned to sample upwind and downwind of the Peace Bridge plaza at the same time to assess the contribution of traffic to the local acrolein concentrations.

Samples were collected on three days, namely July 25 through July 27, 2005. On July 25, duplicate samples were collected every hour at the Chapel site from 07:00 to 19:00 hours. Duplicate samples were collected to provide an estimate of method consistency under the same conditions. Samples were collected hourly in order to determine the temporal cycles of acrolein and other small carbonyls. The time range of 07:00 to 19:00 hours was selected to be consistent with the times utilized by Spengler's group for their cartridge sample collection. On the other two sampling days, we split up the samplers, so one was at the upwind

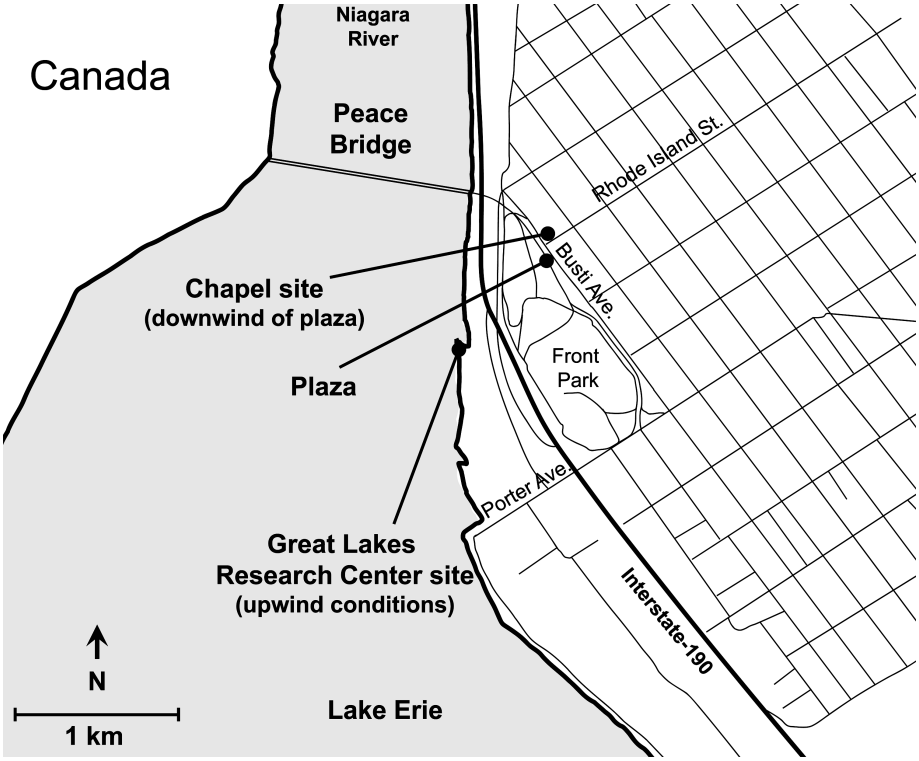

Figure 20. Location of the two sampling sites near the Peace Bridge at Buffalo. The Great Lakes Research Center was the upwind site, while the Chapel site was downwind of the Peace Bridge plaza.

site and one at the downwind site. Samples were collected every-other hour from 07:00 to 19:00 hours. No duplicate samples were collected in this phase of the project. The sample collection procedure described in Appendix A was used with the following exceptions or modifications: meteorologic data were collected by Spengler's research group, rather than by our equipment; one calibration curve was made midway through each sampling day at the Chapel site; two field blanks (one in the morning and one in the afternoon) and one reagent blank were prepared each sampling day at both sites; and the internal standard mixture was spiked into the bisulfite solution of the lower mist chamber between 10 and 30 minutes before the sampling event.

At both sites, the mist chambers were placed on a folding table, with the air intake approximately 1 m off the ground. Line power was used, resulting in flow rates of 15.8 to 16.5 L/min for the two sets of mist chambers. After sample collection, the mist chamber solutions were stored in the reaction tubes in the dark, at ambient temperature, in a rigid plastic cooler. They were shipped by overnight delivery back to the laboratory at the University of California–Davis, and processed 96 hours after collection.

The second objective of sampling at the Peace Bridge was to compare the newly developed mist chamber methodology and other acrolein determination methods. Researchers from Spengler's group collected a series of HMP-coated cartridge samples in accordance with OSHA Method 52. The cartridges, deployed at both the Chapel site and the Great Lakes Research Center site, collected ambient air from 07:00 to 19:00 hours. The cartridges were then shipped to Clayton Group Services for extraction and analyses of the samples. Thus, the analysis of these cartridges was completely independent of the other analytical results.

Another method that was evaluated was the use of DNSH-based passive samplers obtained from Dr. Jim Zhang of Rutgers University (Herrington et al. 2005). Ten cartridges were deployed at the Chapel site alongside the HMP-coated cartridges and the mist chambers. Eight of the ten cartridges were uncapped on the first day. Two cartridges were never uncapped and hence served as blanks. On each of the following 4 days, two of the open cartridges were capped, thus providing cartridge samples representing 1, 2, 3, and 4 days of collection time. The capped cartridges were sent to Zhang for analysis. The results, reported as micrograms of acrolein per cartridge, were then converted into approximate air concentrations by estimating the effective sampling rate of the passive air sampler as reported elsewhere (Herrington et al. 2005).

Ambient Sampling in California

Three sampling campaigns were conducted in California to validate the optimized analytical method under field conditions. In particular, the consistency of the method was evaluated by collecting a large number of samples over a short time period so that the ambient conditions under which the samples were obtained would be as similar as possible. The accuracy of the method was evaluated by the addition of acrolein-d_4 and benzyaldehyde-d_6 to the samples in the field; thus, any chemical loss during collection, derivatization, transport, and extraction would be detected.

The general applicability of the method was tested by collecting samples from two background sites as well as a site impacted by vehicular emissions and other anthropogenic sources (Figure 21). The background sites were used to determine the accuracy, consistency, and sensitivity of the method when very little anthropogenic acrolein was present. These sites also provided measurements of the natural background of acrolein, serving as a baseline for exposure analysis. The urban site, near a busy roadway, was selected to test the method in a situation where the analysis might be confounded by the presence of vehicular and other anthropogenic pollutants.

One background sampling site was at Salt Point along the northern California coast. This site was selected because the meteorologic conditions are dominated by the onshore flow of air from the North Pacific Ocean to the coastal mountains. Therefore, these samples should reflect the concentrations in the marine boundary layer at a hemispheric background level. The area also lacks any development of note, so there are no local anthropogenic sources of acrolein that could confound the analysis.

A total of six samples were collected at Salt Point on August 25, 2005, on a bluff above the Pacific Ocean. The mist chamber collection was identical to that in the optimized methodology described in Appendix A. Two mist chamber apparatuses were set up adjacent to each other to collect duplicate samples. Samples were collected at three times in rapid succession from 12:00 to 14:00 hours to ensure the consistency of the ambient conditions. Each sample collection time was 10 minutes at a flow rate of 15.8 to 16.5 L/min. The collection apparatuses were powered by a deep cycle 12-V battery and a 300-W power inverter.

A calibration curve was prepared in the field and stored alongside the samples to ensure that the derivatization conditions were equivalent for the samples and the calibration curve. This was achieved by bringing a vial containing a calibration solution (target concentration of 10 ng/μL) into the field. Then a volume of the calibration standard (1 to 100 μL) was added to a series of test tubes containing the bisulfite solution randomly selected from the bisulfite

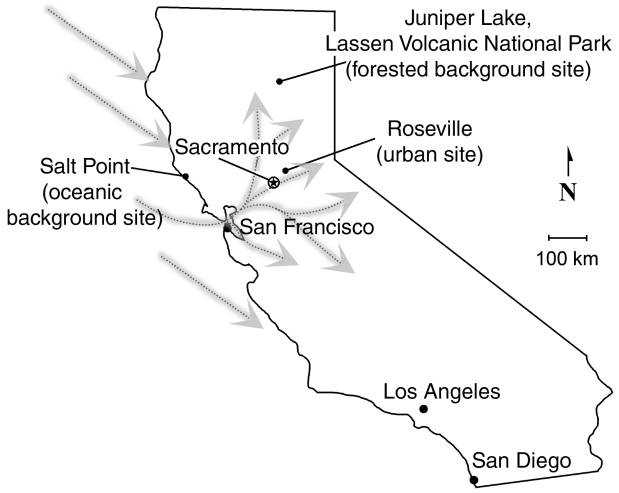

Figure 21. Locations of the three field sampling sites in California. Gray arrows show the dominant surface wind directions for the summer (Hayes et al. 1984), indicating that the samples from the Salt Point site represent oceanic air and that Roseville is downwind of Sacramento.

used in sampling. Next, the internal standards of acrolein-d_4 and benzaldehyde-d_6 were added to the bisulfite solution. The test tubes were capped, shaken, and allowed to react for 10 minutes. After 10 minutes the solutions were poured into the reaction tubes to quench the bisulfite reaction and to derivatize the carbonyls. Five calibration solutions were prepared in this experiment. In addition, two field blanks and two reagent blanks were prepared at the site. The field blanks were prepared in the identical fashion as the test samples (the solution was spiked and poured into the mist chambers, then removed after 10 minutes, and the mist chamber was washed), but the vacuum pumps were not turned on. The field blanks are used to account for any contamination arising from sample handling in the field.

The meteorologic conditions were ideal for sample collection. The wind was gusty and from the southwest, bringing oceanic air. The ambient temperature was between 18° and 24°C during sample collection. Unfortunately, relative humidity measurements were not available, but it was assumed to be high as there was a very thin fog before sampling commenced. The fog burned off to give sunny conditions during sample collection. Ozone measurements were not available at this site.

The other background site was beside Juniper Lake in Lassen Volcanic National Park. This site was chosen because air pollution levels in the park are among the lowest recorded in the 48 contiguous United States (Malm et al. 1994). The sampling area, situated in a mixed conifer forest consisting of *Abies* and *Pinus*, was expected to have biogenic sources of carbonyls but few or no anthropogenic sources of carbonyls.

Nine samples were collected at Juniper Lake from 11:00 to 14:00 hours on September 5, 2005, using the optimized mist chamber methodology (see Appendix A). Triplicate mist chamber apparatuses were used to collect samples three times in rapid succession. Each sample collection time was 10 minutes at a flow rate of 15.8 to 16.5 L/min. The collection apparatuses were again powered by a deep cycle 12-V battery and a power inverter (Figure 22). Two reagent blanks and two field blanks were prepared in the field as before. The temperature ranged from 14° to 24°C during sample collection, while the relative humidity ranged from 35% to 51%, with the lower relative humidity occurring at the end of the sample collection time. The wind was from the west at 3 to 8 km/hr, and the skies were clear during sample collection. Ozone measurements were not available at this site.

The last site was on North Sunrise Boulevard in Roseville, approximately 460 m from Interstate 80 and downwind of a major railroad depot. It is also typically downwind of the Sacramento metropolitan area (see Figure 21). This is not only a vehicle-impacted site downwind of a major metropolitan area, it is also one of the California ARB monitoring sites for numerous air toxics, including acrolein. The median 24-hour average acrolein concentration that the California ARB reported for samples obtained at the site using canisters according to EPA Method TO-15 was 985 ng/m^3 in 2005 and 1240 ng/m^3 in 2006 (with a reported MDL of 609 ng/m^3 or 0.3 ppbv). Although the California ARB was not collecting samples at the same time as our sampling event, its database of reported values (Aerometric Data Analysis and Management System [ADAM] Air Toxics Summary; available at *www.ARB.CA.gov/ADAM/toxics*) gives an indication of the concentrations we should expect at the site. The ozone concentrations during the sampling time ranged from 43 to 54 ppb.

Six samples were collected in Roseville at two 10-minute time intervals between 13:00 and 14:00 hours on September 14, 2005, using triplicate samplers with flow rates of 15.8 to 16.5 L/min. Unlike the sampling at the other two sites, the pumps were powered by line power because it was readily available at the Roseville site. Two reagent blanks and two field blanks were prepared in the field. The temperature was between 29° and 32°C during sample collection, while the relative humidity was 34%. The wind was 19 km/hr from the southwest, which meant the site was directly downwind of Interstate 80 during sample collection. The reasonably high wind may have diluted concentrations of emissions from local sources. The skies were clear and sunny during sample collection.

After each sampling event, the samples were returned to the laboratory, where they were allowed to derivatize in the dark for 4 days. The samples and standards were then extracted and analyzed according to the standard operating procedure described in Appendix A.

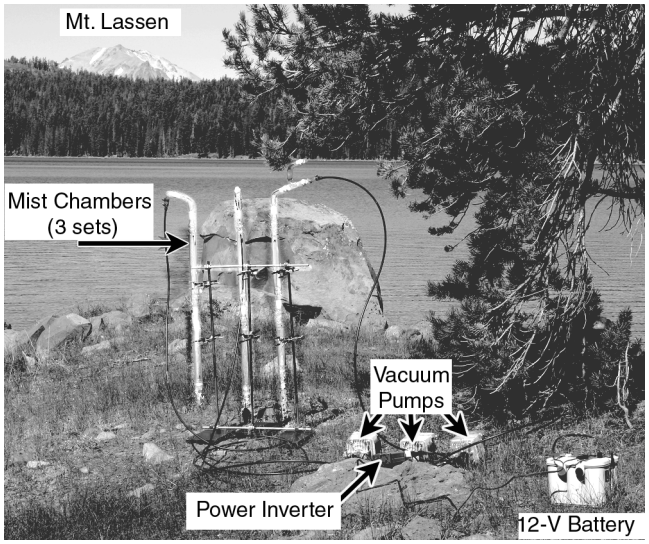

Figure 22. The sample collection system in place at Juniper Lake, Lassen Volcanic National Park. The collection system includes three sets of mist chambers (each with its own pump) to collect triplicate samples simultaneously. Each set consists of two mist chambers in series to determine collection efficiency in the field.

RESULTS

OPTIMIZATION OF THE ANALYTICAL TECHNIQUE

The majority of the research during the first year and a half of the study consisted of the development of a new analytical method for the determination of acrolein concentrations in the ambient environment. A mist chamber methodology was adopted because it allowed for the collection of large volumes of air in relatively short periods of time compared with cartridge-based sampling systems. However, there were several conditions that needed to be optimized to provide the most effective analytical method available. The results from the experiments to optimize these conditions have already been presented in the Methods section because the result from one experiment influenced the next experiment conducted. Therefore, only the final results are summarized here.

The optimal analytical conditions proved to be as follows: (1) a bisulfite concentration of 0.1 M, (2) a very slight molar excess of hydrogen peroxide compared with bisulfite, (3) a PFBHA concentration of 1 mM, (4) a derivatization time of 1 to 4 days, (5) immediate sample derivatization in the field (with no storage time), and (6) the use of acetonitrile as solvent to obtain the best standard stability.

The concentration of bisulfite was critical for the efficient collection and trapping of carbonyls from the gas phase. Lower bisulfite concentrations, as opposed to higher concentrations, resulted in poorer collection efficiencies for acrolein (see Figure 18).

Table 6. Collection Efficiency and Spike Recovery of the Mist Chamber Methodology for a Wide Range of Carbonyls

Compound	10-Minute Sampling Time (n = 3)		30-Minute Sampling Time (n = 3)	
	Collection Efficiency ± SD (%)	Spike Recovery ± SD (%)	Collection Efficiency ± SD (%)	Spike Recovery ± SD (%)
Saturated Aldehydes				
Acetaldehyde	81 ± 2	151 ± 8	66 ± 1	118 ± 4
Propanal	74 ± 3	179 ± 24	62 ± 7	112 ± 7
Butanal	65 ± 10	109 ± 3	49 ± 13	73 ± 13
Pentanal	71 ± 4	87 ± 4	48 ± 7	77 ± 3
Hexanal	68 ± 6	101 ± 4	52 ± 4	91 ± 7
Heptanal	73 ± 21	53 ± 6	47 ± 20	55 ± 17
Octanal	59 ± 10	53 ± 2	27 ± 4	42 ± 5
Nonanal	59 ± 8	44 ± 2	36 ± 8	35 ± 4
Decanal	57 ± 12	41 ± 2	31 ± 7	32 ± 4
2-Methylpropanal	61 ± 13	57 ± 1	43 ± 8	52 ± 2
3-Methylbutanal	63 ± 12	72 ± 2	35 ± 11	61 ± 6
Unsaturated Aldehydes				
Acrolein	80 ± 3	97 ± 1	71 ± 2	73 ± 5
Methacrolein	65 ± 10	31 ± 3	77 ± 2	6 ± 2
Crotonaldehyde	84 ± 4	86 ± 4	74 ± 4	54 ± 8
2-Methyl-2-butenal	62 ± 21	9 ± 3	73 ± 10	< 1
3-Methyl-2-butenal	89 ± 1	83 ± 4	79 ± 2	73 ± 7
2-Hexenal	77 ± 6	62 ± 3	68 ± 5	38 ± 7
2-Heptenal	78 ± 15	47 ± 8	66 ± 5	28 ± 5
4-Decenal	84 ± 23	17 ± 3	80 ± 6	9 ± 6
2,4-Hexadienal	99 ± 1	7 ± 2	95 ± 3	8 ± 5
2,4-Heptadienal	99 ± 1	11 ± 3	97 ± 3	10 ± 6
Aromatic Aldehydes				
Benzaldehyde	88 ± 2	83 ± 2	82 ± 2	89 ± 7
o,m-Tolualdehyde	88 ± 1	67 ± 1	81 ± 1	70 ± 5
p-Tolualdehyde	90 ± 1	66 ± 2	82 ± 2	68 ± 6
2-Ethylbenzaldehyde	84 ± 2	58 ± 4	73 ± 3	63 ± 4
3,4-Dimethylbenzaldehyde	90 ± 1	58 ± 3	83 ± 1	67 ± 5
4-Methoxybenzaldehyde	93 ± 1	53 ± 2	92 ± 1	68 ± 5
3-Hydroxybenzaldehyde	75 ± 4	39 ± 7	76 ± 3	34 ± 4
1-Naphthaldehyde	87 ± 3	138 ± 17	85 ± 2	124 ± 5

(Table continues next page)

The optimal concentration of hydrogen peroxide proved to be a slight molar excess compared with the amount of bisulfite present. Higher amounts of hydrogen peroxide gave lower responses for the unsaturated carbonyls such as acrolein. Presumably, the hydrogen peroxide attacked the derivatized analytes and converted them into other species.

The ideal concentration of PFBHA was 1 mM. Lower concentrations gave poorer responses, while higher concentrations did not improve the responses and created larger reagent peaks in the chromatograms.

Selecting the optimal derivatization time proved to be an exercise in trade-offs. Acrolein was completely derivatized after 24 hours, but the responses slowly dropped with longer derivatization times, presumably owing to disulfonate formation or reactions with hydrogen peroxide. The two dicarbonyls, glyoxal and methylglyoxal, required 4 to 7 days for complete derivatization, most likely because the reaction rate was limited by the release of the dual sulfite groups and subsequent double derivatization. Though no single derivatization time was ideal for all compounds investigated, derivatization times between 1 and 4 days seemed to be optimal over the range of chemicals analyzed.

Table 6 (*Continued*). Collection Efficiency and Spike Recovery of the Mist Chamber Methodology for a Wide Range of Carbonyls

	10-Minute Sampling Time (n = 3)		30-Minute Sampling Time (n = 3)	
Compound	Collection Efficiency ± SD (%)	Spike Recovery ± SD (%)	Collection Efficiency ± SD (%)	Spike Recovery ± SD (%)
Ketones				
Acetone	—[a]	—[a]	—[a]	—[a]
2-Butanone	—[a]	—[a]	—[a]	—[a]
Methyl vinyl ketone	77 ± 5	4 ± 2	0	0
3-Pentanone	0	4 ± 1	0	1 ± 1
2-Pentanone	35 ± 19	11 ± 1	0	1 ± 2
2-Hexanone	—[a]	—[a]	—[a]	—[a]
2-Heptanone	67 ± 31	6 ± 3	82 ± 35	0
2-Octanone	57 ± 36	5 ± 1	0	0
3-Nonanone	0	0	0	0
2-Decanone	48 ± 46	4 ± 1	53 ± 44	1 ± 0.1
Diones				
2,3-Butanedione	88 ± 1	72 ± 10	87 ± 2	91 ± 3
2,3-Pentanedione	88 ± 1	68 ± 5	83 ± 2	84 ± 7
3,4-Hexanedione	83 ± 1	65 ± 2	78 ± 1	76 ± 3
2,4-Pentanedione	75 ± 6	41 ± 5	71 ± 4	32 ± 2
2,3-Hexanedione	86 ± 1	65 ± 1	80 ± 2	71 ± 4
3,5-Heptanedione	59 ± 8	27 ± 4	79 ± 4	12 ± 1
Other Compounds				
Glyoxal	42 ± 31	139 ± 15	61 ± 5	154 ± 11
Methylglyoxal	69 ± 2	60 ± 4	75 ± 2	69 ± 4
3-Phenyl-2-propenal	95 ± 1	49 ± 1	93 ± 1	58 ± 7
Glycolaldehyde	—[b]	—[b]	—[b]	—[b]
Hydroxyacetone	89 ± 5	52 ± 14	99 ± 5	36 ± 7
5-Hexen-2-one	52 ± 25	31 ± 4	81 ± 18	5 ± 3
4-Hexen-2-one	58 ± 15	3 ± 1	73 ± 100	< 1
2-Furaldehyde	96 ± 3	63 ± 4	94 ± 1	49 ± 15
Glutaraldehyde	—[b]	—[b]	—[b]	—[b]
Nopinone	5 ± 22	61 ± 11	50 ± 5	23 ± 7
Pinonaldehyde	69 ± 17	83 ± 11	67 ± 15	88 ± 4
1,4-Benzoquinone	—[c]	—[c]	—[c]	—[c]

[a] Quantification was not reliable owing to high background contamination in the blanks.

[b] Calibration standards were inconsistent, presumably owing to poor derivatization.

[c] Benzoquinone can be derivatized by PFBHA in water, but not in the hydrogen peroxide and bisulfite mixture. This compound is likely oxidized by the peroxide to form hydroquionone, which no longer has any carbonyl functional groups for derivatization.

Because the derivatization time influences the chemical response, it is critical to prepare a calibration curve in the field at the same time as the samples are collected to ensure that the standards are treated in an identical fashion as the samples. Experiments to determine the optimal sample storage time showed that the samples should be derivatized immediately upon collection because some of the unsaturated carbonyls, and methyl vinyl ketone in particular, can react with bisulfite over extended periods of time to form disulfonate adducts that cannot be derivatized or detected with the current analytical methods.

COLLECTION EFFICIENCY AND SPIKE RECOVERY

The results of experiments to determine collection efficiency and spike recovery on a wide range of carbonyls (Table 6) provided important insights into the mechanisms and limitations of the mist chamber methodology. One observation was that many compounds had good collection

efficiency but very poor spike recovery (e.g., methyl vinyl ketone), indicating that the calculated collection efficiency is a rather poor measure of the method's efficacy. It is possible that the collection efficiency calculation is systematically flawed for the mist chamber methods. The second mist chamber experiences a higher vacuum than the first mist chamber, which may result in greater volatilization of chemicals or less partitioning into the chemicals in the aqueous phase to begin with. This would result in systematically lower concentrations in the second chamber relative to the first chamber, thus artificially inflating the collection efficiency values. Therefore, the conditions for the two chambers are not identical, as was assumed in the collection efficiency calculation. We believe that the spike-recovery calculation is probably a more accurate measure of the mist chamber's effectiveness in trapping chemicals from an air stream.

The results of the spike-recovery calculations showed that the method was generally "acceptable" (> 70% recovery) or "marginal" (50% to 69% recovery) for (1) saturated aldehydes with fewer than eight carbons, (2) monounsaturated aldehydes with fewer than six carbons, (3) aromatic aldehydes, (4) diones with fewer than six carbons, and (5) miscellaneous small polar compounds such as glyoxal, methylglyoxal, 2-furaldehyde, nopinone, and pinonaldehyde. The notable exceptions were methacrolein, 2-methyl-2-butenal, 3-hydroxybenzaldehyde, and 2,4-pentanedione. In general, the spike-recovery values tended to decline with increasing molecular mass within a homologous group (e.g., saturated aliphatic aldehydes). This was presumably due to the lower aqueous solubility of the larger, less polar hydrocarbons. The larger chemicals that are less water soluble are less likely to partition into the 0.1 M bisulfite solution and be trapped. For some chemicals the recovery was greater than 100%, which indicates that some background contamination was present. A single set of blanks was used to provide the background values subtracted from these data; these values may not be accurate estimates for chemicals that tend to be present at high and somewhat variable levels (e.g., acetaldehyde and glyoxal).

The method performed very poorly for the ketones, including methyl vinyl ketone. The ketones could be derivatized and produce linear calibration curves, so the problem appears to be with the retention of these compounds in the mist chambers. Many of the diones gave reasonable results. Given that the diones are more water soluble and less volatile, they would be expected to be retained by the mist chamber collection solutions. Thus, it appears that the poor retention of the monoketones was due to their volatility or relative lack of water solubility. We suspect that the bisulfite may not bind to the ketones in the same fashion as to the aldehydes, and thus it may not trap them as well as it does the aldehydes.

Two other groups of chemicals for which the method did not produce accurate results are the doubly unsaturated aldehydes ("dienals") and the quinones. The dienals did not produce very good calibration curves, probably owing to reactions with the bisulfite at two unsaturated functional groups other than the aldehydes' functional group. The quinones, as exemplified by benzoquinone, were easily derivatized by PFBHA in pure water, but they could not be derivatized in the 0.1 M bisulfite–hydrogen peroxide–PFBHA solution, and hence calibration curves could not be created. We suspect that the peroxide was oxidizing the quinone to the hydroquinone, which was then not available for derivatization. Other quinones would likely suffer from the same problem.

The longer 30-minute sampling time resulted in greater volatilization of the lighter compounds and thus poorer spike-recovery values. Conversely, for some of the heavier compounds, recoveries were better with the long sampling times. This is likely an artifact of the spiking methodology in which the spike was applied to a glass tube before entering the mist chamber. Therefore, the chemical must volatilize into the gas phase and enter the mist chamber. The quick rinse of the spiking tube may not have dissolved all of the analyte that remained in it, particularly if the analyte was fairly insoluble in water. Also, there are sites where adsorption could occur in the bottom parts of the mist chambers and in the nebulizer; thus, the chemical may stick on the glassware entering the mist chambers. The longer sampling period gives more time for the chemical to volatilize into the air stream and enter the chamber to be trapped. For field sampling, the higher recovery for the less volatile compounds is probably more representative of their actual collection rate.

The retention of acrolein-d_4 and benzaldehyde-d_6 internal standards (Table 7) agrees well with the spike-recovery data presented above. All the mist chambers were spiked with acetaldehyde-d_4, acrolein-d_4, and benzaldehyde-d_6 in 10 µL of acetonitrile before sample collection. The fraction of the labeled standard at the end of the sample collection could then be compared with the initial mass of chemical added directly to the collection solution. Benzaldehyde-d_6 was unaffected by the longer sampling time, while acrolein-d_4 retention decreased by about 14%. Acetaldehyde-d_4, however, is an enigma. The labeled standard showed extensive loss, probably owing to volatilization, while the spike-recovery values were pretty good despite some background contamination. It is possible, but not likely, that the background contamination in the spike-recovery tests was obscuring a poor sampler collection rate. It is also

Table 7. Retention of Isotopically Labeled Standards Directly Added to Collection Solutions Before Spike-Recovery Sample Collection[a]

Standard	Retention ± SD (%)	
	10-Minute Sampling Time (n = 3)	30-Minute Sampling Time (n = 3)
Acetaldehyde-d_4	7.2 ± 1.4	3.8 ± 0.4
Acrolein-d_4	92.9 ± 3.9	78.7 ± 4.1
Benzaldehyde-d_6	87.8 ± 4.7	87.4 ± 7.0

[a] The retention was calculated for only one (the first) mist chamber.

possible that the labeled acetaldehyde in acetonitrile associated with the solvent in some fashion that allowed it to be more volatile, which could be tested by simply adding the labeled acetaldehyde to the spiking tube and allowing it to volatilize into the mist chambers in the gas phase, as for the "normal" acetaldehyde spike experiment described above. Until this issue is clarified, however, the acetaldehyde values should only be used for qualitative trends.

POSSIBLE INTERFERENCE FROM OZONE

The results showed that the analytical method is effectively immune to interference arising from ozone. The presence of 100 ppb ozone in the air stream did not degrade acrolein that was trapped in the sulfite solution (Figure 23). Moreover, precursor compounds were not converted into acrolein by simply passing ozonated air through the mist chamber containing the precursor compounds. Similarly, methacrolein and crotonaldehyde and their precursors showed no significant positive or negative influences from the addition of ozone; however, the values for methyl vinyl ketone and the dicarbonyls (glyoxal and methylglyoxal) fluctuated widely (Table 8). We believe that the fluctuation in the dicarbonyls was due to poor derivatization because the samples were only derivatized for 24 hours, which we now know is not optimal for these two compounds. Because of the high variability in the results for the dicarbonyls, further studies are necessary to demonstrate their susceptibility to ozone and precursors. However, we would not expect them to be significantly degraded if the unsaturated carbonyls were not degraded by ozone, because these compounds lack an unsaturated functional group that is often the target of ozone attack.

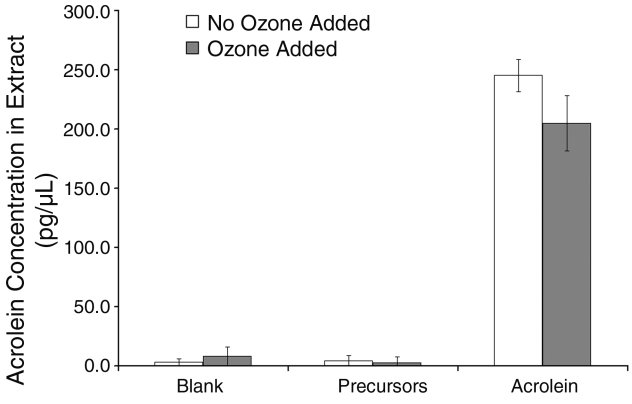

Figure 23. Effects of ozone on acrolein concentrations in mist chambers in which the bisulfite solution is not enriched (blank), or is enriched with precursor compounds or acrolein (n = 3). Error bars are ± 1 SD.

Table 8. Effect of Ozone on Precursors and Carbonyls in the Mist Chamber

Carbonyl	Concentration ± SD (pg/µL)					
	No Ozone			Ozone 100 ppb		
	Bisulfite (Blank)	Bisulfite Precursors	Bisulfite Carbonyls	Bisulfite (Blank)	Bisulfite Precursors	Bisulfite Carbonyls
Acrolein-d_4	0	0	235 ± 12	0	0	214 ± 21
Acrolein	3.3 ± 2.9	4.2 ± 4.7	245 ± 14	8.1 ±7.9	2.8 ± 4.8	205 ± 23
Methacrolein	7.1 ± 2.6	6.7 ± 3.2	32 ± 1	11 ± 7	6.8 ± 7.2	53 ± 16
Methyl vinyl ketone	31 ± 12	70 ± 80	17 ± 4	81 ± 98	103 ± 105	102 ± 60
Crotonaldehyde	0	0	283 ± 22	0	0	227 ± 39
Glyoxal	237 ± 208	411 ± 477	1109 ± 125	678 ± 725	128 ± 222	91 ± 158
Methylglyoxal	56 ± 49	109 ± 108	530 ± 69	300 ± 297	35 ± 61	186 ± 105

Other analytical methods often use an ozone scrubber upstream of the sample collection medium to remove ozone (Helmig and Greenberg 1995; Helmig 1997; Kleindienst et al. 1998; Fick et al. 2001). However, the presence of an ozone scrubber may negatively affect the collection of the desired carbonyls, which may condense in the ozone scrubber as well. Therefore, we consider the new method, which is inherently resistant to the effects of ozone, to be both simpler and less prone to errors than existing methods that require an ozone scrubber.

FIELD SAMPLING

Peace Bridge in Buffalo

The results from sampling upwind and downwind clearly showed that the traffic at the Peace Bridge plaza caused elevated concentrations of acrolein and other carbonyls (Table 9). The average acrolein concentrations detected at the downwind Chapel site ranged from 0.21 to 0.30 μg/m^3, while the average concentrations at the upwind (control) Great Lakes Research Center site were 0.055 μg/m^3 on July 26, 2005, and below the MDL of 0.065 μg/m^3 on July 27, 2005. Therefore, the concentrations of acrolein at the Chapel site were approximately 4-fold to 6-fold higher than those at the control site located approximately 1 km away. In addition, the other targeted carbonyls, except for methyl vinyl ketone, were also detected at the Chapel site, but they were not detected at the control site.

Air samples were collected every hour for the first day, then every-other hour for the second day between 07:00 and 19:00 hours, to assess the potential diurnal cycles of acrolein. The results (Figure 24) showed a trend for higher acrolein concentrations in the middle of the day compared with the morning or evening, although more nighttime samples would be needed to prove this trend. This pattern corresponds well with the number of west-bound automobiles

Table 9. Average Ambient Concentrations of Selected Carbonyls Obtained Using the Mist Chamber at Sites Downwind and Upwind of the Peace Bridge Plaza During Three Days in July 2005[a]

Location and Carbonyl	MDL Range (μg/m^3)	Average Concentration ± SD (μg/m^3) July 25 (n = 26)	July 26 (n = 7)	July 27 (n = 6)
Chapel Site (downwind)				
Acrolein	0.018–0.058	0.30 ± 0.10	0.27 ± 0.063	0.21 ± 0.11
Methacrolein	0.0022–0.0059	0.020 ± 0.013	0.027 ± 0.022	0.055 ± 0.048
Methyl vinyl ketone	—[b]	—[b]	—[b]	—[b]
Crotonaldehyde	0.0035–0.012	0.016 ± 0.0071	0.013 ± 0.0065	0.0084 ± 0.0078
Glyoxal	0.038–0.12	0.26 ± 0.11	0.25 ± 0.17	0.44 ± 0.66
Methylglyoxal	0.018–0.080	0.18 ± 0.094	0.17 ± 0.067	0.17 ± 0.092
Benzaldehyde	0.012–0.047	0.11 ± 0.060	0.081 ± 0.025	0.13 ± 0.15
Great Lakes Research Center (upwind)				
Acrolein	0.032–0.065	—[c]	0.055 ± 0.059	< 0.065
Methacrolein	0.0028–0.037	—[c]	< 0.0028	< 0.037
Methyl vinyl ketone	—[b]		—[b]	—[b]
Crotonaldehyde	0.0020–0.035	—[c]	< 0.0020	< 0.035
Glyoxal		—[c]	1.3 ± 1.9[d]	0.48 ± 0.26
Methylglyoxal	0.10–0.11	—[c]	< 0.10	< 0.11
Benzaldehyde	0.023–0.39	—[c]	< 0.39	< 0.023

[a] The MDL was calculated (mean + 3 × SD) from the two field blanks that were prepared each day at each site. Values listed as "<" indicate that the analyte was below the limit of detection for over half the samples at that time and location.

[b] Methyl vinyl ketone is not reported owing to poor spike-recovery data.

[c] Samples were not collected at the Great Lakes Research Center on this day.

[d] The average and standard deviation for glyoxal on this day were elevated by two high-concentration outliers. We are unsure whether these values reflect a temporally brief local emission or an analytical problem.

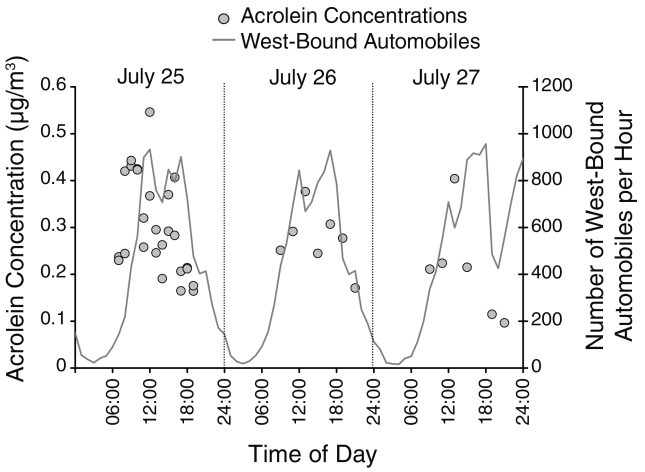

Figure 24. Time series of acrolein concentrations at the Chapel site adjacent to the west-bound traffic at the Peace Bridge plaza. Each sample (or pair) was collected over a 10-minute interval. Duplicate samples were collected every hour for the first day from 07:00 to 19:00 hours. The average difference between replicates was 20%, which was largely the result of three outlier data points. Single samples were collected every 2 hours on the other 2 days.

passing through the Peace Bridge plaza. The correlation between ambient acrolein concentrations and vehicular traffic broke down on the last day of sampling as a result of changing meteorologic conditions, namely a light rain and a northeast wind that made the Chapel site upwind of the Peace Bridge plaza for part of the day.

Comparison of Sampling Methods at the Peace Bridge

One of the objectives of collecting samples at the Peace Bridge was to compare the acrolein concentrations determined by different methods. In addition to our sampling efforts, Jose Vallarino from Spengler's research group collected acrolein samples using OSHA Method 52 at the same locations and times. These were 12-hour samples, as compared with our 10-minute samples, so we averaged our observed concentrations over the course of a day to obtain a concentration comparable to those of the OSHA Method 52 cartridges. The cartridges were analyzed by Clayton Group Services (Novi, MI) independently of our analyses. In addition, DNSH-based passive samplers were deployed at the Chapel site for 4 days, from which two samples were collected and analyzed each day.

The method comparison showed some interesting results (Table 10). First, the results obtained using OSHA Method 52 were all below the limit of quantification (see Appendix B) of 2 µg per cartridge. The cartridges collected approximately 70 L of air during the 12-hour sample. This resulted in the MDL of 28.6 µg/m³ for acrolein, which was approximately 100-fold higher than the acrolein concentrations determined in our analyses. However, this comparison clearly shows that OSHA Method 52 is too insensitive to determine ambient acrolein concentrations, even in a traffic-impacted area. It should be noted that the MDL of 0.2 µg per cartridge claimed by OSHA is a full order of magnitude lower than the MDL that Clayton Group Services reported. Even if the MDL were lower by an order of magnitude than the MDL observed in this study, it would be 2.8 µg/m³, which is still approximately 10-fold higher than the average value observed in our samples and thus inadequate for ambient sampling.

The second analytical method that was simultaneously deployed at the Chapel site was the use of DNSH-based passive samplers supplied by Junfeng (Jim) Zhang at Rutgers

Table 10. Comparison of Acrolein Concentrations Determined by Three Different Methods at the Chapel Site[a]

Date in 2005	Mist Chamber[b] (10-min samples)	OSHA Method 52[c] (12-hr samples)	DNSH Passive Sampler[d] (1- to 4-day samples)		MDL[e]
			Sample 1	Sample 2	
July 25	0.30 ± 0.10 (n = 26)	< 28 (n = 1)	< 1.3	< 1.3	1.3
July 26	0.27 ± 0.063 (n = 7)	< 28 (n = 1)	0.56	< 0.63	0.63
July 27	0.21 ± 0.11 (n = 6)	< 27 (n = 1)	0.44	0.97	0.42
July 28	No samples taken	No samples taken	0.52	< 0.31	0.31

[a] Values are acrolein concentrations (µg/m³); "<" indicates value is below the MDL.

[b] Mist chamber values are average daily concentrations ± SD. The MDL was 0.065 µg/m³.

[c] The OSHA Method 52 MDL was 28.6 µg/m³; these samples were analyzed by Clayton Group Services.

[d] The DNSH values for the fourth day represent the total accumulation from the start of sampling. Thus, the July 28 samples represent the average concentration for July 25 through July 28. These samples were analyzed by Dr. Jim Zhang of Rutgers University.

[e] The DNSH method's MDL was based on 0.01 µg of acrolein per cartridge, so the cartridges with longer accumulation times had lower MDLs.

University (Herrington et al. 2005). Unlike the active samplers of the mist chambers and the cartridges that measure the amount of air that passes through the sampler, the passive samplers utilize the air blowing by the sampler to exchange chemicals with the sampler, then an average exchange rate (or mass transfer coefficient) is used to estimate the amount of air that the sampler contacted (Zhang et al. 2000). Ideally, the carbonyls are trapped and derivatized, so they are no longer volatile.

Ten passive samplers were placed at the Chapel site on July 25, 2005, eight of which were uncapped at 07:00 hours. The two remaining samplers were left capped to serve as blanks. Each morning at 07:00 hours, two of the samplers were capped. Therefore, the first two samples represented 1 day of accumulation, the next two samples represented 2 days of accumulation, while the last two samples represented 4 days of accumulation. Half of the samples fell below the MDL (see Table 10). The other samples were mostly no more than 2-fold greater than the MDL, which is generally in the range where quantification is difficult or unreliable. The last two samples represented 4 days of acrolein accumulation, yet they had lower values than the cartridges with 3 days of accumulation under the same conditions.

Therefore, it would appear that the DNSH-based passive samplers lacked the necessary sensitivity to determine ambient acrolein concentrations over the 4-day sampling period under the field conditions at this site. The cartridges may perform better with higher acrolein concentrations such as those indoors or in occupational exposure situations. The advantage of the DNSH-based cartridges is that they require little effort to deploy in the field, so a large number of samples can be collected with relatively little effort.

Overall, the mist chamber method was the only one of the three methods deployed that consistently detected and quantified acrolein. The precision between duplicate mist chamber systems collecting samples at the same time averaged 20% (n = 13 sample pairs), where the percentage difference between colocated sample pairs was calculated as

$$\text{Difference between sample pairs} = |\text{Sampler 1} - \text{Sampler 2}| / [(\text{Sampler 1} + \text{Sampler 2})/2]) \times 100 \quad (13)$$

or the absolute value of the difference in concentrations, divided by the average of the two concentrations obtained by the sampler pairs. This precision is reasonable for a method that was not fully optimized at the time. OSHA Method 52 proved to be far too insensitive to determine ambient acrolein concentrations, with MDLs 10 to 100 times greater than concentrations determined using the mist chambers. The DNSH passive samplers also proved to be too insensitive for ambient acrolein determination at this site.

Ambient Sampling in California

The optimized method was evaluated by collecting samples at three different locations in California to determine the consistency of the analytical method and its sensitivity in the field, and to verify collection efficiency data obtained in the laboratory. In addition, the three locations were chosen to represent three different situations, namely clean coastal air, clean air in a forested region, and urban air. The first site was Salt Point along the northern Californian coast, where oceanic air was sampled. This site was chosen to represent hemispheric background concentrations in the absence of anthropogenic sources and terrestrial biogenic sources. The second site, Juniper Lake in Lassen Volcanic National Park in northern California, was chosen to represent a remote area with little or no anthropogenic sources but considerable biogenic sources of hydrocarbons that may serve as precursors for acrolein and other carbonyls. The last site was at the California ARB in Roseville. This site is approximately 300 m from Interstate 80, as well as being downwind of a major railroad depot and the Sacramento metropolitan area. Therefore, this site was expected to be impacted by vehicular traffic and other urban pollution sources.

The results (Table 11) showed clear differences in the carbonyl concentrations between the three sites, which was expected. Salt Point showed the lowest concentrations of acrolein, with an average concentration of 0.056 ± 0.011 μg/m^3, which is not surprising as this site was chosen to determine acrolein concentrations in clean oceanic air. All other carbonyl species were below the limit of detection at Salt Point except for a trace amount of benzaldehyde.

The acrolein concentrations at Juniper Lake (0.089 ± 0.013 μg/m^3) were slightly higher than those at Salt Point (t test, $P < 0.001$), but they were still fairly low. In contrast to Salt Point, Juniper Lake had high concentrations of methacrolein and crotonaldehyde. We suspect that a biogenic source contributed to the concentrations of these carbonyls, either directly or through the oxidation of a biogenic emission such as isoprene (Grosjean et al. 1993). The crotonaldehyde concentration, in particular, was approximately 5-fold higher than at the other sites, which represents a substantial contribution from biogenic sources.

Lastly, the concentrations of acrolein were considerably higher at the urban site in Roseville (0.290 ± 0.008 μg/m^3) than at Salt Point (t test, $P < 0.001$), which was expected. The observed acrolein concentrations were approximately 5-fold higher than those at the coastal control site. The concentrations of glyoxal, methylglyoxal, and benzaldehyde at Roseville were considerably higher than those at either of the control sites (t test, $P < 0.05$). Surprisingly, the

Table 11. Average Ambient Concentrations of Selected Carbonyls at the Three Air Monitoring Sites in California[a]

Carbonyl	MDL Range (μg/m³)	Average Concentrations ± SD (μg/m³) Salt Point (n = 6)	Juniper Lake (n = 9)	Roseville (n = 6)
Acrolein	0.012–0.035	0.056 ± 0.011	0.089 ± 0.013	0.290 ± 0.008
Methacrolein	0.007–0.033	< 0.027	0.048 ± 0.013	0.044 ± 0.002
Methyl vinyl ketone		—[b]	—[b]	—[b]
Crotonaldehyde	0.009–0.048	< 0.021	0.112 ± 0.025	0.019 ± 0.009
Glyoxal	0.050–0.216	< 0.050	< 0.091	0.340 ± 0.043
Methylglyoxal	0.029–0.038	< 0.038	0.047 ± 0.018	0.252 ± 0.003
Benzaldehyde	0.020–0.044	0.026 ± 0.007	< 0.044	0.233 ± 0.093
Retention of Internal Standard (%)				
Acrolein-d_4		99.1	109	85.7
Benzaldehyde-d_6		75.4	95.5	96.1

[a] Values lower than the MDL are listed as "<". Salt Point represented a clean coastal site while Juniper Lake represented a clean site in a forested region. Roseville is a vehicle-impacted site near Interstate 80. The average retention (%) of the internal standards added to each sample before sample collection is also given for each sampling episode.

[b] Methyl vinyl ketone is not reported owing to poor spike-recovery results.

concentrations of methacrolein were not significantly different between Roseville and Juniper Lake.

The results demonstrated the sensitivity of the new analytical methods in that they were able to detect and quantify acrolein concentrations at remote sites where concentrations are probably representative of hemispheric background levels. The MDL ranged from 0.012 to 0.035 μg/m³ depending on the site, with the cleaner sites having lower limits of detection. Even at the site with the highest detection limit, namely Roseville, we would still have been able to detect the background concentrations of acrolein. The limit of detection at the clean sites was also lower than the EPA RfC of 0.02 μg/m³. The RfC is an estimate of a continuous inhalation exposure to the human population that is likely to be without appreciable risk of adverse health effects during a lifetime.

The results from the three sites proved the consistency of the analytical method. The relative standard deviation for the acrolein concentrations was 20% at Salt Point, 15% at Juniper Lake, and 3% at Roseville. As with many analytical methods, the precision of this technique improved at higher concentrations that were further from the limit of detection. However, the precision of the method at the site with the worst precision, namely Salt Point, is still acceptable, particularly as this site probably represented hemispheric background concentrations of acrolein.

The use of deuterated acrolein and benzaldehyde as surrogates in the mist chambers, blanks, and calibration curves provides the highest level of quality control, as any losses in the samples during collection, transport, storage, and processing are reflected by the surrogates. In addition, because the calibration curves are prepared in the field at the same time and under the same conditions as the sample collection, any environmental influences will affect the samples and calibration curves in the same manner. To our knowledge, this is the first time that these rigorous controls have been used in the collection and measurement of acrolein in air.

The collection efficiency of the mist chambers was also verified under field conditions by determining the carbonyl concentrations in the two mist chambers independently. The collection efficiency in the field was a little lower than the collection efficiencies determined in the laboratory experiments (Table 12). The field collection of acrolein was approximately 70% per mist chamber; thus, the overall collection efficiency for our system of two mist chambers in series was 91% under field conditions. For the other carbonyls investigated, collection efficiencies were similar to or better than those for acrolein. Therefore, the results from the field sampling show that the mist chamber methodology was effective at trapping the volatile carbonyls under field conditions.

Table 12. Mist Chamber Collection Efficiencies for Selected Carbonyls Under Laboratory and Field Conditions[a]

Carbonyl	Collection Efficiency ± SD (%)		
	Laboratory (n = 3)	Juniper Lake (n = 6)	Roseville (n = 6)
Acrolein	80 ± 3	72 ± 6	70 ± 7
Methacrolein	65 ± 10	< MLQ	< MLQ
Methyl vinyl ketone[b]	77 ± 5	< MLQ	67 ± 6
Crotonaldehyde	84 ± 4	79 ± 6	70 ± 15
Glyoxal	42 ± 31	100 ± 12	< MLQ
Methylglyoxal	69 ± 2	76 ± 10	71 ± 6
Benzaldehyde	88 ± 2	100 ± 17	82 ± 8

[a] If one or both mist chamber concentrations were below the minimum level of quantification (MLQ), then the collection efficiency could not be determined. Collection efficiencies could not be calculated for the Salt Point samples owing to nondetectable concentrations in the second mist chamber.

[b] While methyl vinyl ketone had good calculated collection efficiencies, subsequent spike recovery showed the mist chamber methodology is not good for this compound or other ketones.

DISCUSSION AND CONCLUSIONS

METHOD DEVELOPMENT

The vast majority of this project was dedicated to the development of an accurate and sensitive analytical method that could determine concentrations of acrolein and other small carbonyls in ambient air samples over very short time intervals. DNPH and other cartridge-based analysis systems are often limited by a very low rate of air flow through the sampler, which makes these methods inherently insensitive. The slow flow rate also requires longer sampling times. With long sampling times ozone interference is more likely and the instability of the derivatized analytes becomes a greater problem. The solution is to use a sampler that is capable of much higher flow rates. This led us to investigate the use of mist chambers to collect the samples.

The first step of the method development was to determine how to trap the volatile carbonyls in an aqueous phase. Bisulfite was found to form stable complexes with the carbonyls and thus proved to be an effective trapping agent. Higher concentrations of bisulfite were required to trap the more volatile compounds like acrolein. Unfortunately, the bisulfite could also form disulfonate complexes with the unsaturated carbonyls, which could reduce their response. Therefore, the complexes had to be broken up immediately after collection to prevent the formation of the double adducts.

The use of a bisulfite solution in the mist chamber also made the method immune to ozone interference. Bisulfite rapidly reacts with ozone to produce sulfate; therefore, the trapped analytes present in trace amounts were effectively shielded from ozone by the 0.1 M bisulfite solution. Tests with ozonated air proved that this was the case and that the carbonyls added to the bisulfite solution were not degraded when ozonated air was passed through the mist chamber. For the same reason, the ozone also did not create carbonyls from precursor compounds; the high concentration of bisulfite would react rapidly with ozone before the ozone could attack other compounds. Bisulfite was selected for its carbonyl-trapping properties, but other research groups have used bisulfite as an ozone scrubber. A bisulfite-based ozone scrubber should not be used on systems that are designed for carbonyl analysis, however, because it will remove some of the carbonyls from the air stream.

The mist chamber system's inherent immunity to ozone eliminates the need for a separate ozone scrubber. This reduces the cost and improves the accuracy of the sampling, because the ozone scrubbers, which often use potassium iodide salt, can pick up water and thus cause potential partitioning and reaction of the carbonyls before they enter the sampler.

The carbonyl-bisulfite adducts were disassociated through the addition of hydrogen peroxide, which oxidized the free bisulfite and reversed the adduct formation reaction. Because hydrogen peroxide is an oxidizer, we carefully investigated its potential effects on the carbonyls. After optimizing the hydrogen peroxide concentration, which was a slight molar excess over the bisulfite, we tested the solution for stability. The results showed that peroxide may lower the response of the unsaturated carbonyls after about 4 days, so there was an optimal time window for the peroxide and derivatization reaction for the unsaturated carbonyls. Unfortunately, the dicarbonyls had longer derivatization times owing to the multiple-derivatization process, so they were

not completely derivatized until about 7 days. The overall optimal peroxide and derivatization reaction time for a wide range of carbonyls was between 1 and 4 days.

As the durations of the peroxide and derivatization reactions are important variables, the calibration curve must be prepared at the same time as the samples are collected to ensure identical treatment between the samples and the standards. Although the creation of a calibration curve in the field may sound cumbersome, it can be easily accomplished with either previously prepared standards in ampules or concentrated standards and an accurate measuring device such as a syringe. A calibration curve created in the field is also a good quality control measure because it is more representative of the conditions that the samples were exposed to during transport and storage.

The last main aspect of the method development was the determination of the collection efficiency of the mist chambers with the bisulfite solution. More than 70% of the carbonyls were trapped in the first mist chamber. We conducted our sampling using two mist chambers in series to achieve collection rates greater than 90% for all of the carbonyls investigated. The collection efficiencies in the field were similar to those in the laboratory.

The analytical method developed during this study has both advantages and disadvantages. One major advantage is that it provides greater sensitivity than any other analytical method currently available for acrolein. This sensitivity was good enough to detect acrolein at hemispheric background concentrations. The method was fairly precise (RSD <20%), even for these background sites. The second major advantage of the method is the short time required for sampling, which allows the researcher to determine changes in ambient concentrations over very short time intervals. This would be useful to assess the effects of traffic patterns that vary on an hourly basis, as was done at the Peace Bridge in Buffalo. The third major advantage of the method is that its accuracy can be easily determined for every sample through the addition of acrolein-d_4 and other labeled standards to the collection solution *before* sample collection. This will account for any chemical loss through blow-off, ozone degradation (although this is insignificant), inefficient derivatization, incomplete extraction, or instrumental drift. This is a rigorous quality control mechanism that is absent in other existing methods.

The method developed during this research also has limitations. First, it is relatively labor intensive in the field, making the collection of large numbers of samples difficult. Sample processing in the laboratory is not extensive, but it is longer than that for other simpler methods such as canister sampling. Second, the mist chambers are not commercially available and must be custom-made. Therefore, to start a new research project, the researcher must locate a glass-blower and go through a series of trials with any new batch of mist chambers. Because these mist chambers are hand-made, no two are identical with respect to air flow rates and misting efficiency. Finally, because the method is sensitive to the duration of derivatization time, a calibration curve may have to be prepared each day that samples are collected, depending on the specific carbonyls being measured. Ideally, it would be prepared in the field and stored alongside the samples to ensure similar derivatization time periods. The time-sensitive nature of the sample storage and derivatization makes long-term storage of samples before extraction impossible.

PEACE BRIDGE SAMPLING IN BUFFALO

The time-series data from the Peace Bridge sampling showed that acrolein concentrations appeared to cycle in response to the west-bound automobile traffic that was stopped at the plaza adjacent to the Chapel site. Comparisons between the observed acrolein concentrations at the three California sites and the two Peace Bridge sites in Buffalo showed that the concentrations at the Chapel site downwind of the Peace Bridge plaza (0.28 ± 0.1 μg/m^3) were comparable to those at Roseville, the urban California site (0.29 ± 0.01 μg/m^3) (Figure 25). This suggests that the acrolein concentrations downwind of the Peace Bridge during the 3 days of sampling were similar to those found in other urban and vehicle-impacted environments. Also, the concentrations of acrolein at the Great Lakes Research Center site on July 26, 2005 (average = 0.058 ± 0.057 μg/m^3 when the samples in which acrolein was below the MDL were treated as half of the MDL for the calculation) were comparable to those at the control sites in California (Salt Point and Juniper Lake). This indicates that the Great Lakes Research Center provided an appropriate control site for the Chapel site downwind of the Peace Bridge.

In the comparison of the three sampling methods deployed at the Peace Bridge, the mist chamber method was the only one that consistently detected acrolein at the Chapel site. OSHA Method 52 proved to be too insensitive, by about an order of magnitude, to be applicable to determination of acrolein concentrations in outdoor ambient situations. The DNSH passive sampler approach proved to be more sensitive than OSHA Method 52, but the limit of detection for this method was still slightly above the acrolein concentrations, as determined by the mist chambers in this study. Therefore, acrolein was sporadically detected in the eight DNSH samples, including those that represented acrolein collected for 4 days. While this method shows promise for determining ambient acrolein concentrations in areas impacted by vehicular emissions and other sources

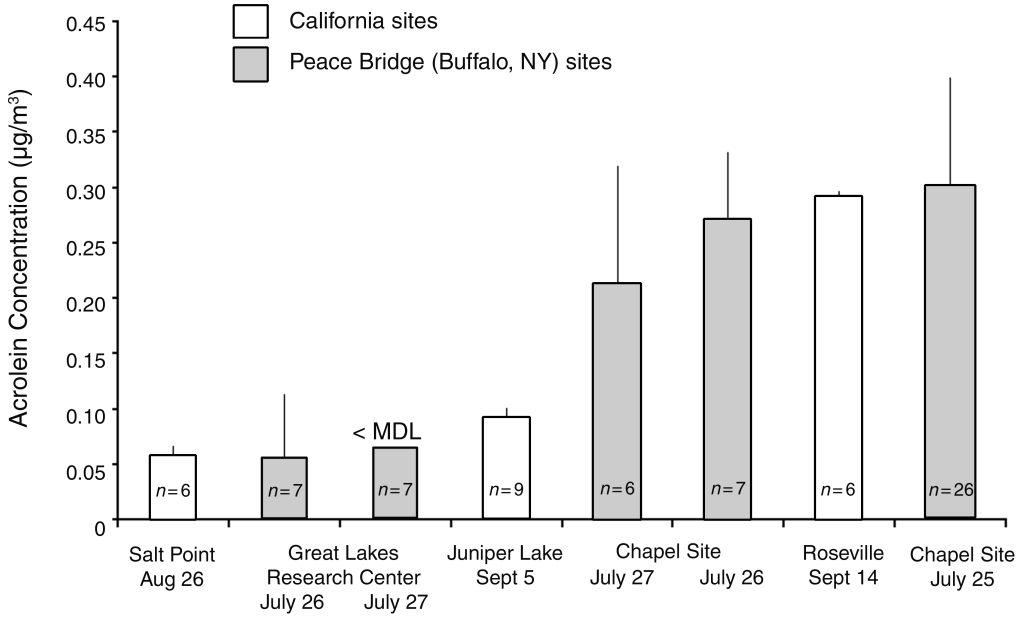

Figure 25. Summary of acrolein concentrations (mean ± SD) at the different sampling sites. The numbers of samples collected and dates of collection at each site are listed below the bars. All samples were collected in 2005. Error bars are ± 1 SD.

of air pollution, it does not have the ability to determine acrolein concentrations over short periods of time, which is needed to assess diurnal cycles. Determining acrolein concentrations at clean background sites may also be difficult with this method.

AMBIENT SAMPLING IN CALIFORNIA

The objective of the ambient sample collection in California was to prove the accuracy, precision, sensitivity, and collection efficiency of the optimized mist chamber methodology for the determination of acrolein concentrations in clean regions and in areas with air pollution. To this end, the sampling efforts were successful in proving that we could detect acrolein in even the cleanest regions of California with good precision.

In addition, the numerical results of the field sampling provided some insight into the sources of acrolein in the environment. Acrolein was detected in the marine air from the North Pacific Ocean, which implies that either acrolein is being transported across the ocean, or there is a natural source of acrolein from direct emission or oxidation from precursor compounds. One possibility is that the acrolein is undergoing long-range transport from Asia. However, the estimated half-life of acrolein is about 15 hours, so it is not likely to cross the Pacific Ocean. In addition, the air sample in this study was collected within the marine boundary layer; hence, chemicals were likely to be scrubbed-out by the ocean or by fog. Another possibility is that acrolein arises from the conversion of other atmospheric hydrocarbons. These hydrocarbons may be either natural or anthropogenic, but we do not have enough data to distinguish between these two types of sources. Therefore, we expect that there is a measurable background concentration of acrolein even in the absence of anthropogenic sources.

It is noteworthy that the background concentration of acrolein determined at Salt Point along the California coast (0.056 ± 0.011 µg/m^3) was higher than the EPA RfC level of 0.02 µg/m^3, as was the background concentration at Juniper Lake in Lassen Volcanic National Park, which is considered to have very clean air (Malm et al. 1994). Therefore, the EPA-recommended chronic exposure limit appears to be lower than the natural background concentration of acrolein. This highlights the problem of conducting health effects studies at high concentrations (ppm concentrations in the case of the EPA studies) and then using extrapolations (interspecies safety factors, sensitive population factors, etc.) to estimate a low concentration that is believed to be safe. The elevated concentrations of acrolein in Roseville were expected because it is an urban site near roadways, but the magnitude of the increase in these urban acrolein concentrations over the rural concentrations was less than expected. The Roseville concentrations were only about 5-fold higher than those on the northern coast and 3-fold higher than those in the clean forested region (see Figure 25). Considering the myriad combustion sources in urban areas, we expected to observe a greater increase in acrolein concentrations in Roseville. The Roseville sampling was

conducted on a windy day, which may have diluted the effect of local emissions. More sampling over the course of several days will be needed to ensure that the observed results were not specific to the particular sampling day.

Another interesting observation is that the California ARB routinely determines acrolein concentrations at the same Roseville site using EPA Method TO-15, in which sample air is collected in a stainless steel canister and then analyzed by thermal-desorption capillary column GC-MS. Their 2006 average concentration was reported as 0.55 ppbv (1.24 μg/m^3) for a 24-hour sample, while the detection limit was 0.3 ppbv (0.69 μg/m^3). The concentrations observed in this research during the middle of the day were much lower. Although it is difficult to compare 10-minute sampling times to 24-hour sampling times, we would expect the concentrations of acrolein to be highest in the middle of the day, as was the case in the Peace Bridge sampling in Buffalo. Therefore, we would expect our short-term values to be higher than the California ARB 24-hour samples. Instead, they were considerably lower. It is also interesting that the reported acrolein concentrations from around the state in 2006 ranged from 0.45 to 0.75 ppb (1.03 to 1.72 μg/m^3), which seems to be a rather limited range given the varied sample locations. In addition, most of the reported values are within a factor of 2 of the reported MDL, a range in which quantification is often difficult. We cannot compare the two sampling approaches because the samples were not obtained at the same time; however, it is noteworthy that our method gave lower concentrations than the California ARB typically reports at that site.

DIRECTIONS FOR FUTURE RESEARCH

The current research provided many suggestive observations about ambient acrolein concentrations that need further investigation.

One direction for future method development that may lead to easier and more widespread sample collection is to take advantage of the stable disulfonate adducts of unsaturated carbonyls that are formed over time in a bisulfite solution. The current method deliberately avoids the formation of disulfonates because the reaction is irreversible and the product cannot be derivatized for GC-MS analysis, which was necessary in this study to achieve chromatographic separation of different isomers (e.g., methacrolein, methyl vinyl ketone, and crotonaldehyde). However, these disulfonate adducts may be quantified directly using liquid chromatography–tandem mass spectrometry (LC-MS-MS) techniques, thus bypassing the steps of hydrogen peroxide disassociation, PFBHA derivatization, and extraction. Recent improvements in liquid chromatography, such as the ultra-performance liquid chromatograph, may provide sufficient chromatographic separation of the different isomers of the unsaturated carbonyls.

If the bisulfite extract can be directly analyzed for the carbonyl adducts, then a much simpler collection and analysis system can be created. For example, a simple cartridge could be coated with bisulfite that would trap the carbonyls and eliminate ozone interference. The cartridge could then be extracted with water and directly analyzed for the bisulfite adducts. As the disulfonate adducts of the unsaturated carbonyls are stable, the sampling system will not be as time sensitive, so longer sample collection times can be used. This long sampling time is necessary for cartridge-based sampling systems because of their low air flow rates. This would then result in a simple procedure for sample collection, similar to the DNPH cartridges that are commonly used, except the derivatives would be more, if not completely, stable. Therefore, the storage stability problems that have plagued the DNPH cartridges could be avoided. The development of a direct bisulfite adduct analysis method could result in a far simpler and more widely applicable method than the current mist chamber method, which requires specialized equipment and procedures.

Another direction for future research is the determination of natural background concentrations of acrolein. The current research has shown that the background concentration of acrolein appears to be higher than the EPA RfC of 0.02 μg/m^3. However, the natural background concentration of acrolein was only really estimated from 2 days of sampling in California, rather than from many independent measurements of the background concentrations. Knowing the natural background of acrolein is essential for any exposure assessment because it is used to set the baseline exposure in the absence of anthropogenic emissions. Also, the accurate determination of natural background concentrations of acrolein may prompt a reevaluation of the EPA RfC if they are indeed greater than the RfC for acrolein.

Determination of acrolein at near-road receptors would also be helpful. The third year of the project, which was not funded by HEI, would have primarily focused on determining the concentrations of acrolein and other small carbonyls in a variety of near-road exposure situations, including tollbooths occupied by attendants, residential areas adjacent to busy roadways, fast-food plazas adjacent to freeways, and "in-car" exposure of people in commuter traffic. These situations would represent some of the highest levels of vehicle-related exposure, and thus they would set an upper limit to the acrolein exposure resulting from vehicles.

Finally, acrolein has many domestic sources, such as tobacco smoke, cooking, incense burning, and wood-fires; thus, significant human exposure to acrolein may occur within homes. This assessment would help to determine

the relative importance of the different pathways of exposure to acrolein. If domestic exposure is the dominant exposure route, then the ambient exposure may be relatively unimportant. The estimation of domestic exposure will be needed for any thorough evaluation of acrolein exposure.

EPILOGUE

HEI discontinued this project after the second year because the methods were deemed "time-consuming, laborious, and not easily replicated by other groups." However, the acrolein research has continued, with funding by other groups such as the California ARB. Subsequent projects evaluated in-home acrolein concentrations and potential sources of indoor acrolein such as cooking oil and building materials. Approximately 217 samples (80 samples of indoor and outdoor air, 107 of cooking oil emissions, and 30 of building materials) were collected and analyzed by a graduate student and a research scientist. In the summer of 2006, the California ARB funded a project to investigate the diurnal cycles of acrolein and other carbonyls in urban and rural regions. A research scientist and three undergraduate students collected a total of 235 samples over 2 months. The results of this ongoing research are starting to be published in the scientific literature (see Other Publications Resulting from This Research). The analytical methods described here are considerably more difficult and time-consuming than canisters, cartridges, or passive samplers, but large numbers of samples can be collected and processed once the equipment and personnel are prepared. Therefore, though the methods presented here are not applicable to widespread regulatory monitoring, they can be very useful to answer specific questions about the occurrence of acrolein and other carbonyls.

IMPLICATIONS OF FINDINGS

This research produced three major findings that have implications for the assessment of human exposure to acrolein. The first of these is that an analytical method has now been developed that is capable of detecting low part-per-trillion concentrations of acrolein with a sampling time of only 10 minutes. The accuracy of each sample determination can be verified through the addition of acrolein-d_4 to each sample before sample collection. Given the uncertainty regarding the acrolein concentrations determined by other analytical approaches, the ability to prove the absolute accuracy of the results is a great improvement. The newly developed analytical approach has the ability to collect the data necessary to answer key questions about human acrolein exposure that could not be answered by previous methods. For example, the method can determine rapid changes in acrolein concentrations over short time scales, which is essential for determining acrolein emissions from traffic that change on an hourly basis. In addition, the analytical method has the sensitivity to accurately quantify background concentrations of acrolein, which sets the baseline for human exposure.

The second major finding from this research is that vehicles contributed to ambient acrolein concentrations. The samples collected downwind of the Peace Bridge plaza had concentrations that were approximately 5-fold higher than the upwind site located only 1 km away. The results also showed that acrolein concentrations appeared to follow the temporal pattern of west-bound automobile traffic, which stops at the plaza before passing over the bridge. The acrolein concentrations at the Chapel site correlated with the automobile traffic ($r^2 = 0.40$), but not the truck traffic, which raises questions about the relative contribution of the two types of vehicles to ambient acrolein concentrations. Of all the carbonyls investigated, acrolein had one of the best correlations with the automobile traffic pattern, which further suggests that vehicular emissions are very important to local acrolein concentrations.

The third major finding from this research is that the natural background concentrations exceed the EPA RfC for acrolein. The results from the two background sites in remote areas of California, one on the north coast and one in Lassen Volcanic National Park, showed quantifiable concentrations of acrolein that were higher than expected and exceeded the EPA RfC for acrolein. This raises the question whether this exposure limit is valid. The EPA's chronic exposure RfC for acrolein of 0.02 $\mu g/m^3$ was based on subchronic animal exposure studies performed in 1985 (Kutzman et al. 1985). The lowest exposure concentration used in these studies was 0.4 ppm or 1 mg/m^3, which was also the lowest level at which adverse effects were seen. A series of uncertainty factors was then applied to obtain the action level of 0.02 $\mu g/m^3$. The concentrations at both of the remote sites in California and the control site upwind of the Peace Bridge in Buffalo were more than twice the EPA RfC. In light of this information, it would seem prudent to reevaluate the effects of chronic exposure to these lower levels of acrolein.

The acrolein concentrations in the background locations were higher than expected. The urban acrolein concentrations in Roseville were only about 5-fold higher than those in the remote areas. Given the many anthropogenic sources of acrolein in Roseville, including vehicular emissions, a major rail yard, and urban combustion sources, it was surprising that the difference between concentrations there and those in the remote sites was not greater. Some of

the other carbonyls investigated, such as benzaldehyde, showed a much greater degree of urban enrichment. The same trend was observed at the Peace Bridge in Buffalo, with the downwind acrolein concentrations being about 5-fold greater than the upwind concentrations. The similar results from these two field studies suggest that the natural background of acrolein may be more important than previously suspected. Further research into the background concentrations of acrolein is necessary for more accurate assessment of both human exposure to acrolein and the relative contribution of anthropogenic activity to ambient acrolein concentrations.

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APPENDIX A. Standard Operating Procedures for Carbonyl Collection and Analysis

Created by Thomas M. Cahill on April 29, 2005; revised July 4, 2006

PURPOSE

To collect and determine concentrations of acrolein and other small carbonyls in the ambient atmosphere using mist chambers and a bisulfite trapping solution.

HAZARDS

Use all solvents and perform all extractions in the fume hood. Hexane, which is used in the extractions, is flammable and should be considered toxic. Hydrogen peroxide is an oxidizing agent and should be stored away from other organic solvents. Sulfuric acid is a corrosive agent that should be stored with other acids. Be sure to wear protective gear when making solutions of sulfuric acid. Pentafluorobenzylhydroxylamine (PFBHA) has not been fully characterized as to its hazards; therefore, it should be treated with care as a potential toxicant.

REAGENTS

1. **Bisulfite 0.1 M Solution**

   Prepare solution by adding 12.6 g of sodium sulfite to 1 L of HPLC-grade or 18 MΩ-resistance water. Adjust pH to approximately 5.0 by adding 55 mL 1.0 M H_2SO_4. Allow solution to equilibrate for 24 hours before use. The solution appears to be stable for at least 6 months.

2. **PFBHA 50 mM Solution**

   Add 62.5 mg of PFBHA to 5.0 mL of methanol. Use the PFBHA as received from the manufacturer. The solution appears to be stable for at least 1 month.

3. **Hydrogen Peroxide**

   Use the 30% solution as purchased. Keep the bottle sealed when it is not in use to prevent contamination. Do not pipette directly from the source bottle.

4. **Internal Standard Solution**

   Acrolein-d_4, benzaldehyde-d_6, and acetaldehyde-d_4 are prepared at a concentration of 10 ng/μL in methanol. Additional internal standards will be added to the mixture as they become available.

   For field sampling, the internal standard mixture (10 μL of solution) will be added to an ampule containing 200 μL of acetonitrile and then sealed in the laboratory. The ampule can then be transported and used in the field without fear of chemical loss or contamination. The internal standard mixture will be added to the samples before collection to account for blow-off, degradation, or incomplete derivatization of the analytes.

5. **Injection Standard Solution**

   Octafluoronaphthalene (10 ng/μL), 1,2,3-tribromo-5-fluorobenzene (50 ng/μL), dibromonaphthalene (50 ng/μL), and hexabromobenzene (100 ng/μL) are combined into a single hexane solution containing the stated concentrations. Then 10 μL of the injection standard is added to a 0.5-mL sample just before instrumental analysis to quantify any instrumental drift.

6. **Calibration Standards**

   Calibration standards are mixtures of the carbonyls of interest in methanol which result in a final carbonyl concentration of 5, 10, 50, 100, or 500 pg/μL. The current compound list includes acrolein, methacrolein, methyl vinyl ketone, crotonaldehyde, glyoxal, methylglyoxal, and acetaldehyde. The calibration solutions also contain the internal standard compounds of acrolein-d_4 and acetaldehyde-d_4 at a constant concentration of 100 pg/μL, which is the same concentration as would be present in the field samples if there were no losses.

GLASSWARE CLEANING

All glassware is washed in hot soapy water, rinsed twice with deionized water, rinsed once with acetone (to remove soap residues), and baked at 550°C for 8 hours. After baking, either the glassware is capped (in the case of test tubes and centrifuge tubes) or the openings are covered with aluminum foil. This is intended to reduce glassware exposure to air, which might cause contamination.

SAMPLING EQUIPMENT

Two mist chambers per sampling train (and backup chambers in case of breakage)

Medo vacuum pump

DryCal lite (preferred) or rotometer to measure air flow rate

Vacuum tubing and connectors

Snyder column (to act as an aerosol trap and protect pump from any bisulfite solution leakage)

HPLC-grade water (for rinsing mist chambers), approximately 4 L per day of sampling

A syringe (2.5 to 5 mL) or WireTols for measuring internal standards and calibration curves

Large syringe (preferred) or pasteur pipettes and bulbs for water rinses

Equipment for measuring meteorologic conditions (temperature, relative humidity, and wind speed)

Ozone meter

Laboratory notebook

For sampling in remote areas away from line power, the following additional equipment is needed:

12-V deep cycle battery

Power inverter (300 W or greater, one per pump)

Battery recharger

BEFORE FIELD COLLECTION

1. Measure 10 mL of the 0.1 M bisulfite solution into amber 15-mL vials. These are the "collection" solutions. Prepare enough vials for all the samples (with 2 vials per sampling train), reagent blanks, field blanks, and calibration curve. In addition, prepare approximately 15% extra vials in case of breakage.
2. Prepare the "reaction" tubes that will neutralize the bisulfite and derivatize the carbonyls. These are the tubes that contain H_2O_2, PFBHA, sulfuric acid, water, and hexane. This mix is stable for a least 1 week, but try to prepare these solutions as close to sampling time as possible.

If the two mist chambers are going to be combined (i.e., there is no collection efficiency measurement), then add the following to a 50-mL test tube:

2 mL of 1.8 M H_2SO_4
200 µL of H_2O_2
400 µL of 75 mM PFBHA
5 mL of hexane

If the two mist chambers are going to be processed separately (for collection efficiency determination), then add the following to a 30-mL test tube:

1 mL of 1.8 M H_2SO_4
100 µL of H_2O_2
200 µL of 75 mM PFBHA
5 mL of hexane

The choice to combine the two sequential mist chamber solutions or process them separately is a matter of logistics. Processing the two mist chambers separately allows the investigators to determine the collection efficiencies of the analytes for the field samples. However, this results in processing two samples for every mist chamber collection run. Combining the two mist chambers reduces the number of samples that need to be processed by half, but then the collection efficiency cannot be determined for the field samples. A second disadvantage to combining the samples is that the combined sample will have a higher background blank, so the sensitivity of the combined sample is lower. If the mist chamber samples are processed separately, then the blank (which is largely due to reagents) is lower. Since the first mist chamber collects most of the chemical mass, this creates a better signal-to-noise ratio.

Therefore, combining the two mist chamber solutions is recommended when large numbers of samples will be processed. The solutions should be processed separately when only a few samples will be processed and the expected concentrations are low, such as at background sites.

COLLECTION AND DERIVATIZATION

1. Assemble vacuum pump and flow monitoring system.
2. Fill two mist chambers with 10 mL of the 0.1 M bisulfite solution. Keep the two mist chambers in the same order for all sampling times during the campaign, so label one chamber "A" and always put it as the first mist chamber.
3. Add 100 ng of each internal standard chemical to mist chamber A by adding 10 µL of the 10-ng/µL solution directly to the collection solution. Allow the collection solution to sit for 10 minutes. If the experiment calls for the determination of collection efficiency, then add the internal standards to both mist chambers as they will be processed separately.
4. Connect the two mist chambers in series, making sure that mist chamber A is first.
5. Turn on the vacuum pump and ensure that the flow rate is between 10 and 20 L/min. Make sure the chambers are forming mist. Record the exact start time and flow rate in the sample log book.
6. Record meteorologic conditions such as temperature, relative humidity, and wind speed and direction.
7. After 10 minutes, turn off the vacuum pump and record the exact end time in the sample log book. Make any comments relevant to the sampling (local conditions, etc.).
8. Empty both mist chambers into a single 50-mL reaction tube. If the chambers are going to be processed separately, then add the solutions from the two chambers to two different reaction tubes, being sure to label each as either the "A" or "B" chamber. Rinse each chamber twice with approximately 5 mL of HPLC-grade or 18-MΩ-resistance water. Add these rinses to the appropriate sample in the reaction tubes.
9. Label the sample on both the test tube and the cap with a sticky label and a pencil. (Pencil lead does not come off in organic solvents, so accidental erasure is less likely.)
10. Prepare a calibration curve in the field at the time (within 6 hours) of the sample collection. Add the internal standard mixture (10 µL of the 10-ng/µL solution) to each of six collection solution vials. Then add the appropriate amount of the standard solution to

each vial (see below). Allow the chemicals to react for 10 minutes and then pour the collection solution into a reaction tube. The amount of standard to add is as follows:

0 pg/µL standard uses 0 µL of standard solution
10 pg/µL standard uses 2 µL of standard solution
50 pg/µL standard uses 10 µL of standard solution
100 pg/µL standard uses 20 µL of standard solution
250 pg/µL standard uses 50 µL of standard solution
500 pg/µL standard uses 100 µL of standard solution

11. Store the samples at room temperature for 24 to 96 hours to allow them to react. The samples should be extracted before 96 hours for the best results.

SAMPLE EXTRACTION

Sample extraction needs to be conducted 24 to 96 hours after sample collection. For each sample and standard:

1. Shake vigorously and allow the aqueous and hexane layers to separate. Remove the hexane layer and add it to a graduated, 15-mL conical glass centrifuge vial by passing the hexane through a sodium sulfate pasteur pipette column to remove any traces of water.
2. Conduct an additional extraction by adding another 5 mL of hexane to the sample and processing it as in step 1.
3. Reduce the volume of the extract to 0.5 µL by nitrogen evaporation. Vortex the centrifuge tube to wash the walls before transferring the solution to an amber GC vial.
4. Add 10 µL of the injection standard solution to each sample and standard to serve as an injection standard.
5. Store samples at 4°C in a sealed container with desiccant until instrumental analysis. The samples are stable for at least 30 days in this condition.

INSTRUMENTAL ANALYSIS

The samples are best determined by gas chromatography followed by negative chemical ionization mass spectrometry owing to the electronegative properties of the pentafluorohydroxyl functional group. Note that carbonyls may give rise to more than one peak because of isomers arising from the double bond in the derivatization reagent. Chromatographic separation of different isomers (e.g., methacrolein, methyl vinyl ketone, and crotonaldehyde) is easily accomplished by gas chromatography. Our instrumental conditions are as follows:

1. Instrument: Agilent 6890GC and 5973MS
2. Column: DB-5MS or DB-XLB (30 m, 0.25-mm I.D., 0.25-µm film thickness)
3. Helium carrier gas at a linear velocity of 35 cm/sec.
4. GC Program: Initial temperature of 50°C, increase 5°C/min to 150°C, increase 20°C/min to 260°C, increase 30°C/min to 325°C, hold for 5 minutes.
5. MS source temperature is 150°C; mode is negative EC/CI; reagent gas is CH_4.

Typically, the PFBHA-derivatized carbonyls ionize to give $[M–20]^-$ as the dominant ion, which represents the loss of hydrofluoric acid (HF) from the molecule. This is typically the quantification ion for our analytes.

APPENDIX B. Clayton Group Services Laboratory Report for the Analysis of Acrolein from HMP-Coated Cartridges

These cartridges were collected at the Peace Bridge in Buffalo during the same time as the mist chamber samples were collected. Therefore, the results from these samples could be used to assess the three different analysis methods for colocated samples collected in the field.

Details about the cartridge samples are given in **Table B.1**.

Table B.1. Cartridge Samples Analyzed by Clayton Group Services

Site of Collection	Date in 2005	Sample ID	Clayton ID Number	Volume of Air Collected (L)	MDL (µg/m^3)
Chapel	July 25	316	7	71.5	28.0
Chapel	July 26	9	4	71.9	27.8
Great Lakes Research Center	July 26	4	2	68.5	29.2
Chapel	July 27	1	1	73.4	27.3
Great Lakes Research Center	July 27	17	5	30.2	66.2
Great Lakes Research Center - blank	July 26	8	3		
Great Lakes Research Center - blank	July 25	310	6		

ABOUT THE AUTHORS

Thomas M. Cahill is an assistant professor at Arizona State University at the West Campus in the Department of Integrated Natural Sciences. His research has focused on determining the sources and environmental fate of anthropogenic pollutants through both field measurements and multimedia computer models. Recent research projects include determining the emission rates of polybrominated diphenyl ethers from automotive and electronics recycling facilities as well as estimating the behavior of fluorinated acids and surfactants in the environment. He received his Ph.D. from the University of Nevada, Reno.

M. Judith Charles was an assistant professor in the Department of Environmental Toxicology at the University of California–Davis. Her research focused on investigating the linkages between the laboratory and field domains to advance an understanding of the generation, fate, and health effects of pollutants. One area of particular interest was the formation of oxygenated organic molecules, from both biogenic and vehicular emissions, and their contribution to aerosol formation. Another area of research was the sources and impacts of halogenated compounds on occupationally exposed groups. One common thread between all her research projects was the development of new analytical methodologies to measure trace amounts of pollutants in environmentally relevant matrices. She received her Ph.D. from the Department of Environmental and Industrial Health at the University of Michigan.

Judi Charles passed away in October 2004 after a long fight with cancer.

Vincent Y. Seaman is currently at the Centers for Disease Control and Prevention in Atlanta. The research presented in this report was the core of his Ph.D. dissertation in Pharmacology and Toxicology at the University of California–Davis. In addition to his work at UC–Davis, he has undergraduate degrees in chemistry and biology and has worked as a research and manufacturing chemist, a pharmacist, and a public high school teacher.

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ABBREVIATIONS AND OTHER TERMS

2-HMP	2-(hydroxymethyl)piperidine
ARB	Air Resources Board (California)
CAS	Chemical Abstract Society
DNPH	dinitrophenylhydrazine
DNSH	dansylhydrazine
ECNI	electron-capture negative ionization
ECNI-MS	electron-capture negative ionization mass spectrometry
EPA	U.S. Environmental Protection Agency
GC	gas chromatography
GC-MS	gas chromatography with mass spectrometry
IUPAC	International Union of Pure and Applied Chemistry
LC-MS-MS	liquid chromatography with tandem mass spectrometry
MDL	minimum detection limit
MS	mass spectrometry
MTBE	methyl-*tert*-butyl ether
m/z	mass-to-charge ratio
$NaHSO_3$	sodium bisulfite
$NaHSO_4$	sodium bisulfate
Na_2SO_3	sodium sulfite
OSHA	Occupational Safety and Health Administration
PAKS	Personal Aldehydes and Keytones Sampler
PFB	pentafluorobenzyl
PFBHA	*o*-(2,3,4,5,6-pentafluorobenzyl) hydroxylamine
PFPH	2,3,4,5,6-pentafluorophenylhydrazine
ppb	parts per billion

ppbv	parts per billion by volume
PTFE	poly(tetrafluoroethylene)
RfC	reference concentration
RFPA	Request for Preliminary Applications
RIOPA	Relationships of Indoor, Outdoor, and Personal Air Study
RSD	relative standard deviation
XAD-2	trade name for a styrene divinylbenzene polymer based adsorbent

Research Report 149, *Development and Application of a Sensitive Method to Determine Concentrations of Acrolein and Other Carbonyls in Ambient Air,* T.M. Cahill et al.

INTRODUCTION

Acrolein is a reactive aldehyde that injures the airways in humans and other species. Aldehydes (also referred to as carbonyls because of their chemical structure) are part of a diverse group of air pollutants called air toxics whose levels are not regulated by National Ambient Air Quality Standards, but which are known or suspected to cause adverse health effects in humans. They are, however, subject to a set of rules promulgated by the U.S. Environmental Protection Agency (EPA*) as part of its mandate to characterize, prioritize, and reduce the impacts of air toxics on public health and the environment. In 2001 the EPA targeted 21 air toxics emitted, at least in part, from mobile sources that needed to be reduced (U.S. EPA 2001); subsequently, it identified 8 of these mobile-source air toxics that, based on their emissions and reported toxicity, pose the greatest health risk (U.S. EPA 2007). Among these are three aldehydes: formaldehyde, acetaldehyde, and acrolein. Information on the concentrations of these pollutants to which people are exposed is important for assessing the risk to human health.

Despite some technological improvements, it remains difficult to accurately measure acrolein and other reactive aldehydes in ambient air at low levels because, upon collection, they rapidly form unstable intermediates that are difficult to differentiate and quantify. HEI has supported several studies aimed at improving methods for measuring aldehydes in ambient air as part of the air toxics research program.

In 2001 Dr. Judith Charles of the University of California–Davis and colleagues submitted a proposal, entitled "Exposure of Tollbooth Attendants to Acrolein and Other Toxic Carbonyls in the San Francisco Bay Area," in response to Request for Preliminary Applications (RFPA) 00-3. Through RFPAs, HEI funds studies that are compatible with its overall research priorities but fall outside the areas targeted in its Requests for Applications. The applicant and her colleagues proposed to develop a new method to collect and measure low levels of acrolein, crotonaldehyde, and other unstable carbonyls (involving the formation of a stable chemical intermediate), and then use this method to examine the exposure of tollbooth attendants in the San Francisco Bay area. The Research Committee thought that it was important to develop more sensitive methods for measuring acrolein and other unsaturated carbonyls in ambient air and asked for a full application. After reviewing the full application, the Committee recommended that the investigators limit the study to the development of the sampling and analytic methods to determine whether the approach would be successful, but it left open the possibility of a field study that might allow comparison with existing techniques at a later date. The Committee believed that the proposed method might be useful for accurately measuring low levels of these carbonyls.

During the middle of the second, and last, year of this work, Dr. Charles became ill, and Dr. Thomas Cahill replaced her as the principal investigator and completed the study. The Committee did not fund a third year of work because it was not convinced that the technology was ready for field application. Nevertheless, Cahill and colleagues made some limited outdoor measurements independently and included them in the Investigators' Report with the approval of the Review Committee. This critique is intended to aid HEI sponsors and the public by highlighting the strengths of the study and the advantages and disadvantages of the technique, and by comparing it with other available techniques.

SCIENTIFIC BACKGROUND

CHEMISTRY

Aldehydes and ketones are two types of volatile organic molecules that contain a carbonyl group (C = O). Aldehydes

The 2-year study of Drs. Thomas M. Cahill, M. Judith Charles, and Vincent Y. Seaman, "Development and Application of a Sensitive Method to Determine Concentrations of Acrolein and Other Carbonyls in Ambient Air," began in January 2003. Total expenditures were $430,230. The draft Investigators' Report from Cahill and colleagues was received for review in December 2005. A revised report was received in July 2006. A second revision of the report, received in December 2006, was accepted for publication in March 2007. During the review process, the HEI Health Review Committee and the investigators had the opportunity to exchange comments and to clarify issues in both the Investigators' Report and the Review Committee's Critique.

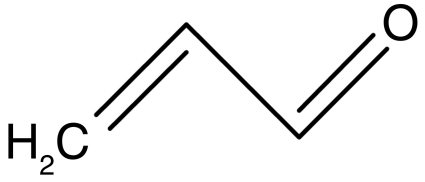
* A list of abbreviations and other terms appears at the end of the Investigators' Report.

contain a hydrogen molecule attached to the carbonyl group and have the general formula of RCHO, where R is a hydrocarbon group (except for formaldehyde, where R is hydrogen). Ketones have the general formula R_1R_2CO, where R_1 and R_2 represent carbon chains. There are two broad classes of aldehydes: saturated (with no double bonds between carbon atoms), such as formaldehyde and acetaldehyde, and unsaturated (with a double bond between the α and β carbons, such as acrolein (see chemical structure in Critique Figure 1) and crotonaldehyde. The presence of an α,β-unsaturated bond in aldehydes increases their reactivity (Witz 1989).

EXPOSURE AND HEALTH EFFECTS

Acrolein is emitted by a variety of indoor and outdoor sources but primarily from the incomplete combustion of automotive fuels, tobacco, wood, and cooking oils and fats. Nationwide, on-road mobile sources accounted for 14% of acrolein emissions in 1999 (U.S. EPA 1999b). Levels of acrolein are usually low in outdoor air in the United States, ranging from 0.5 to 11.9 μg/m^3 (HEI Air Toxics Review Panel 2007); indoor levels where there is combustion of tobacco products can be much higher (Agency for Toxic Substances and Disease Registry 2007). The oxidation by ozone of atmospheric 1,3-butadiene, which is emitted from motor vehicles, is an important source of acrolein in ambient air (Kramp and Paulson 2000; Agency for Toxic Substances and Disease Registry 2007). Acrolein can also form when ozone reacts with terpenes (naturally occurring hydrocarbons from trees and plants) (Nazaroff and Weschler 2004).

Acrolein is a respiratory irritant in humans: exposure to a relatively high concentration (700 μg/m^3) induces eye, nose, and throat irritation (HEI Air Toxics Review Panel 2007). Acrolein exposure also damages rodent airways. Acute exposure to acrolein at 1.6 mg/m^3 and 14 mg/m^3 depressed respiratory rates in mice and rats, respectively (Steinhagen and Barrow 1984), and acrolein at 0.4 mg/m^3 induced bronchial hyperresponsiveness and airway inflammation in guinea pigs (Leikauf et al. 1989; Leikauf 1991). Exposure of rodents to 1.8 ppm (0.8 mg/m^3) acrolein for 13 weeks was associated with nasal and lower-airway inflammation; hyperplasia and squamous metaplasia were also observed in the lower airways (Dorman et al. 2008). Other studies of acrolein exposure have reported changes in airway structure and histologic and biochemical alterations associated with chronic obstructive pulmonary disease, including airspace enlargement, mucous-cell metaplasia, and increased mucin gene expression (e.g., Costa et al. 1986; Borchers et al. 1998, 1999). The International Agency for Research on Cancer (1995) concluded that there was inadequate evidence to determine the carcinogenicity of acrolein, and the EPA concluded in its latest update of the evidence that the potential "carcinogenicity of acrolein cannot be determined by the inhalation route because of a lack of human data and adequate chronic bioassays in laboratory animals" (U.S. EPA 2003).



Critique Figure 1. Chemical structure of acrolein.

CURRENT TECHNIQUES FOR MEASURING ACROLEIN

Currently, there is no federal reference method for measuring acrolein and other unsaturated carbonyls. Method TO-11A, the EPA's conventional method for measuring carbonyls, primarily formaldehyde, uses an active sampler consisting of a cartridge coated with dinitrophenylhydrazine (DNPH) adsorbed on silica gel (U.S. EPA 1999a), but it is not suitable for the unsaturated carbonyls because the product of their reaction with the DNPH (a carbonyl hydrazone) is unstable (Tejada 1986; Kieber and Mopper 1990). After collection the carbonyls are desorbed from the cartridge and separated by high-performance liquid chromatography with ultraviolet analysis. This method has been adapted for passive samplers and used to measure acrolein by various research groups (e.g., Grosjean and Williams 1992; Uchiyama and Hasegawa 1999). The instability of the hydrazone derivative for unsaturated carbonyls in the DNPH-based method led Dr. Junfeng (Jim) Zhang and colleagues to develop, as part of the study Relationships of Indoor, Outdoor, and Personal Air (RIOPA), funded by HEI and the Mickey Leland National Urban Air Toxics Research Center, a passive sampler using a fluorogenic reagent, 5-dimethylaminonaphthalene-1-sulfohydrazide or dansylhydrazine (DNSH) (Zhang et al. 2000). Binding of the unsaturated carbonyls with DNSH results in a more stable derivative than binding with DNPH. Furthermore, the method for analyzing this product relies on fluorescence, which has higher sensitivity than ultraviolet detection. The DNSH-based Personal Aldehydes and Ketones Sampler (PAKS) developed by Zhang and colleagues had a minimum detection limit (MDL) of 0.14 μg/m^3 for acrolein, as determined during the RIOPA study, versus the MDL range of 0.57 to 1.04 μg/m^3 determined with an active DNPH-based sampler (Weisel et al. 2005). Like the DNPH-based method, it requires relatively long sampling

times (24 to 48 hours). Although the DNSH-based method was an improvement over the method using DNPH, it still recovered only 60% of the acrolein (Zhang et al. 2000).

To further improve their method, the RIOPA investigators examined the chemical reactions between the carbonyls and DNSH. They discovered that unsaturated carbonyls can undergo further derivatization at the carbon–carbon double bond, resulting in additional peaks in the chromatographic profile that were not detected using their original method. On the basis of this finding, the method for analysis of the DNSH-based cartridge samples was modified to maximize the conditions for derivatization of acrolein. The new method recovered 99% of the acrolein (Herrington et al. 2005). Subsequently, the same group developed an active sampler that collects acrolein from 30 minutes to 24 hours. However, this sampler has not been tested in the field for short sampling periods.

Ho and Yu (2004) developed a glass sampling tube coated with a mesh with 2,3,4,5,6-pentafluorophenylhydrazine (PFPH) that relies on the thermal desorption of the carbonyl by gas chromatography with mass spectrometry (GS-MS) and appears to provide good separation of acrolein. The MDL for acrolein (0.23 $\mu g/m^3$) during a 4-hour sampling period was lower with this method than the MDL obtained with the DNPH-based method (1.41 $\mu g/m^3$) in the same study.

The EPA also developed a method specific to acrolein, Method TO-15 (Eastern Research Group 2005). Canisters are used to collect acrolein in the gas phase, which is then measured by GC-MS. The MDL for acrolein was reported to be 0.18 $\mu g/m^3$ when samples were collected in the field during a period of 24 hours (Swift et al. 2006). Method TO-15 has several advantages: canister preparation for collection is simple, a variety of sampling times can be used, and the analyte does not require derivatization. Finally, Occupational Safety and Health Administration (OSHA) Method 52 for measuring acrolein and formaldehyde in occupational settings uses XAD-2 absorbent cartridges coated with 2-(hydroxymethyl)piperdine. The method has a reported overall MDL of 6.1 $\mu g/m^3$ for acrolein (OSHA 1989) and is not sensitive enough to detect it in ambient air.

STUDY DESIGN AND SPECIFIC AIMS

Charles and Cahill, with Dr. Vincent Seaman, explored a mist chamber technique for measuring low levels of acrolein and other unsaturated carbonyls. The method relies on trapping the carbonyls in an aqueous medium in which they form stable chemical reaction products. The overall aim of the study was to develop and optimize the technique. The methods were developed in several distinct phases: (1) investigation and optimization of conditions for trapping acrolein and other carbonyls in the mist chamber and obtaining a stable carbonyl derivative for analysis; (2) evaluation of the effects of both positive and negative artifacts arising from ozone interactions; and (3) investigation of collection efficiency and recovery of the analyte.

The investigators also measured acrolein levels in two field studies and compared the results with those obtained using other methods.

METHODS AND RESULTS

DEVELOPMENT AND OPTIMIZATION OF MIST CHAMBER METHODOLOGY

The methods development focused on optimizing the collection and quantification of acrolein, but many other carbonyls were also tested. Specifically, four unsaturated carbonyls (acrolein, methacrolein, methyl vinyl ketone, and crotonaldehyde) and two small dicarbonyls (glyoxal and methylglyoxal) were used for validation of the device during all stages of laboratory testing and in the field studies. At later stages in the methods development, benzaldehyde and other carbonyls were included. Some of the experimental work described in the Investigators' Report is also reported by Seaman and colleagues (2006).

Mist Chamber Description

The mist chamber consists of a custom-made glass cylinder containing a solution through which air is drawn by a vacuum pump. Before the air enters the chamber, it passes through a nebulizer (see Figure 1 of the Investigators' Report). The nebulizer produces a fine mist that facilitates adsorption of the carbonyls from the gas phase into the liquid phase in which they are trapped. Baffles or Teflon filters are used to prevent the escape of the carbonyls from the chamber.

Carbonyl Trapping

In previous research using the mist chamber, the investigators showed that water-soluble gaseous chemicals of low volatility, when pulled into the chamber through a nebulizer, dissolve in an aqueous solution containing *o*-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine (PFBHA) and form stable derivatives for GC-MS analysis (Spaulding et al. 2002). However, acrolein is highly volatile and could

not be collected and measured by that method. Cahill and coworkers found that a sodium bisulfite solution was very effective in trapping acrolein and other volatile carbonyls. Bisulfite attacks the electrophilic carbon of the carbonyl group, forming a carbonyl-bisulfite adduct that is highly water soluble and quite stable. Experiments to determine the rate of this reaction for six carbonyls (acrolein, methacrolein, crotonaldehyde, glyoxal, methylglyoxal, and formaldehyde) were conducted by adding each carbonyl to a solution containing an excess amount of bisulfite and monitoring the adduct formation. The reaction was allowed to proceed for 40 minutes at room temperature (21°C). After 10 minutes, 96% of the acrolein was in the form of an acrolein-bisulfite adduct (shown in Table 2 of the Investigators' Report). A bisulfite concentration of 0.1 M was selected because separate experiments had shown that it yielded the highest collection efficiency for carbonyls in the mist chamber (described below).

Carbonyl Derivatization and Extraction of Derivatives

To measure the acrolein collected in the mist chamber, the first step was to convert the trapped carbonyl to a stable derivative for GC-MS analysis. The investigators evaluated two fluorinated derivatizing agents and selected PFBHA, which was used in the earlier studies (Spaulding et al. 2002). However, the bisulfite in the adducts prevented the carbonyls from binding to the PFBHA, and the amount of carbonyl derivatized was minimal. Hydrogen peroxide was added to oxidize the bisulfite to sulfate, freeing the carbonyls (equations 8, 9, and 10 in the Investigators' Report). A 1.06:1 molar ratio of peroxide to bisulfite allowed for maximum derivatization of acrolein (Table 5 and Figure 6 of the Investigators' Report). The minimum concentration of PFBHA needed for maximum yield of acrolein and most of the other carbonyls tested was determined to be 1 mM for a 24-hour derivatization time (Figure 7 of the Investigators' Report). Higher concentrations yielded no significant increases in derivatization (t test, $P > 0.05$ for all compounds tested).

As part of this work, experiments were also conducted to determine the optimal time for the derivatization reaction and the stability of the carbonyl-bisulfite adducts over time. The investigators found that the derivatization reaction for individual carbonyls was complete within 24 to 168 hours, but there was not a common optimal derivatization time for all the carbonyls (Figure 8 of the Investigators' Report). The authors chose a derivatization time of 4 days (96 hours), which appeared to be optimal for acrolein and many of the other carbonyls analyzed.

The stability of the different carbonyls in the bisulfite solution also varied, ranging from 1.1 day for methyl vinyl ketone to 13.6 days for acrolein (Figure 9 of the Investigators' Report). This finding led the authors to derivatize the carbonyl-bisulfite adducts immediately after the end of sampling. Thus all the field samples had to be derivatized in the field. The stability of the carbonyl derivatives is not reported. For consistent calibration, the investigators recommend that the calibration standards be brought to the field and processed in parallel with the collected samples. This protocol was applied to the field studies described below.

The next step was to extract the carbonyl derivatives from the mist chamber solution. Two solvents, methyl-*tert*-butyl ether and hexane, were tested. Hexane was chosen because it yielded fewer contaminants in the chromatogram. After extraction and storage in anhydrous hexane, the acrolein appeared to be stable for extended periods of time. No losses were noted when derivatized acrolein extracts were stored at 4°C for 6 months. The standard operating procedures for sample collection, extraction, and analysis can be found in Appendix A of the Investigators' Report.

Evaluation of Interference by Ozone

Ozone is a highly reactive gas present in ambient air and in common atmospheric precursors of hydroxyl radicals (reactive species that oxidize many atmospheric compounds), which could create artifacts when trapped in the mist chamber. The role of ozone in the chamber was explored by adding a known concentration of acrolein into the mist chambers and comparing the effects of zero-grade (purified) air and zero-grade air with ozone, which were passed through the mist chamber for 10 minutes. Ozone at 100 ppb did not cause any degradation of acrolein or other unsaturated carbonyls in the bisulfite solution.

Internal Standards

Isotope-labeled (deuterated) internal standards were added to the mist chambers before sample collection both in laboratory experiments and in field studies to account, and correct, for potential losses during collection (due to volatization), derivatization, and extraction. Acrolein-d_4 was used as a standard for unsaturated carbonyls with low molecular weights (acrolein, methacrolein, methyl vinyl ketone, and crotonaldehyde); benzaldehyde-d_6 was used for all other less-volatile unsaturated carbonyls. To correct for losses, the peak area of the analyte on the chromatogram was divided by the peak area of the internal standard. The investigators assumed that the deuterated standards performed the same as the analytes being measured.

EVALUATION OF MIST CHAMBER COLLECTION EFFICIENCY, RECOVERY, AND RETENTION

Three different approaches were used to evaluate the ability of the mist chamber methodology to collect, derivatize, extract, and accurately measure the concentrations of acrolein and other carbonyls: (1) measuring the collection efficiency of a carbonyl sample in one chamber relative to that in a second chamber in series; (2) determining the recovery of a carbonyl delivered to the chamber from a "spiking tube" placed upstream of the chamber, using the mass balance approach; and (3) tracking the retention of an internal standard carbonyl added directly to the mist chamber. Critique Table 1 summarizes the results of the experiments described in this section.

Collection Efficiency

The collection efficiency for the two mist chambers connected in series was determined as the amount of acrolein in the first chamber relative to the amount in the second chamber, expressed as a percentage. The result is a relative measure of the efficiency of trapping the carbonyl that is not dependent on the initial carbonyl concentration and can be determined in the field. This approach does not provide an absolute value for the collection of a carbonyl.

The mist chamber's collection efficiency was initially determined to establish the effect of varying the bisulfite concentration on the derivatization process. In those experiments, the investigators filled a Tedlar bag with zero-grade air containing the carbonyls to be measured. The content of the bag was drawn into the mist chamber at a flow rate of 20 L/min. The collection efficiency was dependent on the concentration of bisulfite. It reached a maximum of 83% at 0.1 M bisulfite (as estimated from Figure 18 of the Investigators' Report). Based on these results, the investigators decided to use two mist chambers in series for all future experiments.

In subsequent experiments the investigators put a known amount of acrolein in a spiking tube placed upstream of the two mist chambers and delivered the acrolein to the mist chamber by blowing pure nitrogen through the tube to simulate ambient collection conditions. The measured collection efficiency was 80% for a 10-minute period (Table 6 of the Investigators' Report). Collection efficiencies (at flow rates of 15.8 to 16.5 L/min) determined in field studies at two locations in California were generally lower than those in the laboratory, where the air flow rate was higher. For acrolein the collection efficiency was 72% and 70% at the two California sites, Juniper Lake and Roseville, respectively (Table 12 of the Investigators' Report).

Spike Recovery

Spike recovery (also defined as the mass balance) is a measure of the overall carbonyl recovery, from collection to analysis. It was determined by adding a known concentration of the carbonyl (dissolved in a solvent) to the spiking tube placed upstream of the chamber as described above. The recovery is calculated by determining the mass of the carbonyl in each chamber and the mass remaining in the spiking tube relative to the mass of carbonyl added initially, expressed as a percentage.

The spike recovery and the collection efficiency were determined in the same experiments for 57 common aldehydes and ketones. Two different sampling times were evaluated in triplicate, 5 minutes and 25 minutes (the sampling times were actually 10 minutes and 30 minutes, but the spike analyte was added 5 minutes after sampling started). The results demonstrate that 97% of the acrolein was recovered after a 10-minute sampling period (the sampling duration yielding higher recovery). Of the 50 other carbonyls for which results are presented, 37 had a recovery of less than 70% (Table 6 of the Investigators' Report). The effect of sampling time on the retention rates depended on the specific chemical, with the shorter 10-minute sampling time providing better recoveries for the low-molecular-weight compounds and the longer 30-minute sampling time resulting in higher recovery for the higher-molecular-weight compounds (such as aromatic aldehydes).

Critique Table 1. Summary Results for Laboratory Tests of Mist Chamber Performance

	Results for 10-Minute Sampling Period (%)		
Carbonyl	Collection Efficiency (Using the Spiking Tube)	Spike Recovery	Retention of Internal Standards
Acrolein	80	97	93
Crotonaldehdye	84	86	
Benzaldehyde	88	83	88
Acetaldehyde	81	151	7

Retention of Internal Standards

The measure of the retention of internal standards (acrolein-d_4, benzaldehyde-d_6, and acetaldehyde-d_4) that were added directly to the mist chamber before sample collection was used to provide an indication of losses due to volatilization, degradation, and sample processing for specific classes of carbonyls.

The retention of acrolein-d_4 and benzaldehyde-d_6 was very high (93% and 88%, respectively), while that of acetaldehyde was very low (7%) for a 10-minute sampling period. The retention of acrolein decreased by 14% with the longer sampling time, suggesting possible loss due to volatilization. The low retention of acetaldehyde was explained by a high degree of volatilization or degradation during sample processing.

FIELD TESTING

After the methods development and optimization were completed, the investigators conducted two short field studies. In these studies, acrolein-d_4 and benzylaldehyde-d_6 were added to the mist chamber to correct for any chemical loss during collection, transport, derivatization, or extraction. The flow rate used for these studies was 15.8 to 16.5 L/min.

In the first field study, Cahill and colleagues had an opportunity to compare their mist chamber method with conventional methods for measuring acrolein being used in an ongoing HEI study conducted at the Peace Bridge in Buffalo, New York, by Dr. John Spengler of the Harvard School of Public Health and colleagues. In the Spengler study, part of the HEI air toxics hot spot program, acrolein was sampled for 1 to 4 days using OSHA Method 52 and DNSH-based samplers (Zhang et al. 2000), with the goal of assessing the impact of vehicle emissions on the local community. Two sites were selected, one directly downwind of the tollbooth plaza, and one upwind. Cahill and colleagues collected samples using the mist chamber technique for 10 minutes every hour on 3 days in July 2005, during 12-hour periods, to be consistent with the 12-hour sampling time in the study by Spengler and colleagues. Measurements from each sampling period over the course of a day were averaged.

Of the three methods, only the mist chamber technique was able to consistently detect and measure acrolein during the 3 days of sampling (Tables 9 and 10 of the Investigators' Report). The levels of acrolein determined using OSHA Method 52 (n = 3) were all below the MDL determined for that set of samples. The results from the DNSH-based samplers show that about half of the values (5 of 8) fell below the MDL. The few values above the MDL were slightly higher than those measured with the mist chamber.

In the second set of field studies, the investigators collected samples from three sites in California. Two sites in northern California, Salt Point and Juniper Lake in Lassen Volcanic National Park, were selected for their remoteness, and samples obtained there were assumed to represent background concentrations of acrolein. The third site was in an urban location (in Roseville) close to a highway and downwind from a railroad depot. The consistency of the mist chamber method was evaluated by collecting several samples over a very short time, when ambient conditions remained relatively stable.

There were differences among the carbonyl measurements at the three test sites, reflecting different carbonyl sources nearby (Table 11 of the Investigators' Report). The average acrolein concentrations at the two background sites were 0.056 ± 0.011 μg/m^3 and 0.089 ± 0.013 μg/m^3, respectively, while the concentration at the urban site in Roseville was significantly higher at 0.290 ± 0.008 μg/m^3. The MDL for acrolein at the three sites ranged from 0.012 to 0.035 μg/m^3.

HEI REVIEW COMMITTEE EVALUATION

In its independent review of the study, the HEI Review Committee concluded that Dr. Cahill and colleagues conducted a thorough study aimed at developing a new method for measuring acrolein and other unsaturated carbonyls in ambient air. Before this study, efforts to measure ambient levels of acrolein had been limited by the lack of sensitive methods. The Investigators' Report describes in detail the experiments conducted to optimize the collection and analysis of acrolein using a mist chamber as a sampling device. By taking advantage of ongoing field studies, the authors were also able to compare the performance of their methodology with that of other current methods. Although the mist chamber methodology was optimized for measuring acrolein, other carbonyls were also tested.

METHOD DEVELOPMENT

The sampler consists of a custom-built glass mist chamber. The mist chamber samples air at high flow rates and collects carbonyls by trapping them in a solution of bisulfite as carbonyl-bisulfite adducts. This reaction was quite rapid (on the order of seconds) for all the carbonyls tested, and the rate was dependent on the concentration of bisulfite at room temperature. The optimal sampling time for acrolein was 10 to 30 minutes at a flow rate of 20 L/min. Longer sampling times, lower flow rates, and different

temperatures were not evaluated. The optimal setup for collection of the carbonyls appears to be two chambers in series, owing to the fact that some of collected carbonyls can volatilize from the solution and escape from the mist chamber. The calculated MDL for acrolein varied between experiments, but the range of 0.012 μg/m^3 (0.005 ppb) to 0.035 μg/m^3 (0.015 ppb) is much lower than the MDL range of other methods, as shown in Critique Table 2.

The overall sampling protocol, as also noted by the authors, appears to be quite laborious and time-consuming, with possible failure if each step of the protocol, such as mist chamber construction and in situ derivatization of samples and calibration standards, is not carefully followed. This could lead to differences in sampler performance for different research groups, making it difficult to separate operational problems from actual differences in concentration. The method appeared to be highly reproducible in Cahill's study, however, based on the results of multiple measurements in a few locations.

The investigators used several measures to evaluate the performance of the mist chamber and analytic methods, but they did not discuss what relationships they expected to find between them. For acrolein the collection efficiency (the percentage of the carbonyl concentration in the first chamber relative to the concentration in the second chamber) was 80%. The determination of the collection efficiency using two chambers in series is a useful approach because it does not require knowledge of the starting concentration of the analyte. However, it does not provide an absolute collection value. Moreover, the assumption that the two chambers are identical in their collection efficiency has not been verified. In fact, the authors report that the second chamber is under a higher vacuum, which could possibly cause volatization of the carbonyl. It is noteworthy that the collection efficiency measured in the field (71%) was lower than that measured in the laboratory (80%). This could be due to differences in atmospheric conditions (such as humidity) or in flow rate, but this issue is not discussed. If one assumes that the collection efficiency is the same in the two chambers, the collection efficiency of the whole system should be approximately 91% in the field.

Spike recovery provides an approximate measure of the absolute collection recovery, which was 97%. For this test acrolein was dissolved in solvent and volatilized into a nitrogen stream. Although this approach was designed to simulate sampling in the field, it may not reflect entirely the actual conditions to which acrolein is exposed when sampled in ambient air.

The retention of deuterated acrolein-d_4 added to the bisulfite solution before sampling showed that, once the carbonyl was trapped, the retention of acrolein throughout the process was high (93%). Because the deuterated species were dissolved directly in the bisulfite solution, rather than bubbled into the solution in an air stream, this approach does not evaluate the efficiency with which the carbonyl in the ambient air stream is trapped in the solution. Experiments that examined the difference in recovery with spiking before versus after sampling would have been useful. Deuterated acrolein, benzaldehyde, and acetaldehyde were used as representatives of various classes of aldehydes for the determination of the recovery of individual species. However, there is uncertainty about extending the results to the other analytes because the standards only approximate their chemical and physical properties.

Overall, the Review Committee thought that these analyses were useful and showed a high level of acrolein recovery under laboratory conditions. However, the dynamic processes that lead to absorption of acrolein in the field may vary.

Critique Table 2. MDLs of Available Methods for Measuring Acrolein

Method	MDL (μg/m^3)	Sampling Time
DNPH-based	0.57–1.04[a]	48 hr
	1.41[b]	4 hr
DNSH-based (2000)	0.14[a]	48 hr
Modified DNSH-based (2005)	0.25[c]	24 hr
PFPH-based	0.23[b]	4 hr
EPA Method TO-15	0.18[d]	24 hr
OSHA Method 52	6.1[e]	8 hr
Mist chamber	0.012–0.035[f]	10 min

[a] Values were determined in the RIOPA study (Weisel et al. 2005) based on the sampler described in Zhang et al. 2000.

[b] Ho and Yu 2004.

[c] Herrington et al. 2005.

[d] Swift et al. 2006.

[e] Occupational Safety and Health Administration 1989.

[f] This study (values are from the field studies).

FIELD STUDIES

The comparison of the mist chamber with the DNSH-based passive cartridge and the OSHA sampler is difficult to evaluate because sampling times varied widely, with the mist chamber sampling for 10 minutes and the other two devices sampling for 12 to 24 hours. A more rigorous comparison of the methods would be useful and should include EPA Method TO-15. However, such work was not

part of the scope of the HEI study. Overall, the results showed that the mist chamber methodology has greater sensitivity than the other two samplers and can detect lower ambient levels of acrolein than the other existing methods.

CONCLUSIONS

The mist chamber methodology offers greater sensitivity than other existing methods for measuring acrolein. The analytic steps allow good separation of several carbonyls, but more work would be needed to use the mist chamber to measure other carbonyls. The chamber performance was evaluated using a variety of approaches, but the expected relationships between the different measures are not discussed. The overall acrolein recovery, from collection to analysis, was 97% under laboratory conditions.

Some limitations that might prevent the use of this method in population exposure studies are that the mist chamber has to be custom-built and is quite costly and that the method is labor-intensive, requiring several steps in the field, such as setting up a calibration curve, adding the internal standard, and adding hydrogen peroxide. In addition, the sampler can only be used as a stationary monitor. Development of more practical and less expensive approaches will be important if this method is to be more widely used. The performance of the method is optimal for very short sampling periods (10 minutes). The investigators provide a good rationale for having a sampler with a short sampling time to track short-term changes in acrolein concentrations. The Review Committee thought that a sampler with a wider range of sampling times would be more useful for measuring variations in ambient levels and personal exposures, without having to combine data from repeated measurements taken over very short periods. Despite its potential limitations, the report shows that the mist chamber methodology can provide useful information when detailed temporal characterization of acrolein concentrations is needed.

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