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Development of Samplers for Measuring Human Exposures to Ozone

Active and Passive Ozone Samplers Based on a Reaction with a Binary Reagent
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A Passive Ozone Sampler Based on a Reaction with Nitrite
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A Passive Ozone Sampler Based on a Reaction with Iodide
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Includes the Commentary of the Institute's Health Review Committee

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HEI HEALTH EFFECTS INSTITUTE

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HEI Statement

Synopsis of Research Report Number 63

Development of Personal Ozone Samplers: Three Approaches

BACKGROUND

Ozone is formed in the lower atmosphere when emissions from mobile and industrial sources react in the presence of sunlight. Because ozone is a highly reactive gas and a major component of urban smog, the Environmental Protection Agency has set a standard for ozone of 120 parts per billion for one hour, a level not to be exceeded more than once per year. Ozone is a major public health concern because exercising subjects experience transient decrements in lung function when exposed to ambient air containing ozone at concentrations equal to, or slightly below, the level of the current standard. In addition, because indoor ozone concentrations can exceed 50% of outdoor concentrations, people may be exposed to ozone for several hours each day. Assessing the risk of adverse health effects from such exposures is difficult because only limited data are available on the actual ozone concentrations that people experience.

Fixed-site monitors, which measure ambient ozone levels over widely spaced areas, are large and expensive to operate. Thus, these monitors cannot be used to measure individual exposures of large numbers of human subjects; in addition, their readings may not accurately reflect ozone levels in different microenvironments. In contrast, small personal ozone samplers measure total accumulated exposure as a person moves from one setting to another. Thus, personal samplers can improve the estimate of the exposure that an individual experiences and can provide better information for assessing the risk of exposure to ozone.

The Health Effects Institute supported three studies to advance the development and testing of personal ozone samplers. The results of these studies are discussed in the accompanying Research Report.

APPROACHES AND RESULTS

The investigators funded under the HEI ozone sampler program, Drs. Hackney, Yanagisawa, and Koutrakis, and their collaborators used different approaches to develop personal ozone samples that would be sensitive, accurate, and amenable to use in epidemiological studies.

Dr. Hackney and colleagues designed active and passive samplers based on ozone-induced changes in the intensity of a color formed by a chemical reagent. (Passive samplers depend on the natural diffusion of air and gases to the collection site, and active samplers use a pump to draw air into the device.) Dr. Hackney and associates coated filter papers with a reagent that forms a pink color after ozone exposure. By extracting the reaction product from the paper and measuring the intensity of the colored solution, they determined the amount of ozone that had reacted with the reagent. The investigators also designed a light-tight sample holder to mitigate the reagent's sensitivity to light. When tested in an indoor exposure chamber using mixtures of filtered air and pure ozone, the samplers detected ozone relatively accurately at several combinations of temperature and humidity. The active sampler was less accurate at lower humidity than at higher humidity, and the passive sampler's performance declined when it was tested at a combination of high temperature and high humidity. Both active and passive samplers performed less satisfactorily outdoors than indoors. The active device was accurate only for one- to two-hour exposures; the passive device overestimated ozone levels. Based on these results, the investigators concluded that the slower process of air diffusion, inherent in the passive design, allowed an unknown interfering component of ambient air to contact the reagent for a longer time

(*Continued on next page.*)

This Statement is a summary, prepared by the Health Effects Institute (HEI) and approved by the Board of Directors, of three research projects sponsored by HEI from 1989 through 1992. Dr. Jack D. Hackney and his associates from Rancho Los Amigos Medical Center conducted the first study, Active and Passive Samplers Based on Ozone's Reaction with a Binary Reagent; Dr. Petros Koutrakis and his colleagues from the Harvard School of Public Health conducted the second study, A Passive Sampler Based on Ozone's Reaction with Nitrite; and Dr. Yukio Yanagisawa also of the Harvard School of Public Health conducted the third study, A Passive Sampler Based on Ozone's Reaction with Iodide. The following Research Report contains the three detailed Investigators' Reports and a Commentary on the studies prepared by the Institute's Health Review Committee.

than in the active sampler. For these reasons, the samplers based on the reagent used by Dr. Hackney and colleagues were not considered for further development. Although the reagent appeared promising in early laboratory tests, the investigators' careful experimental work indicated that it was problematic in a practical application.

Dr. Yanagisawa's passive sampler is based on ozone oxidizing iodide ion to molecular iodine. The unique feature of this sampler is that as the reaction proceeds on a carbon disk coated with a nylon derivative and potassium iodide, the volatile iodine product stabilizes by forming an electrically charged complex with nylon. The amount of current discharged by the complex then is a measure of the amount of iodine bound to nylon, and thus, the amount of ozone that had reacted with iodide ion to form molecular iodine. In chamber studies, the amount of charged complex formed increased with increasing ozone exposure levels. The sampler was generally unaffected by wind, temperature, or relative humidity, except at very low humidity levels (12%). Sulfur dioxide decreased iodine formation by ozone, but this interference was eliminated by adding a filter to absorb the sulfur dioxide. However, nitrogen dioxide also was detected, thus interfering with ozone detection. Therefore, Dr. Yanagisawa's sampler must be considered a total oxidant sampler, rather than an ozone-specific sampler.

The third study evaluated the performance of a passive sampler previously designed by Dr. Koutrakis and colleagues. The sampler is based on ozone oxidizing nitrite ion, which is coated onto glass fiber filters, to nitrate ion. After extracting the ions from the filters with water, the investigators separated the nitrate ion from the nitrite ion by a process called ion chromatography. Although it requires a certain technical expertise, this method is efficient and rapid, both positive features when multiple samples from large epidemiological studies must be analyzed. In both indoor chamber experiments and outdoor field tests, good agreement was found between the ozone levels detected by Dr. Koutrakis' sampler and a reference ozone monitor; however, these comparisons need to be made systematically over a wider range of ozone levels than was done in this study. Initial chamber experiments indicated that the sampler was affected by wind velocity. However, wind velocity effects were adequately minimized by the use of a plastic wind shield. The investigators themselves did not perform interference studies as part of their HEI project. Results from another laboratory indicate that nitrogen dioxide, sulfur dioxide, and peroxyacetylnitrate do not interfere significantly with the sampler's performance. The sampler's performance also was not affected by temperature or relative humidity. A major uncertainty that needs to be addressed before the sampler is used in field studies is the method the investigators used to assess the sampler's accuracy. (A similar concern is also relevant to the accuracy of the other samplers discussed in this Research Report.) Sampling rates were determined by an equation that used ozone concentrations derived from a standard reference ozone monitor, and the calculated ozone levels were compared with those obtained with the reference monitor to assess accuracy. Using sampling rate data that are independent of a standard monitor would be a more scientifically rigorous method to estimate an experimental sampler's accuracy. An independent validation of Dr. Koutrakis' sampler would allow researchers to determine if its performance is adequate to meet the objectives of a proposed study.

CONCLUSIONS

In summary, HEI-funded investigators examined the performance of ozone samplers based on three different experimental approaches. The binary organic reagent used by Dr. Hackney and colleagues in their active and passive samplers proved unsuitable for accurate colorimetric ozone determination. Dr. Yanagisawa's sampler shows promise, but its ability to detect ozone at low concentrations requires improvement before it is ready for validation studies. If the detection limits can be improved, this sampler may be attractive to many analysts because of its simplicity. At the present time, of the samplers described in this Research Report, Dr. Koutrakis' is the closest to being ready for use in epidemiologic studies.

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The paper in this publication meets the minimum standard requirements of the ANSI Standard Z39.48-1984 (Permanence of Paper) effective with Report Number 21, December 1988, and with Report Numbers 25, 26, 32, and 51 excepted. Reports 1 through 20, 25, 26, 32, and 51 are printed on acid-free coated paper.

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When an HEI-funded study is completed, the investigators submit a final report. The Investigators' Report is first examined by three outside technical reviewers and a biostatistician. The Report and the reviewers' comments are then evaluated by members of the HEI Health Review Committee, who had no role in the selection or management of the project. During the review process, the investigators have an opportunity to exchange comments with the Review Committee, and, if necessary, revise their report. This Research Report contains three Investigators' Reports.

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Active and Passive Ozone Samplers Based on a Reaction with a Binary Reagent

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ABSTRACT

Ozone is one of the most toxic common air pollutants (judging from short-term animal and human exposure studies at realistic concentrations) and one of the most difficult and expensive pollutants to control. Because of ozone's high chemical reactivity, its concentrations may vary greatly over short distances, and fixed-site air quality monitors may not accurately estimate exposures of human populations. Epidemiologic research on ozone's long-term health effects has been inconclusive, partly because of the lack of reliable personal exposure information. The objective of this project was to develop a practical personal ozone exposure monitoring technique, and to document its precision and accuracy in actual use by representatives of freely ranging, ozone-exposed populations. The project site, Los Angeles, is the nation's metropolitan area with the highest level of ozone pollution and, thus, probably the most important locale for personal exposure assessment.

Our overall strategy was (1) to select the most promising laboratory technique for ozone detection from published literature and private communications; (2) to design and test personal monitors using this technique; and (3) when feasible, to evaluate concurrently alternative methodologies developed by others. As indicated below, parts 1 and 2 of our strategy yielded a limited success with respect to short-term active sampling, i.e., measuring personal ozone exposure levels during one to two hours with a monitor incorporating a battery-powered air pump of the type used in industrial hygiene investigations. The same approach was not successful in passive sampling, i.e., measuring exposure levels during multihour or multiday periods with a lightweight, diffusion-controlled "badge" sampler having no moving parts. Passive badge samplers could be calibrated reasonably well in laboratory exposures to ozone in otherwise pure air, but they greatly overestimated ozone levels in outdoor ambient air. Part 3 of our strategy yielded more promising information on an alternative passive badge design.

After testing and rejecting two other possibilities, we chose a binary organic reagent, 3-methyl-2-benzothiazolinone acetone azine with 2-phenylphenol, as the most promising chemical detector of ozone. Filter papers impregnated with the binary reagent develop a characteristic intense pink color when exposed to ozone. The inventors, J.E. Lambert and associates of Kansas State University, had intended only to develop a rough qualitative ozone monitor (Lambert et al. 1989). However, our initial laboratory testing (in exposure chambers containing ozone in otherwise very clean air, away from humans), revealed a fairly accurate quantitative response. The amount of pink product, as determined by conventional solvent extraction and absorption spectroscopy, bore an approximately linear relationship to ozone exposure (concentration × time). However, ambient light disrupted the ozone reaction and caused formation of a differently colored product. We therefore designed a light-tight sample holder in collaboration with B.R. Daube of the California Institute of Technology, Pasadena, CA. Active samplers were laboratory-tested at fixed concentrations of ozone (0.05 to 0.25 parts per million) in our exposure chambers, with a background of highly purified air. Next, they were tested by volunteers exercising outdoors on summer afternoons in Los Angeles, in ambient pollution containing ozone at concentrations ranging from 0.04 to 0.20 parts per million. Conventional ultraviolet photometric monitors, calibrated against a standard certified by the local air quality monitoring agency, provided the reference ozone measurements. Active samplers showed a nearly linear response to ozone, with sensitivity adequate to measure one-hour average exposures. Variability among individual samples was appreciable, but not great enough to preclude useful personal exposure assessments. Response diminished somewhat with very high temperature and low humidity. Lambert and coworkers empirically tested numerous alternative

This Investigators' Report is one part of the Health Effects Institute Research Report Number 63, which also includes an Investigators' Report by Koutrakis and colleagues, an Investigator's Report by Yanagisawa, a Commentary on the three Investigators' Reports by the Health Review Committee, and an HEI Statement about the research projects. Correspondence concerning the Investigators' Report by Hackney and associates may be addressed to Dr. Jack D. Hackney, Los Amigos Research and Education Institute, 51 Medical Science Building, Downey, CA 90242.

Although this document was produced with partial funding by the United States Environmental Protection Agency under assistance agreement 816285 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 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.

azines and related hydroxy-aromatic compounds in an unsuccessful effort to eliminate the light sensitivity and temperature and humidity dependence (see Appendix A). W.S. Trahanovsky and associates at Iowa State University isolated the colored compound formed from ozone by the original binary reagent, and determined most of its molecular structure (see Appendix B). Their results should help elucidate the reaction mechanism and may suggest an appropriate redesign of the reagents to reduce interferences.

For passive sampling, we used the same design for a light-tight sample holder, with increased size, thereby allowing ambient air to diffuse to the reagent-coated surface at a reasonable rate. Initially, passive samplers were laboratory-tested in our exposure chambers, with exposure periods lasting from several hours to several days. Under these indoor ozone conditions, the samplers showed an approximately linear response, with substantial but acceptable variability among individual samples, much as with the active samplers. Next, passive samplers were exposed outdoors, both in direct sunlight and in the shade, during periods of light ambient ozone pollution (daily peak one-hour average concentrations usually between 0.05 and 0.1 part per million). Serious anomalies of response were observed outdoors: the amount of pink reaction product ranged from about 10 to 50 times higher than expected, on the basis of indoor laboratory tests. The cause of this phenomenon is uncertain. It may relate to some highly reactive trace photochemical oxidant or free radical that is present in outdoor Los Angeles air but not in highly filtered chamber air with generated ozone. In any case, this phenomenon seems to limit use of the original binary organic reagent to active personal sampling during short periods (approximately one to two hours). Passive sampling with the original binary reagent clearly is not feasible outdoors in the Los Angeles area. Indoor passive sampling still might be considered, but further testing would be necessary to determine whether strong interferences may occur in typical indoor atmospheres with multiple pollutants (as opposed to atmospheres of ozone in highly purified air, as tested here).

We also performed limited laboratory testing of a different passive sampler, developed by Koutrakis and coworkers (1990, 1991, 1992) at Harvard School of Public Health, that employs an inorganic nitrite reagent. The response of this sampler was more precise and linear than responses for the binary organic reagent samplers in laboratory tests under conditions of mild temperature and humidity. Koutrakis and associates (1990, 1992) reported success in limited outdoor testing of their samplers under mild ozone pollution conditions in the Northeast. They also observed that the response was greater for outdoor ambient air than for ozone generated indoors, but only by a factor of approximately 1.3. This excess outdoor response can be accounted for by higher average air velocity across the face of the sampler outdoors (P. Koutrakis, private communication), which should be preventable by redesigning the holder to create a longer diffusion path. Accordingly, the nitrite badge is at present the most promising approach to a practical personal ozone exposure monitor. We recommend further laboratory testing of the nitrite badge, followed by field testing in Los Angeles, to identify any important interferences.

INTRODUCTION

The specific aim of this project was to develop and validate a practical device to measure short-term personal ozone (O_3)* exposures experienced by residents of O_3-polluted communities, Los Angeles in particular. The broader objective was to obtain improved estimates of personal exposure to O_3 in residents of communities where ambient O_3 pollution violates health-based federal air quality standards. (These include a large fraction of urban areas in the United States, as well as many rural areas downwind of large pollution sources.) Of common air pollutants, ozone is perhaps the most toxic to the respiratory system at exposure concentrations near or within the ambient range, according to a wide variety of studies on animals and human volunteers (Lippmann 1989). Ozone also is one of the most difficult and expensive pollutants to control. As a result, the margin of safety provided by the existing primary National Ambient Air Quality Standard for O_3 is narrow or nonexistent, and regulatory policymakers face strong socioeconomic pressures both for and against stricter regulation. Credible epidemiologic studies of the short- and long-term influences of O_3 pollution on respiratory health would help resolve the regulatory issues. Some past epidemiologic investigations suggested that long-term residence in an O_3-polluted area increases the rate of lung function loss; but these investigations have not been accepted as an adequate basis for regulatory policy (Lippmann 1989), partly because they lack personal exposure information. Most people spend most of their time indoors, and being indoors confers an appreciable (though variable) degree of protection against outdoor O_3. In conventional buildings without specific equipment to remove O_3, indoor concentrations may range from 20% to 80% of outdoor concentrations; indoor and outdoor concentrations usually correlate strongly (Yocum 1982; Contant et al. 1985; Hayes 1989; Johnson et al. 1990). Exposure models are used to predict the actual amounts of O_3 breathed by members of exposed populations, using a combination of outdoor air monitoring data,

* A list of abbreviations appears at the end of this report for your reference.

time-activity data, and proportionality factors to relate outdoor background O_3 concentrations to concentrations in definable "microenvironments" occupied by exposed individuals. Existing models provide better estimates of personal exposure than outdoor monitoring data alone. However, because of the difficulty of monitoring personal exposures with conventional instruments, models are often based on few data, and data to test the accuracy of their exposure predictions are scarce. Thus, better models, based on more extensive personal and "microenvironmental" monitoring data, are needed.

The successful development of a convenient, low-cost personal exposure monitor for O_3 would allow greatly expanded personal and "microenvironmental" monitoring. Exposure models then could be refined and validated to a much greater degree, and epidemiologists could employ direct exposure measurements to supplement or replace modeling estimates. Practical personal monitors have been developed for nitrogen dioxide (NO_2) (Palmes et al. 1976; Yanagisawa and Nishimura 1982), based on the principle of passive diffusion of the pollutant gas along a gradient from the sampler and atmosphere interface (at atmospheric concentration) to the reactive surface (at zero concentration). Ideally, the rate of diffusion at any point in time is proportional to the gradient (and thus to the atmospheric concentration) at that point in time; and over a given time interval, the total consumption of pollutant gas (or formation of analyzable product) is proportional to the time-weighted average atmospheric concentration during that interval. In practice, the NO_2 monitors do not behave ideally, but they still yield useful personal exposure estimates. Several investigators have reported possible means of adapting the same principle to O_3 monitoring (Surgi and Hodgeson 1985; Koutrakis et al. 1990; Monn and Hangartner 1990; Yanagisawa and Kanno 1991; Grosjean and Hisham 1992). It seems unlikely that exposure estimates from any economical, readily portable monitor can approach the quantitative accuracy obtainable from laboratory instruments. But valid epidemiologic studies do not necessarily require that high a degree of accuracy; their primary need is to rank individuals' and communities' levels of exposure accurately, and then determine whether higher exposures correlate consistently with poorer health.

Our investigative strategy included the following components:

1. Identifying several promising chemical methods for personal O_3 monitoring, through the published literature and consultants experienced in the field.
2. Testing these methods, through exposures to O_3 in laboratory chambers under realistic conditions of air flow and concentration, and identifying one method as the most promising.
3. Designing and constructing practical sampling devices employing the most promising chemical method. (Wearable sample holders, or "badges," for personal monitoring, were the primary focus. Nonwearable area sampling devices were considered also. Both active samplers, employing an air pump, as is commonly used in industrial hygiene, and passive-diffusion samplers were evaluated.)
4. Testing these sampling devices in the laboratory, i.e., performing further exposures in chambers with O_3 in pure background air under controlled conditions, away from people.
5. Testing the devices under conditions of realistic use (field testing), i.e., having volunteers wear them while exposed to ambient O_3.
6. Concurrently testing any promising alternative personal sampling methods that might become available from other laboratories.

As indicated in the following sections, the active-sampling development effort in steps 2 through 5 achieved some success; although the passive-sampling development effort began promisingly, it ultimately was unsuccessful. In step 6, a passive sampler developed by Koutrakis and associates (1990) at the Harvard School of Public Health performed well in a limited range of laboratory testing here. Given that passive sampling is potentially far more widely applicable than active sampling, the findings from step 6 may turn out to be the most important results from this project. However, these passive samplers will require field testing under Los Angeles pollution conditions to rule out the kinds of serious problems experienced with our passive samplers.

Our investigation was initiated with support from the American Petroleum Institute and the Motor Vehicle Manufacturers Association, and continued with Health Effects Institute support under the present project. This report focuses on the Health Effects Institute–supported work. For the sake of clarity and completeness, it also summarizes the earlier work supported by the American Petroleum Institute and the Motor Vehicle Manufacturers Association, much of which has been reported previously (Avol et al. 1990).

EXPERIMENTAL PLAN AND METHODOLOGY

EVALUATION OF ANALYTICAL TECHNIQUES

The first passive badge sampling technology we evaluated was originally developed by Surgi and Hodgeson (1985). For the O_3-reactive agent, we used 10,10′-dimethyl-9,9′-biacridylidene (DBA) suspended in a gas-permeable polymer film, MEM-213 (GE Membrane Products Division, Schenectady, NY). The DBA and polymer badges showed

much lower sensitivity and more erratic response to O_3 than the findings of Surgi and Hodgeson (1985) indicated, even when prepared by one of the original inventors. Discussions with the manufacturer suggested that the original success had related to a special formulation of MEM-213, which was no longer reproducible. Experiments with DBA deposited on filter paper were also unrewarding, so this approach was abandoned.

The second sampling technology we investigated was based on phenoxazine. Lambert and colleagues (1987) had reported that filter paper impregnated with phenoxazine can be used as a qualitative colorimetric detector for O_3, which yields a brown product, or for NO_2, which yields an orange product. In the laboratory, we tested phenoxazine-impregnated filter papers in otherwise clean air containing O_3 alone or NO_2 alone, extracted the colored products in aliquots of organic solvents and quantitatively analyzed them by absorption spectrophotometry. We found reasonably linear and reproducible exposure-response curves for each pollutant. However, the absorption spectra of the NO_2 and O_3 products overlapped, and the NO_2 product's absorbance was approximately three times greater, thus precluding quantitative O_3 monitoring in atmospheres that also contained NO_2. Chromatographic separation might have overcome the NO_2 interference problem, but would have made analysis considerably more expensive and time consuming. That possibility was not pursued because Lambert and associates (1989) discovered a new, more O_3-specific sampling method employing a binary organic reagent: 3-methyl-2-benzothiazolinone acetone azine with 2-phenylphenol. This combination reacts with ambient O_3 to yield an intensely pink product, the structure of which has since been worked out by M.G. Ranasinghe and W.S. Trahanovsky at Iowa State University (see Appendix B). A number of modified binary organic reagents were tested by Lambert and coworkers (see Appendix A), but none appeared to offer a substantial advantage over the original reagent.

Initial tests with the binary reagent indicated that it did not react appreciably with NO_2, but could be decomposed by ambient light, forming a brown product that interfered with analysis of the O_3-derived product. We therefore designed and constructed light-tight sample holders to use with the binary reagent, as described later. Most of this project involved testing the light-tight samplers with binary reagent, both in the active (pump-driven) mode and in the passive (diffusion) mode, under a variety of environmental conditions. As the Results section indicates, the samplers worked reasonably well indoors, except under extreme temperature and humidity conditions. Outdoors, only active sampling during periods of about one hour appeared successful; multihour and multiday passive sampling proved to be subject to large positive interferences from unknown sources. Unfortunately, this did not become apparent until near the end of the project, when too little time was left to pursue other alternatives seriously. However, with the cooperation of Dr. Koutrakis and coworkers at Harvard School of Public Health, we were able to perform limited indoor laboratory testing of their prototype passive O_3 sampler, which is based on an inorganic nitrite reagent (Koutrakis et al. 1990). Compared with the binary reagent, their approach appears to offer better linearity and precision in indoor sampling at moderate temperature and humidity, although its sensitivity may be lower.

PREPARATION AND USE OF BINARY ORGANIC REAGENT

Reagent grade 2-phenylphenol was obtained from Aldrich Chemical Co. (Milwaukee, WI). Synthesis of 3-methyl-2-benzothiazolinone acetone azine was carried out according to the procedure of Lambert and coworkers (1989). To prepare badge filters (reagent-impregnated filter papers for use in personal samplers), an acetone solution was prepared with concentrations of 1.1 g azine and 5.1 g 2-phenylphenol per 50 mL of solution. Whatman No. 1 filter papers were soaked in this solution for 20 minutes, suspended for 20 minutes in an O_3-free atmosphere to dry, then refrigerated in the dark in airtight containers until use. The papers were exposed to O_3-containing atmospheres in light-tight sample holders (see next section) for periods ranging from 30 minutes to two hours in the active mode, or from 12 hours to seven days in the passive mode. After exposure, a filter was removed from its sample holder and placed in an airtight container protected from light. Initial testing indicated that the reaction product decomposed at a rate of approximately 5% per 24 hours; therefore, all filters were analyzed immediately after exposure. Each filter was extracted with a precise volume of spectrophotometric grade acetone (delivered by a volumetric pipet) by 30 seconds of vigorous shaking. The volume of acetone was changed from sample to sample in rough proportion to the amount of colored product on the filter. This kept the resulting solution concentration within the appropriate absorbance range for spectrophotometry. Solutions were analyzed in a Varian (San Fernando, CA) 635 ultraviolet-visible spectrophotometer at wavelength 492 nm and with a slit width of 0.2 mm. Zero absorbance was set with acetone in both the reference and sample cuvettes. In order not to move the sample cuvette, prior to each analysis, it was emptied by a vacuum aspirator, filled with analyte by pipet, emptied again, and refilled with a second aliquot of analyte for the absorbance measurement. Absorbance was generally measured in the range 0 to 1 units. In the Results section, graphed "absorbance" readings relate to the most concentrated solution in a series

of analyses, so that they are always proportional to the quantity of O_3-derived product in the sample. Thus, for example, if an extract of one filter with 10 mL acetone showed an absorbance of one, and an extract of a second filter with 20 mL acetone showed an absorbance of one, the second filter would have contained twice as much O_3-related product, and its reading would be graphed as two. During each test run, blank filters were stored and analyzed in the same manner as the exposed filters. The blanks were neither placed in sample holders nor transported like exposed filters, because not enough sample holders were available.

On the basis of his earlier findings (Lambert et al. 1987, 1989) Lambert recommended use of a spectrophotometer accessory to read the intensity of color on filters by reflectance measurements. One disadvantage of this approach is an inherently nonlinear calibration curve; however, an overriding potential advantage is the elimination of the acetone extraction step in the analysis. Accordingly, we fabricated and tested a reflectance accessory similar to that used by Lambert and associates (1987, 1989) at Kansas State, and tested the reflectance technique on filters from passive samplers. In terms of variability and sensitivity, our direct reflectance measurements of filters generally were inferior to extraction and absorbance measurements. Accordingly, we chose to rely on the extraction and absorbance measurement approach.

DESIGN AND CONSTRUCTION OF SAMPLE HOLDERS

Figure 1 shows a front view and cutaway side view of an active sampler. The active samplers had an outside diameter of approximately 55 mm and employed 47-mm filter papers. Passive samplers differed only in that they were larger (outside diameter of approximately 80 mm, using 70-mm filter papers) and lacked the air outlet and tubing connector shown at the top of the figure. Air entered the front cover of the sampler through the six holes surrounding the central mounting screw. In order that essentially all light would be excluded, the air passed seven blind 90-degree bends before reaching the surface of the filter, which was mounted against the backing plate. (Note that the active sampler drew air over the filter surface, rather than through the filter.) Photometric tests were performed by the designer (B.R. Daube, California Institute of Technology) using a Siemens (Karlsruhe, Germany) BP103B-3 phototransistor with appropriate precision power supply and digital voltage readout. Results showed that light intensity at the filter surface was reduced to approximately 1/625 the intensity of external light outdoors on a clear day, with the sampler directly facing the sun. The sampler body was machined from black Nylatron, a comparatively inert form of nylon. Air was drawn through active samplers by battery-powered

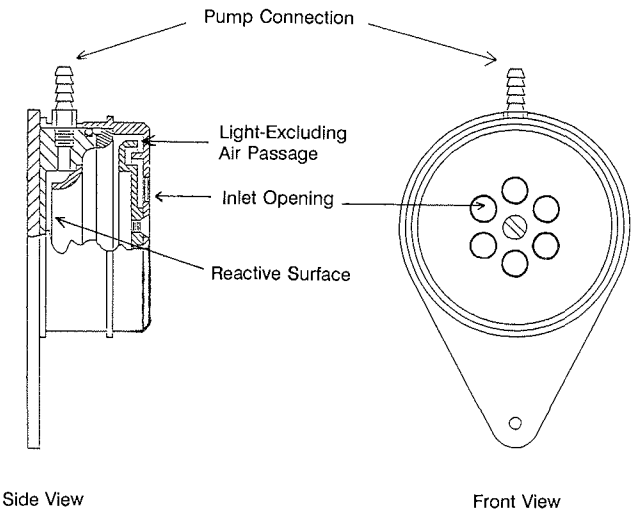

Figure 1. Front view and cutaway side view of an active ozone sampler.

industrial hygiene sampling pumps at a flow rate of 1 L/min or 2.5 L/min, depending on the O_3 concentration and sampling time.

EXPOSURE FACILITIES AND LABORATORY TESTING TECHNIQUES

Otherwise pure atmospheres containing O_3 were generated for laboratory testing either in the Environmental Health Service's main exposure chamber at the Rancho Los Amigos Medical Center (Hackney et al. 1975) or in the movable laboratory chamber (Avol et al. 1979). The main chamber has stainless-steel walls and a volume of approximately 60 m^3. The movable laboratory chamber has vinyl-surfaced walls with a low-emission coating and a volume near 25 m^3. Tests at extreme temperatures or humidity levels were conducted in the main chamber because of its broader environmental-control capabilities; other tests usually were conducted in the movable chamber because of its lower operating costs. In both chambers, background O_3, NO_2, and most other common pollutant gases and particles were removed by a combination of activated carbon, permanganate and alumina chemisorbent, and high-efficiency paper particulate filters. The main chamber also incorporated a high-temperature catalytic converter to remove carbon monoxide and less reactive hydrocarbon pollutants. Air exchange rates were approximately 10 air changes/hour in the main chamber and 30 air changes/hour in the movable chamber; this was sufficient to maintain stable O_3 generation conditions without a perceptible draft. Chamber performance tests prior to this project had demonstrated substantially uniform O_3 concentrations throughout the free volume of the chambers. Nevertheless, reference O_3 mon-

itoring instruments were placed in the immediate vicinity of samplers being tested. Ozone was generated in the main chamber by high-voltage discharge, and in the movable chamber by ultraviolet lamps. There was no noticeable difference in the samplers' response with the different chambers.

During all indoor and outdoor testing, reference O_3 concentrations were measured with commercial ultraviolet photometers (model 1003-AH and 1003-PC, Environics Series 300, Dasibi, Glendale CA). Flow, zero, and span checks were performed on the reference monitors at least once per week. Multipoint calibrations were performed at least twice per month, using a model 8500R calibrator (Monitor Labs, San Diego, CA) to generate controlled levels of O_3, and to compare these readings with those from a transfer standard Dasibi photometer, which was tested and certified every six months by the local air pollution monitoring agency (the South Coast Air Quality Management District). Signals from the O_3 reference monitors were recorded by an on-line minicomputer that displayed and stored an average concentration reading for every five-minute interval. The appropriate five-minute readings were averaged to calculate the time-weighted average concentration throughout each sampler's period of exposure. In active sampling, the total volume of air pumped through the sampler was known, along with the concentration, so the total mass of O_3 that had contacted the filter was directly calculated in micrograms. In passive sampling, the mass of O_3 contacting the filter was not readily determinable, so exposure levels were expressed in parts per million (ppm) (time-weighted average) $\times$ minutes.

When tested in the chambers, samplers were suspended from metal laboratory racks to insure free access of light and air. Reference O_3 monitor air inlets were placed no more than 1 m away. No personnel were in the chamber except for brief periods, as necessary, to place and remove the samplers. Three nominal O_3 concentrations were employed (0.05, 0.15, and 0.25 ppm) in order to cover most of the range expected in field use. To cover most of the meteorological ranges expected in field use, responses were tested at temperatures between 25°C and 40°C, and at relative humidity levels between 25% and 75%. (Relative humidity during one high-temperature test series was still lower, roughly 12%, due to an air conditioning malfunction.) Because the sample holders were not totally light-tight, three different incident light levels were tested to rule out interference by residual light: "dark" (near-total darkness, illuminance at sampler face less than 0.5 foot-candles [ft-c]); "low" (variable incandescent lighting at minimum power, approximately 5 ft-c), and "high" (fluorescent lighting plus incandescent lighting at maximum power, approximately 125 ft-c). The effect of light level was tested only at the lower temperature and humidity levels.

Nitrite-based sampling badges (Koutrakis et al. 1990) were obtained from Dr. Koutrakis' staff at Harvard School of Public Health and exposed alongside a set of binary-reagent badges in the main chamber at 25°C, with low humidity. Exposed badges and blanks were numerically coded and returned to Harvard, where they were analyzed without knowledge of the exposure levels.

FIELD TESTING OF SAMPLERS BY VOLUNTEERS

Active samplers were tested on summer afternoons outdoors near our laboratory in Downey, CA. Two successive one-hour exposure measurements were made for each volunteer. Usually, two people were studied concurrently on a given day; 20 subjects were studied in all. The volunteer wore a sample holder on his or her shirt collar, connected by lightweight tubing to a battery-powered pump attached to a belt, as in conventional industrial hygiene sampling. During each hour, the volunteer successively rested, walked, and jogged along a 260-m paved course near the edge of a large parking lot, away from heavy vehicle traffic. At the center of the course, ambient O_3 was sampled approximately 2 m above the ground by a Dasibi monitor and by a second active sampler. Weather was generally clear during the tests, with temperatures ranging from 25°C to 35°C. Hourly average ambient O_3 concentrations, as determined by the Dasibi, ranged from 0.04 to 0.20 ppm. Because passive samplers failed to perform satisfactorily in outdoor laboratory tests, they were not tested by volunteers.

RESULTS

ACTIVE SAMPLERS WITH BINARY ORGANIC REAGENT

Figure 2 summarizes results from numerous laboratory tests of active samplers that employed the binary reagent at 31°C and 35% relative humidity and lasted for one to six hours. The active samplers' responses, in terms of absorbance of the extract (i.e., quantity of colored product on the filter) versus the quantity of O_3 passed through the sampler, appeared fairly linear and consistent at concentrations of 0.05 to 0.25 ppm and sampling rates of 1 to 2.5 L/min, provided the total quantity of O_3 remained below 100 µg. With more than 100 µg total O_3 exposure, the response appeared to drop off somewhat, but this should not present a problem during typical intended monitoring periods of one to two hours.

Scatterplots in Figures 3 and 4 summarize the results of all volunteers' outdoor field tests of the active samplers. Each point indicates a time-weighted average concentration

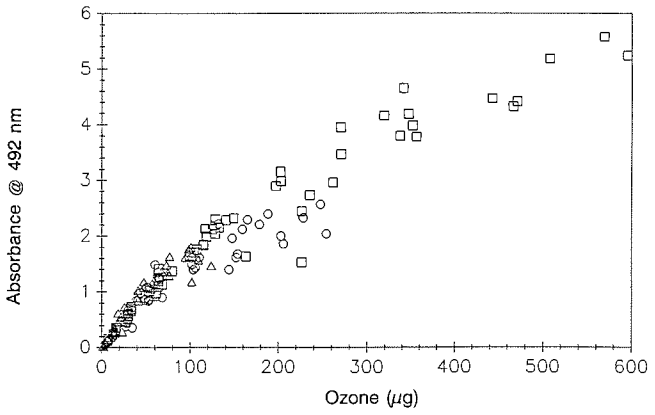

Figure 2. Tests of active samplers in controlled exposure chamber at three different ozone concentrations: △ = 0.05 ppm; ○ = 0.10 ppm; □ = 0.25 ppm. Absorbance of filter extract was measured as a function of the ozone mass that passed through the sampler.

of O_3, as determined during approximately a one-hour period by an active sampler (calibrated from laboratory testing data) versus the time-weighted average concentration during the same time period, measured by a Dasibi photometer. (Concentrations are plotted in $\mu g/m^3$; 200 $\mu g/m^3$ = 0.1 ppm). The darker diagonal line on each plot is the line of identity, the line on which all points would fall if the photometer and badge agreed perfectly. The lighter line is the best-fit first-order regression line based on all points, for which the intercept b, the slope m, and the correlation coefficient r are also shown. The majority of time-weighted

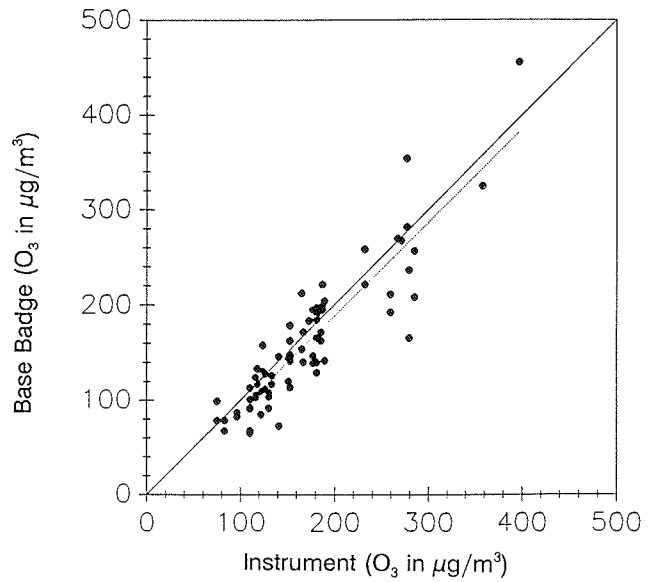

Figure 3. Comparative one-hour average ozone concentration readings of active sampling badge and reference instrument, both located at the base site during outdoor testing by volunteers. Solid diagonal line is the line of identity; dotted diagonal line is the best-fit first-order regression based on all points, for which intercept b = 0.800, slope m = 0.982, and correlation coefficient r = 0.904.

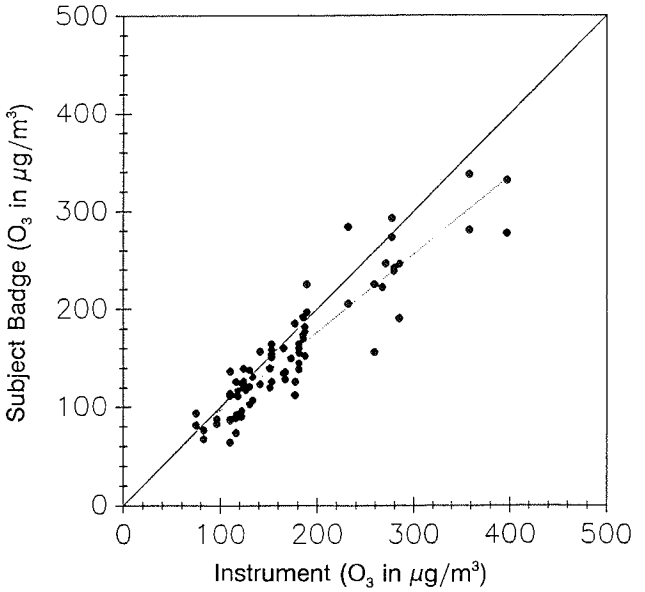

Figure 4. Comparative one-hour average ozone concentration readings of active sampling badges worn by volunteer subjects on outdoor exercise course and reference instrument at the base site. Solid diagonal line is the line of identity; dotted diagonal line is the best-fit first-order regression based on all points, for which intercept b = 16.816, slope m = 0.798, and correlation coefficient r = 0.919.

average ambient O_3 concentrations during these one-hour tests were below 0.10 ppm; however, on a few especially polluted days the concentrations were higher, reaching 0.20 ppm (400 $\mu g/m^3$) on one occasion. Figure 3 shows results from samplers operating immediately adjacent to the Dasibi photometer reference instrument at a fixed site at the center of the outdoor exercise course. The active samplers and reference instruments located together showed good overall agreement, despite some scatter in the data. Figure 4 shows results from samplers worn by volunteers during exercise along the course compared with results from the centrally located reference instrument. Again the active samplers agreed reasonably well with the reference instrument. The lower slope of the Figure 4 data, when compared with the Figure 3 data, might suggest that O_3 concentrations near volunteers' body surfaces are slightly less than the background concentration in their outdoor microenvironment. The average concentration difference, as predicted by the regression lines, would amount to roughly 10% in the middle of the observed concentration range. If real, the difference would be readily explainable in terms of O_3 reacting with surface components of clothing or skin. These data would suggest that any such reactions should not interfere seriously with exposure estimation.

Figure 5 summarizes the results of one-hour and two-hour active sampler laboratory tests at varying light levels. There was no obvious difference in response between near-

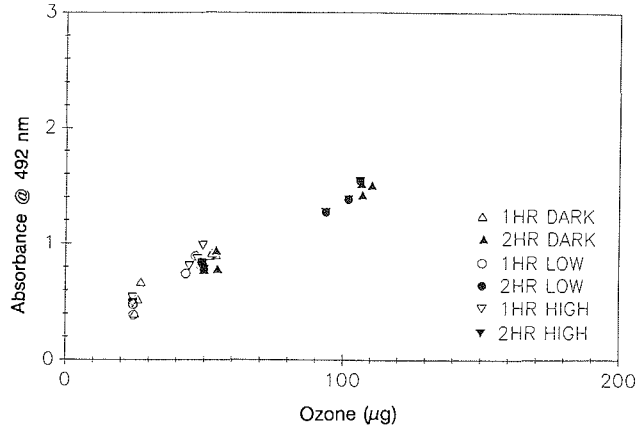

Figure 5. Response of active sampler at different light levels in exposure chamber (chamber temperature 23°C, with 21% relative humidity).

total darkness and a very high intensity of indoor lighting. Thus, the design was considered satisfactory to eliminate light interference.

Figure 6 summarizes results of active sampler laboratory tests at different temperatures and relative humidities for periods of one to six hours. Visual examination suggested a drop-off in response during longer exposures at 40°C and 25% relative humidity, and a less consistent drop-off at 40°C and 75% relative humidity. A mean response index (absorbance units per microgram of O_3) and its coefficient of variation (standard deviation as percentage of mean) were calculated for each set of three similarly exposed filters. The response index averaged 0.0164 and varied consistently with O_3 concentration and relative humidity, as discussed below. The coefficient of variation averaged 8% and did not vary significantly with different exposure conditions. Linear regression analysis of the Figure 6 data (summarized in Table 1) showed that temperature had no consistent effect on the samplers' response. However, relative humidity showed a highly significant positive effect: the colored product was formed more rapidly (or lost more slowly) during an exposure at high humidity than during a similar exposure at low humidity. The O_3 regression coefficient decreased significantly from 0.05- to 0.15- to 0.25-ppm exposures, suggesting that collection efficiency increased at lower O_3 concentrations. These effects remained significant when the regression analysis was limited to exposure times of one or two hours. The regression results strongly suggest real (although not necessarily large) concentration dependence and humidity effects in active sampling; such effects are chemically plausible. However, more testing is needed to confirm the existence of these effects because the present data represent comparatively few test runs and are possibly biased as a result of unavoidable batch-to-batch variability in filters.

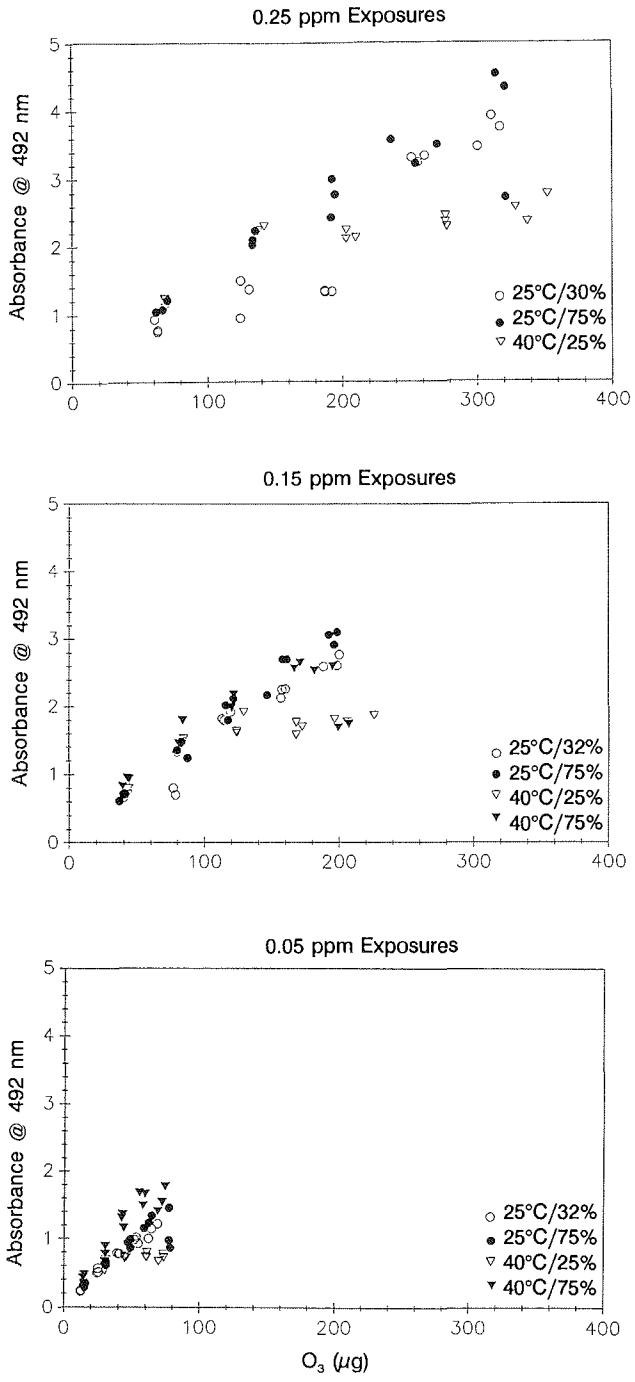

Figure 6. Response of active sampler at different ozone concentrations, temperatures, and levels of relative humidity in the exposure chamber. See Table 1 for statistical analysis.

PASSIVE SAMPLERS WITH BINARY ORGANIC REAGENT

Figures 7, 8, and 9 summarize the results from multiple series of passive sampler laboratory tests in chambers con-

Table 1. Effects of Ozone Exposure Level, Temperature, and Relative Humidity on Absorbance of Extracts from Active Sampler Filters Exposed in Chamber[a]

	Exposures Included in Analysis[b]			
	All	0.05 ppm[c]	0.15 ppm[c]	0.25 ppm[c]
Intercept	−0.051	−0.260	0.542	−0.397
Temperature coefficient	0.0008	0.0059	−0.0122	0.0090
Humidity coefficient	0.0096	0.0059	0.0064	0.0161
O_3 Exposure coefficient	0.0100	0.0139	0.0102	0.0088
Multiple correlation coefficient	0.849	0.714	0.771	0.779

[a] Regression analyses of data plotted in Figure 6. Data fit to equation $A = I + C_T T + C_H H + C_O O$, in which A = absorbance (dependent variable), I = intercept, C_x = regression coefficient for each independent variable as follows: T = temperature, H = relative humidity, O = ozone exposure level (micrograms of O_3 passed through active sampler).

[b] Temperature coefficients are not significantly different from zero ($p > 0.05$), except in 0.15 ppm exposures ($p = 0.04$). All humidity and O_3 coefficients are significant ($p < 0.005$).

[c] Regression lines for 0.05-, 0.15-, and 0.25-ppm exposures differ significantly ($p = 0.0003$).

taining O_3 in highly purified background air, at different conditions of temperature and relative humidity. In the aggregate, the data show a reasonably linear response that is not strongly dependent on temperature and humidity, except at 39°C (102° F) and 75%, points at which the response seemed to increase. That result might actually relate to decreased response by the reference O_3 analyzer under extreme conditions. As the figures illustrate, sample-to-sample variability within one test series was appreciable, and different batches of filters exposed under similar conditions might respond somewhat differently (compare Figures 8 and 9). Figure 9, representing extraction and absorbance measurements, may be compared with Figure 10, representing reflectance measurements on some of the same filters

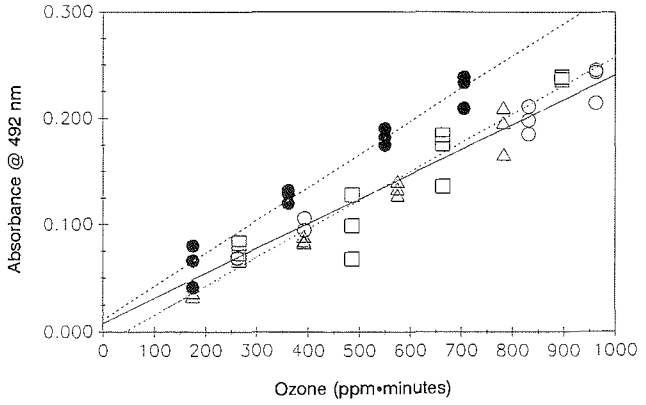

Figure 7. Response of passive samplers (70-mm Daube design) in exposure chamber, in four series of studies at different temperatures and relative humidities. □ with dotted line/solid line = experiment was conducted in 10/90, at 39°C and 25% relative humidity; ○ with solid line = experiment was conducted in 11/90, at 39°C and 12% relative humidity; △ with dotted line = experiment was conducted in 12/90, at 24°C and 26% relative humidity; ● with dashed line = experiment was conducted in 2/91, at 39°C and 75% relative humidity.

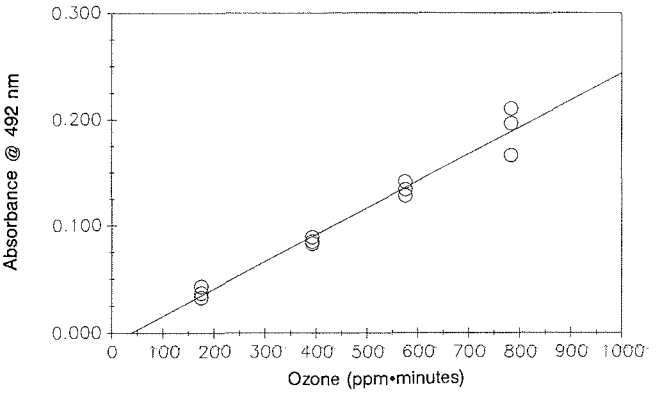

Figure 8. Additional test of passive samplers (70-mm Daube design) in an exposure chamber at moderate temperature and low humidity. Experiment was conducted 12/17/90 through 12/20/90, at 24°C and 26% relative humidity. Intercept b determined by linear regression = -9.535×10^{-3}; slope m = 2.527×10^{-4}; and correlation coefficient r = 0.984. Diagonal line represents best fit by linear regression.

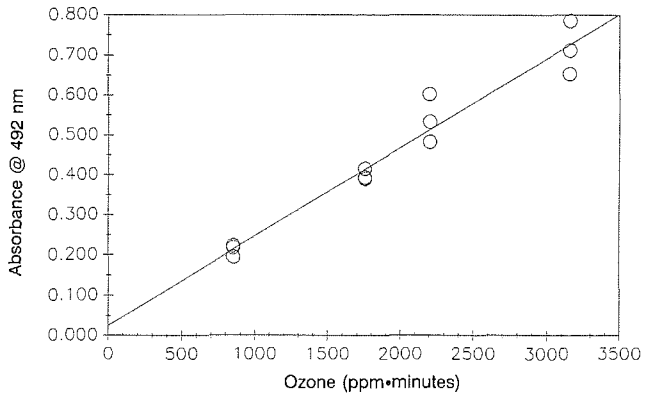

Figure 9. Test of passive samplers (70-mm Daube design) at high levels of total exposure, moderate temperature, and low humidity. Experiment was conducted on 1/11/91, at 25°C and 35% relative humidity. Intercept b determined by linear regression = 2.476×10^{-2}; slope m = 2.222×10^{-4}; and correlation coefficient r = 0.977. Diagonal line represents best fit by linear regression.

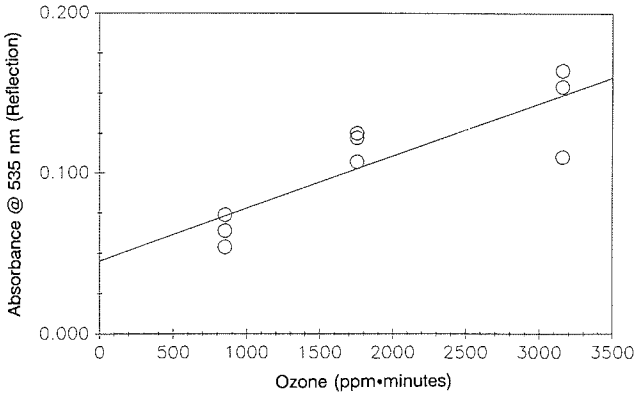

Figure 10. Results from the same passive samplers represented in Figure 9, but analyzed by reflectance spectrophotometry prior to extraction. Experiment was conducted on 1/11/91, at 25°C and 35% relative humidity. Intercept b determined by linear regression = 4.545×10^{-2}; slope m = 3.268×10^{-5}; and correlation coefficient r = 0.858. Diagonal line represents best fit by linear regression.

prior to extraction, to illustrate the superior precision of the extraction and absorbance analytical procedure.

Given the reasonably satisfactory performance by binary-reagent passive samplers in indoor laboratory tests and by binary-reagent active samplers in field tests outdoors, we expected no serious problems in field tests of passive samplers. However, a serious problem did occur. Prior to scheduling field tests with volunteers, we set up an outdoor laboratory test of passive samplers during a period from late winter to early spring, to see how they would perform during long exposure periods with low ambient O_3 levels. Samplers were exposed for periods of three days or longer on the roof of the movable chamber facility, where ambient O_3 was being monitored continuously by a Dasibi photometer and computer system. During each test period, three samplers were exposed in direct sunlight, and three more were shaded during exposure. Table 2 shows the average time-weighted average O_3 level calculated from each set of three passive samplers, along with the mean and standard deviation of concurrent readings from the Dasibi reference instrument. The calibration curve for the passive samplers was derived from the four most recent indoor pure air and O_3 laboratory tests. Compared with the reference instrument, passive sampler readings varied widely and were always too high by more than an order of magnitude. Samplers exposed in direct sunlight read consistently higher than those exposed in the shade. Exposed filters appeared to contain only the usual pink product; the brown contaminant previously found in unprotected light-exposed filters was not evident. In light of these results, we canceled the originally planned field tests, replacing them with experiments intended to help explain the interference.

The interference might have been due to some reactive species other than O_3, which is commonly present in outdoor air but not in the purified air of the exposure chambers. In that case, there would be little hope of practical passive sampling with the original binary reagent. Alternatively, some potentially correctable problems with the passive sample holders, interacting with some component of the outdoor environment, might have caused the interference. The observations described below support the alternative involving a reactive pollutant other than O_3 in outdoor air.

AVERAGE READING FROM THREE SIDE-BY-SIDE SAMPLERS

One experiment tested whether the interference related to some inherent difference between the larger passive sample holders (which had never worked as expected outdoors) and the smaller active sample holders (which had worked as expected outdoors, albeit for short times). Three active sample holders were converted to the passive mode by sealing off their air pump tubing connectors. These sample holders were exposed outdoors, along with three unmodified passive samplers, during three days of relatively cool weather and good air quality. At the conclusion of exposure, the filters from all six sample holders showed comparatively intense color, indicating gross overprediction of O_3 concen-

Table 2. Initial Ozone Readings for Outdoor Laboratory Tests of Passive Samplers

Days of Sampling	Ozone (ppm)		
	Reference Instrument[a]	Passive Samplers in Sun[b]	Passive Samplers in Shade[b]
3	0.028 ± 0.027	0.679	0.373
6	0.015 ± 0.015	1.349	0.321
21	0.019 ± 0.016	0.956	0.606

[a] Based on successive five-minute average readings throughout sampling period. Values are given as means ± SD.

[b] Values are time-weighted averages.

trations, as found in previous outdoor passive sampling. Absorbance readings of filter extracts averaged about the same for modified active sample holders and passive sample holders, after adjusting for the difference in surface areas. Thus, an inherent difference in interference between active and passive sample holders was ruled out.

Another experiment tested for an inherent difference in behavior between active and passive sampling outdoors. Three active samplers were operated continuously outdoors for three days. Three passive samplers were exposed concurrently at the same location. A Dasibi photometer was operated continuously as the reference instrument; over the three-day period, it showed a mean ambient O_3 concentration of 0.037 ppm (SD ± 0.023 ppm). The passive samplers again grossly overestimated the time-weighted average ambient O_3 concentration, yielding an average reading of 0.64 ppm (determined by the calibration curve from recent indoor pure air and O_3 laboratory tests described above). The active samplers underestimated ambient O_3 levels, relative to the Dasibi, yielding an average reading of 0.019 ppm. Thus, the binary reagent's behavior was influenced strongly by large differences in air flow characteristics. However, as mentioned earlier, the behavior was not much influenced by modest changes in flow rate during active sampling.

A third experiment assessed the binary reagent's responses to outdoor air, heat, and the sample holders in a different manner. Two passive samplers were exposed in the usual manner outdoors in direct sunlight for a three-day period, during which the Dasibi reference instrument indicated a mean ambient concentration of 0.022 ppm (SD ± 0.036 ppm) (based on successive five-minute average readings). Two more passive samplers were set out at the same location for the same time period, with their inlets covered with Parafilm to exclude air. During the same three-day period, two more passive samplers were kept in a laboratory drying oven at 41°C, wrapped in Parafilm to exclude air and aluminum foil to exclude light. Two additional filters were exposed to heat in the same manner but away from sample holders: they were kept in the oven in sealed glass jars wrapped in aluminum foil. At the conclusion of the three-day period, filters from all the aforementioned samples were analyzed, and predicted O_3 exposure levels were determined using the calibration curve from recent pure air and O_3 laboratory tests, as described previously. Results are shown in Table 3. Samplers exposed conventionally outdoors gave the usual large overestimate of O_3 level. When air was excluded from the samplers, even outdoors in the sun, there was no such "false-positive" response. A small amount of colored product was found at the edges of filters from sample holders kept in the oven. This might reflect a reaction of the binary reagent with some component of the sample holder, but is more plausibly explained by slight contamination left in the holder after previous sampling efforts. In any event, the series of experiments clearly demonstrated that the large "false-positive" response depended on some component of outdoor air that manifested itself only when ambient air diffused passively to the filter surface, not when air was drawn through filters at a finite flow rate.

TESTING OF PASSIVE SAMPLERS WITH INORGANIC NITRITE REAGENT

In one of the previously discussed series of laboratory tests (results illustrated in Figure 8), we simultaneously exposed a set of passive sampling badges based on inorganic nitrate, supplied through the courtesy of Dr. Koutrakis. Figure 11 shows blank-corrected concentrations of nitrate ion in extracts from the sampling badges exposed to O_3 in otherwise pure air in the main chamber, as a function of O_3 exposure level in ppm•minutes. As mentioned before, analyses were performed under blind conditions by the Harvard laboratory staff. In this one series of tests under conditions of mild temperature and low humidity, the nitrate-based badges outperformed the binary-reagent passive samplers with respect to precision and linearity of response, as can be seen by comparing Figures 8 and 11. Logistic constraints precluded any broader testing of the badges here. Dr. Koutrakis has reported success in limited outdoor testing of the samplers under mild O_3 pollution conditions in the Northeast, with sampling for 24 hours or longer (Koutrakis et al.

Table 3. Responses of Filters Subjected to Various Conditions

Container	Exposure	Ozone[a] (ppm)
Glass jar	In oven (41°C), air and light excluded	0.006[b]
Sample holder	In oven (41°C), air and light excluded	0.013[b]
Sample holder	Outdoors in sunlight, air excluded	0.005
Sample holder	Outdoors in sunlight, air admitted as usual	1.921

[a] Hypothetical time-weighted averages over three days; average of two samples that differed by less than 20%, except where indicated.

[b] Average of two samples that differed by approximately 40%.

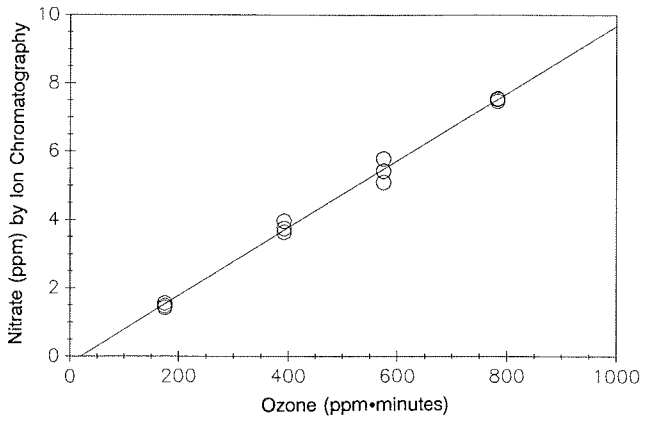

Figure 11. Nitrate content of passive samplers based on inorganic nitrate exposed in the chamber, expressed as a function of total ozone exposure. Experiment was conducted from 12/17/90 through 12/20/90, at 24°C and 26% relative humidity. Exposures were at 0.25 ppm for 12 to 48 hours. Nitrate analyses were performed by Harvard personnel without knowledge of exposure conditions. Intercept b determined by linear regression = -1.950×10^{-1}; slope m = 9.862×10^{-3}; and correlation coefficient r = 0.9971. Diagonal line represents best fit by linear regression.

1990). Dr. Koutrakis recently reported a higer response for outdoor ambient air than for O_3 generated indoors, but (unlike the case of our binary organic reagent passive sampler) the difference appeared small enough to not seriously interfere with practical use (Koutrakis et al. 1991). The increased response appears to result from higher wind speed outdoors, i.e., higher average air velocity at the badge face outdoors (P. Koutrakis, private communication). In these sample holders, the path length for diffusion of ambient air to the reagent surface is much shorter than in our sample holders. Thus, if the difference for the indoor and outdoor responses is indeed due to face velocity differences, it might be reduced or eliminated by redesigning the holder to lengthen the diffusion path.

DISCUSSION

This project has demonstrated that a comparatively simple solid-phase device, filter paper impregnated with 3-methyl-2-benzothiazolinone acetone azine with 2-phenylphenol, is potentially useful for active sampling to estimate one- or two-hour average personal O_3 exposures under atmospheric conditions prevalent in the Los Angeles area. The skilled staff and equipment found in most chemistry laboratories are sufficient to make and use these devices. However, the devices must be protected from ambient light both while in storage and in use. With the current state of the art, their accuracy is somewhat limited by unexplained variations in response for different batches of filters. Moreover, their response appears to decrease somewhat with increasing O_3 concentration and with decreasing relative humidity. Further development efforts might mitigate these problems. Such efforts may or may not be worthwhile, depending on the degree of success with alternative O_3 sampling methods (discussed further below).

Unfortunately, the solid-phase binary-reagent sampling technique proved unsuccessful in the potentially more important application of multihour or multiday passive sampling. Two important general questions thus arise: (1) What other alternative passive sampling methods may prove useful in studies of O_3 exposure and health effects? and (2) What are the possible explanations for the failure of binary-reagent passive samplers, and what are their implications for studies of exposure and health?

With regard to the first question, the O_3 badge developed by Koutrakis and associates based on the conversion of nitrite ion to nitrate ion, has been mentioned as highly promising, with the limited testing in this project and findings from the inventors (Koutrakis et al. 1990, 1992). Another personal sampling technology is based on the conversion of iodide ion to iodine (Yanagisawa and Kanno 1991). This approach requires special equipment both to fabricate the sampling badges and to analyze them after exposure. One problem observed so far is a positive interference by NO_2 that is equal to approximately 30% of the O_3 response if both gases are at equal concentrations. Interference from NO_2 might not be very important in monitoring maximum Southern California afternoon summer outdoor O_3 exposures in which O_3 concentrations far exceed NO_2 concentrations. However, in any situation with less extreme O_3 pollution and more NO_2 pollution, particularly in indoor exposures, the NO_2 interference might seriously compromise O_3 exposure estimates. Concurrent use of O_3 and NO_2 sampling badges would help overcome this problem. However, accuracy still might be poor because O_3 exposures would have to be estimated from the difference of two relatively imprecise analytical results. As previously mentioned, the phenoxazine passive monitoring technique (Lambert et al. 1987) yields different products from O_3 and NO_2, offering the potential to monitor both pollutants simultaneously if a cost-efficient separation technology can be developed and if no important interferences are found. Another passive sampling technology, based on O_3's cleavage of the carbon-carbon double bond in di-(4-pyridyl)ethylene to form 4-pyridylaldehyde, has shown some promise in an initial area sampling study in Europe (Monn and Hangartner 1990). Analyzing exposed samplers is more complex than analysis with the binary organic reagent, and protection from sunlight is required. Another passive O_3 monitor employs a

colored organic reagent (indigo carmine) that decomposes into a colorless product upon exposure; this has shown promise for multiday sampling (Grosjean and Hisham 1992). Any further investigation of these or other possible O_3 sampling technologies will require both indoor laboratory tests under a variety of controlled conditions and outdoor tests covering a meaningful range of real pollution exposures.

A thorough answer to the second question regarding the solid-phase binary reagent sampling technique would require extensive chemical research beyond the scope of this project. Nevertheless, our observations may yield some useful insights. The quantitative relationship of atmospheric O_3 and the pink-colored product from the binary reagent appeared relatively straightforward, except under the combination of two factors: outdoor air and passive sampling (i.e., a very slow air exchange rate at the filter surface). With these factors, product formation increased by one to two orders of magnitude beyond what was expected under other conditions. The requirement for outdoor air indicates that the "excess" reaction depended on some unidentified trace component of outdoor air other than O_3, which was removed from exposure chamber air by chemisorbents or physical filters. The requirement for a slow air exchange rate implies that the reagent's reaction with the unidentified trace component required a finite period of time and proceeded through a somewhat volatile intermediate substance. Thus, the higher air exchange rate in active sampling would continuously remove the intermediate substance and prevent the excess reaction.

In this project, or in any chemical analysis of personal exposure, the pollutant-sampling reagent is implicitly a surrogate for substances within the human body that might be damaged by inhaled pollution. Thus, the excess reaction with outdoor air raises the question of whether Southern California oxidant pollution contains some substance more damaging than O_3. We previously addressed that question in the mobile chamber facility, by exposing volunteers to O_3 at several concentrations in otherwise pure air to determine personal O_3 dose-response curves, and also by exposing them to ambient air on summer afternoons when high oxidant levels were expected (Avol et al. 1984). We found that typical responses to the ambient oxidant mixture were about equal to predictions from O_3 dose-response information. Thus, the intensity of lung dysfunction and respiratory irritant symptoms during ambient oxidant exposures was entirely explainable by the amount of O_3 present; there was no indication that any coexisting pollutant increased the atmosphere's respiratory irritancy. Thus, some evidence (albeit very limited) indicates that the excess reaction found here in outdoor passive sampling is not relevant to short-term human health risks from Southern California's ambient oxidant pollution.

ACKNOWLEDGMENTS

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APPENDIX A. Attempts to Improve the Binary Reagent

(This appendix was written by Jack Lambert and Steve Leggans, Department of Chemistry, Kansas State University, Manhattan, KS 66506.)

Since the summer of 1990, a study has been underway on the components previously used to make the two-component ozone reagent, along with several previously untested compounds. Sensitivity and specificity for ozone are required in any new reagent formulation. Reducing or eliminating the photosensitivity observed with the 3-methyl-2-benzothiazolinone with 2-phenylphenol reagent is a highly desirable goal, as is reducing or eliminating the decrease in sensitivity under conditions of high temperature and low relative humidity.

The azine compounds of 3-methyl-2-benzothiazolinone hydrazone (MBTH) we prepared were as follows (those previously reported are identified by an asterisk):

* acetone
  acetylaldehyde
* cyclohexanone
  cyclopentanone
  dihydroxyacetone
  formaldehyde
* 4-phenylcyclohexanone

The aromatic hydroxy compounds used as the second component in the 1:6 ratio of components included the following (those previously reported are identified by an asterisk):

* 2,2′-dihydroxydiphenyl
  6,7-dihydroxy-2-naphthalenesulfonic acid
  3,5-dihydroxy-2-naphthoic acid
  3,7-dihydroxy-2-naphthoic acid
  1,3-dihydroxynaphthalene
  1,5-dihydroxynaphthalene
  1,6-dihydroxynaphthalene
* 2,6-diphenylphenol
* 1-naphthol
* 2-naphthol
  1-naphthol-8-sulfonic acid
  1-naphthol-3,6-disulfonic acid
* 2-phenylphenol
* 4-phenylphenol

Several compounds have been obtained, but not yet studied, as the second component of the reagent:

2,2′-bipyridine-3,3′-diol
2-methoxybiphenyl
1,3,5-trimethoxybenzene

Thus far, reagent combinations of the above compounds have not eliminated the photosensitivity or the high temperature and low humidity problem. The graduate student who worked on this problem, Mr. Steve Leggans, has taken it on as his thesis research and will continue this work. Dr. Walter Trahanovsky of Iowa State University has identified the chromophore produced by the action of ozone on the original reagent, 3-methyl-2-benzothiazolinone acetone azine with 2-phenylphenol, that we reported (Lambert et al. 1989). See Appendix B for these results.

APPENDIX B. Isolation and Characterization of the Product Formed by the Reaction of the Binary Reagent and Ozone

(This appendix was written by M.G. Ranasinghe and W.S. Trahanovsky, Department of Chemistry, Iowa State University, Ames, IA 50015.)

3-Methyl-2-benzothiazolinone acetone azine (200 mg, 0.913 mmol) and 2-phenylphenol (621 mg, 3.65 mmol) were dissolved in 25 mL of ethyl acetate. This was mixed with 70 g of fine silica gel and evaporated to dryness. This mixture was further dried under vacuum and exposed to a stream of ozone for two to three minutes, until the mixture turned pink. Unreacted hydrazone and 2-phenylphenol were removed by chromatography on silica gel using a mixture of 10% ethyl acetate and hexane as eluent. The pink material was eluted with a mixture of 20% ethyl acetate and hexane. Further purification by high-performance liquid chromatography on reverse-phase column using methanol for the mobile phase yielded approximately 10 mg of a dark red solid, which was characterized by infrared spectroscopy (IR), mass spectroscopy (MS), and proton and carbon nuclear magnetic resonance (NMR).

Spectroscopic findings were as follows: ^{1}H NMR ($CDCl_3$) δ 8.16 (d, 1H), 8.10 (dd, 1H), 7.63–7.49 (m, 10H), 7.47–7.35 (m, 12H), 3.83 & 3.81 (2 × s, 6H, two methyl group); ^{13}C NMR ($CDCl_3$) δ 186.9 (C = 0), 140.5, 139.6, 137.8, 131.2, 129.7, 129.4, 129.0, 128.3, 128.2, 128.0, 126.9, 125.6, 125.2, 123.7, 124.6, 122.8, 110.8, 31.94, 31.89 (two methyl group); IR (thin film) 1622 cm^{-1}, 1605 cm^{-1}; MS (EI) 345.2 (M^+), 316, 288, 168, 150, 139.2; (CI) 346 (100%, $M^+ + 1$), 263, 197, 185, 165, 150; UVδ_{max} ($CHCl_3$) 495 nm.

Based on the above data, the structures in Figure B.1 were proposed. The pink material is a mixture of two of those four isomers.

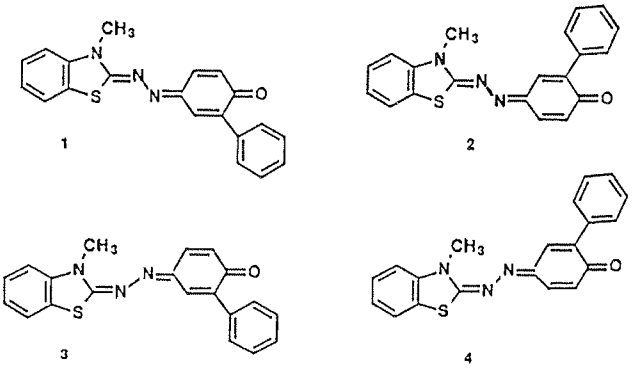

Figure B.1. Possible structures for reaction product of Kansas State two-component reagent with ozone.

APPENDIX C. Numerical Data for Ozone and Absorbance

Table C.1. Ozone Mass and Absorbance at Various Concentrations, Temperatures, and Levels of Relative Humidity[a]

Ozone Mass[b] (μg)	Absorbance
0.25 ppm, 25°C, 30%	
317.00	3.74
310.80	3.91
300.60	3.46
60.60	0.93
62.70	0.74
63.00	0.77
124.00	0.94
124.40	1.48
130.70	1.36
251.50	3.30
261.20	3.32
256.10	3.23
187.20	1.34
187.10	1.32
192.20	1.32
0.25 ppm, 25°C, 75%	
66.50	1.06
69.90	1.20
61.70	1.03
133.00	2.01
135.10	2.22
133.50	2.08
314.30	4.53
321.10	2.70
321.10	4.33
254.50	3.22
270.60	3.50
236.30	3.57
191.70	2.42
194.70	2.75
192.50	2.98
0.25 ppm, 40°C, 25%	
337.40	2.34
352.20	2.75
328.60	2.56
67.90	1.23
68.40	1.22
68.50	1.10
135.70	2.15
137.50	2.23
141.90	2.29
276.60	2.35
276.80	2.44
277.80	2.28

(Table continues next column)

Table C.1. (*continued*)

Ozone Mass[b] (μg)	Absorbance
202.80	2.10
203.00	2.23
210.00	2.12
0.25 ppm, 40°C, 75%	
337.40	2.34
352.20	2.75
328.60	2.56
67.90	1.23
68.40	1.22
68.50	1.10
135.70	2.15
137.50	2.23
141.90	2.29
276.60	2.35
276.80	2.44
277.80	2.28
202.80	2.10
203.00	2.23
210.00	2.12
0.15 ppm, 25°C, 32%	
198.40	2.60
200.20	2.76
188.50	2.58
38.70	0.68
40.20	0.70
39.60	0.66
78.60	0.69
76.70	0.79
79.80	1.32
156.80	2.11
160.10	2.25
157.60	2.24
114.70	1.79
113.10	1.81
119.50	1.91
0.15 ppm, 25°C, 75%	
39.40	0.71
40.60	0.71
36.60	0.61
80.00	1.34
87.10	1.23
82.90	1.46
192.30	3.05
196.40	2.90
198.40	3.09
157.90	2.69
161.10	2.69
146.60	2.16
115.90	2.01
121.30	2.10
117.50	1.78

(Table continues next page.)

Table C.1. (*continued*)

Ozone Mass[b] (μg)	Absorbance
0.15 ppm, 40°C, 25%	
206.30	1.76
226.40	1.86
196.90	1.80
42.40	0.79
43.70	0.79
42.90	0.71
81.90	1.42
83.50	1.47
84.70	1.52
168.30	1.75
172.70	1.69
168.30	1.57
123.90	1.63
124.00	1.60
129.10	1.91
0.15 ppm, 40°C, 75%	
42.40	0.94
43.80	0.93
39.10	0.82
81.30	1.44
84.10	1.78
83.30	1.44
199.50	1.68
195.20	2.59
207.50	1.73
181.70	2.53
171.00	2.64
166.80	2.56
119.70	1.98
121.60	2.17
120.10	1.97
0.05 ppm, 25°C, 32%	
64.20	1.15
68.90	1.22
62.00	1.00
12.20	0.25
12.60	0.24
12.50	0.25
24.50	0.51
25.00	0.57
25.40	0.52
51.50	0.99
54.20	0.93
52.80	1.03
39.10	0.78
40.30	0.78
40.90	0.78

(*Table continues next column*)

Table C.1. (*continued*)

Ozone Mass[b] (μg)	Absorbance
0.05 ppm, 25°C, 75%	
15.00	0.30
15.60	0.36
14.20	0.33
29.70	0.64
30.80	0.62
30.70	0.67
78.30	0.87
77.40	1.45
77.40	0.98
61.90	1.23
64.40	1.34
58.70	1.16
46.70	0.95
48.50	0.99
48.40	0.87
0.05 ppm, 40°C, 25%	
73.40	0.73
73.00	0.77
69.60	0.67
14.60	0.29
14.90	0.33
14.80	0.34
29.60	0.60
29.90	0.55
30.80	0.70
60.10	0.74
60.90	0.80
60.60	0.73
44.30	0.72
44.40	0.74
45.80	0.74
0.05 ppm, 40°C, 75%	
14.70	0.36
15.10	0.48
14.10	0.44
30.30	0.89
30.40	0.78
29.70	0.68
72.10	1.54
69.00	1.40
74.40	1.77
57.70	1.49
59.50	1.66
55.30	1.68
42.90	1.36
43.70	1.16
42.10	1.30

[a] For details of the measurement procedures, refer to the main body of the report.

[b] The mass of O_3 that passed through an active sampler, i.e., the product of O_3 concentration, sampling flow rate, and sampling time.

[c] The spectrophotometrically measured absorbance of the extract from the sampler's filter.

ABOUT THE AUTHORS

Jack D. Hackney, M.D., project director for this study, is a Professor of Medicine at the University of Southern California. He received his M.D. degree from Saint Louis University. He recently retired as Chief of the Environmental Health Service at Rancho Los Amigos Medical Center, where the study was performed, and remains active as a consultant in the group's research program on human health effects of air pollution.

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ABBREVIATIONS

DBA	10,10′-dimethyl-9,9′-biacridylidene
ft-c	foot-candles
NO_2	nitrogen dioxide
O_3	ozone
ppm	parts per million

A Passive Ozone Sampler Based on a Reaction with Nitrite

Petros Koutrakis, Jack M. Wolfson, Arnold Bunyaviroch, and Susan Froehlich

ABSTRACT

Standard ozone monitoring techniques utilize large, heavy, and expensive instruments that are not easily adapted for personal or microenvironmental monitoring. For large-scale monitoring projects that examine spatial variations of a pollutant and human exposure assessments, passive sampling devices can provide the methodology to meet monitoring and statistical goals.

Recently, we developed a coated filter for ozone collection that we used in a commercially available passive sampling device. Successful preliminary results merited further validation tests, which are presented in this report.

The passive ozone sampler used in field and laboratory experiments consists of a badge clip supporting a barrel-shaped body that contains two coated glass fiber filters. The principle component of the coating is nitrite ion, which in the presence of ozone is oxidized to nitrate ion on the filter medium (NO_2^- + O_3 produces NO_3^- + O_2). After sample collection, the filters were extracted with ultrapure water and analyzed for nitrate ion by ion chromatography. The results from laboratory and field validation tests indicated excellent agreement between the passive method and standard ozone monitoring techniques. We determined that relative humidity (ranging from 10% to 80%) and temperature (ranging from 0°C to 40°C) at typical ambient ozone levels (40 to 100 parts per billion) do not influence sampler performance.

Face velocity and sampler orientation with respect to wind direction were found to affect the sampler's collection rate of ozone. Using a protective cup, which acts as both a wind screen and a rain cover, we were able to obtain a constant collection rate over a wide range of wind speeds.

INTRODUCTION

Ozone is an atmospheric oxidant formed through photochemical reactions of volatile organic compounds and nitrogen oxides. Although a great deal of effort has been made to decrease emissions of these ozone precursors, ambient concentrations of ozone have only decreased approximately 10% over the last decade (U.S. Environmental Protection Agency 1991). Daily maximum one-hour ozone concentrations can range from 50 to 300 parts per billion (ppb)*, often exceeding the National Ambient Air Quality Standard (NAAQS) of 120 ppb. In fact, more than half of the U.S. population resides in areas that do not comply with the current NAAQS for ozone (Lippmann 1989). At these ambient concentrations, ozone exposure can cause respiratory health effects, including changes in lung capacity, flow resistance, and epithelial permeability (Lippmann 1989).

It was traditionally thought that indoor ozone concentrations were negligible because of ozone's rapid depletion on indoor surfaces. However, recent studies suggest ozone is present indoors and may represent a significant fraction of a person's total ozone exposure (Allen et al. 1978; Allen and Wadden 1982; Davies et al. 1984; Weschler et al. 1989). Indoor concentrations were found to be as high as 60% to 80% of the outdoor concentration (in an art gallery and in office buildings) and to depend upon building geometry, interior surfaces, ventilation systems, and indoor sources, such as electrostatic precipitators and copying machines. Thus, investigating the human health effects associated with ozone exposure requires the knowledge of both outdoor and indoor concentrations, as well as measurements of personal exposures.

Although there is a great deal of information about outdoor ozone concentrations, very little is known about indoor concentrations and personal exposures. One reason for this is the lack of lightweight, inexpensive, and reliable ozone monitors suitable for personal or indoor monitoring.

This Investigators' Report is one part of the Health Effects Institute Research Report Number 63, which also includes an Investigators' Report by Hackney and colleagues, an Investigator's Report by Yanagisawa, a Commentary on the three Investigators' Reports by the Health Review Committee, and an HEI Statement about the research projects. Correspondence concerning the Investigators' Report by Dr. Koutrakis and associates may be addressed to Dr. Petros Koutrakis, Department of Environmental Health, Harvard School of Public Health, 665 Huntington Avenue, Boston, MA 02115.

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* A list of abbreviations appears at the end of this report for your reference.

The indoor studies discussed above required bulky instruments that can be invasive on site and labor intensive. Although the techniques used by previous indoor studies provided accurate data, the effort needed to implement such studies seriously limits the scope of investigations.

Passive monitoring devices offer the flexibility to undertake more ambitious sampling schemes, which can include both indoor and personal monitoring. Nonetheless, ozone is difficult to measure with a passive monitor because of its high reactivity and the potential for interference. Although there are many passive devices to monitor other pollutants (volatile organics, nitrogen dioxide [NO_2]), particularly at occupational concentrations, until recently, passive ozone monitoring rarely has been attempted.

Only a few passive ozone monitors employing conventional chemical analysis techniques have been developed. A passive ozone monitor developed by Monn and Hangartner (1990) is based on ozone reacting with 1,2-di-(4-pyridyl)-ethylene to produce an ozonide, and eventually forming an aldehyde that is determined spectrophotometrically. Although these investigators' results were promising, the evaluation presented by their research does not fully validate their sampler. Interference by ultraviolet (UV) light is also possible with their method, which would limit its usefulness as a personal monitor. Grosjean and Hisham (1992) developed a colorimetric passive ozone monitor using indigo carmine as the colorant; however, this monitor displays a positive interference from NO_2 (approximately 15%), which is another important atmospheric oxidant often present in high concentrations. Kanno and Yanagisawa (1992) developed a passive ozone and oxidant monitor that is based on ozone reacting with potassium iodide to liberate iodine, which is determined via constant-current coulometry. The drawback to this method is that it is a total oxidant monitor. It is not ozone-specific and displays a positive interference from NO_2.

The passive ozone sampling method presented in this report allows for the specific collection and measurement of ozone. Initially, we tested the filter coating in an active rather than a passive monitor, including critical NO_2 and UV interference tests. The promising results prompted us to apply the method to a passive design. This design is a passive device that is commercially available (Ogawa & Co., USA, Pompano Beach, FL). It was initially designed to sample nitric oxide (NO) and NO_2.

Validation tests in a controlled environment are crucial to understanding passive sampler response and the limitations of its use. Ozone diffusion and reaction on the filter can be affected by various sampling conditions that must be simulated in the laboratory. Because ozone is an oxidant, it can react with surfaces near the filters. Also, passive samplers can be highly affected by variation in wind velocities at the sampler face. Some passive samplers are inappropriate for the lower exposures encountered in an outdoor, rather than an occupational, environment. These issues must be considered when designing the validation tests and interpreting their results.

The development and use of this ozone sampling monitor provides us with the potential to:

1. Assess personal exposures to ozone;
2. Monitor a variety of environments that may be inaccessible to standard monitoring techniques, e.g., confined work spaces or remote sites; and
3. Measure ozone using simple and relatively inexpensive techniques.

EXPERIMENTAL METHODS

DESCRIPTION OF THE OZONE COATING SOLUTION

Laboratory tests conducted by Febo and associates (1986) suggested that nitrite collected by alkaline-coated denuders was oxidized to nitrate when ozone was present in the air sample. Sickles and Hodson (1989) noted oxidation of nitrite, presumably by ozone, on sodium carbonate–coated filters after exposure to ambient air. The nitrite-based oxidation reaction, confounding one sampling methodology by producing nitrate, became the focus in developing an ozone-specific sampling medium.

The solution used to coat the collecting filters included sodium and potassium salts of nitrite and carbonate in a solution of glycerol, methanol, and water. In the presence of ozone, the nitrite ions are oxidized to nitrate ions:

$$NO_2^- + O_3 \rightarrow NO_3^- + O_2$$

Solution components were chosen to ensure that oxidation would be specific to ozone and not caused by other gaseous pollutants. Prior to the passive sampler validation tests, the composition of the coating solution was tested using active samplers, with both denuders and coated filters. The optimal coating was used initially in an active sampler with a filter pack, and exceptional results encouraged use of this in a passive device.

Optimum collection efficiency is obtained when the nitrite and carbonate in the coating have sodium as the cation for one and potassium for the other. Results from collection efficiency tests (using an active system with either a diffusion denuder or a coated glass fiber filter) showed that ozone reacts optimally with nitrite when the nitrite and carbonate come from salts of different metals. This may be ex-

plained by the fact that the mixture of sodium and potassium crystals formed on the coated glass fiber filter collection medium is more hygroscopic than if either sodium or potassium were used alone. Increasing the number of water molecules at the surface of the crystals enhances the oxidation reaction of nitrite by ozone. For this reason, the hygroscopic compound glycerol is also added to the solution. Therefore, we speculate that the reaction between ozone and the collecting medium occurs through homogeneous aqueous reactions that take place inside microscopic droplets.

Rate equations for aqueous nitrogen chemistry (Seinfeld 1986) indicate that the reaction described above is dependent on pH, with a rate constant that increases with pH. Thus, potassium carbonate is used to keep the collecting medium alkaline. Because the oxidation of nitrite by hydrogen peroxide is fast only at low pH values, this coating is insensitive to the presence of this important atmospheric oxidant.

DESIGN OF THE OGAWA PASSIVE SAMPLING DEVICE

The Ogawa passive sampler (Ogawa & Co., USA) chosen for testing the coating solution consists of a cylindrical polymer body (2 cm in diameter × 3 cm long) and a plastic pin-clip holder (4 × 3 cm) (Figure 1). There are two cavities on the ends of the cylinder, each of which holds one coated filter between two stainless-steel screens. Because the core of the body is solid, each cavity is isolated from the other. The diffusion barrier end caps hold the screens and filters in place by friction fit. Prior to exposure, the assembled sampler is sealed in a reusable plastic bag and placed in a polystyrene bottle. The sampler is lightweight, relatively inexpensive, and easy to use.

FILTER AND SAMPLER PREPARATION

The following filter cleaning protocol was critical for eliminating chemical interferences due to filter impurities. All filters were cleaned vigorously before being coated, and all sampler parts were cleaned carefully before use. Grade #30 glass fiber filters were obtained from Schleicher & Schuell (Keene, NH) and were custom-cut by the manufacturer to a 14-mm diameter. The filters were soaked successively in the following concentrated acids and base: nitric acid (two hours), chromic and sulfuric acid (one hour), hydrochloric acid (0.5 hour), and 10 N sodium hydroxide (one hour). Between each soaking, the filters were rinsed several times with ultrapure water (Milli-Q, Millipore Corp., Bedford, MA). Finally, the filters were placed on a porcelain funnel under low vacuum, and methanol was poured through them. The funnel was covered with Kimwipe tissues and the filters were allowed to dry with room air passing through them. When fully dried, the filters were stored in 10-mL polyethylene bottles.

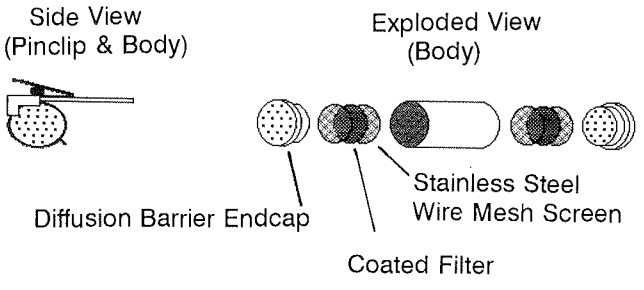

Figure 1. Exploded diagram of the Ogawa passive sampler.

Filter coating was done in a glove box purged with clean air from a system containing potassium permanganate–coated alumina, activated charcoal, and silica gel. The filters were laid out in the glove box on clean, ridged acrylic sheets. Then, 100 µl of the coating solution was pipetted onto each filter, and the filters were allowed to dry. The coated filters were stored in the glove box at room temperature in 10-mL polyethylene bottles that had been sealed in resealable plastic bags until ready for sampler assembly. All sampler parts were rinsed with ultrapure water, or wiped clean with moist Kimwipes, or both, before being used. The samplers were assembled with coated filters inside the glove box.

TEST APPARATUS

Four different exposure chambers were used for the sampler validation studies performed at the Harvard School of Public Health (HSPH). Most of the initial laboratory testing was done in a rectangular Plexiglas chamber. Some of this initial testing also used a smaller rectangular glass (aquarium) chamber. A polyethylene container was used as an exposure chamber for temperature experiments. Wind velocity and relative humidity experiments were conducted in a cylindrical Plexiglas chamber designed to function as a wind tunnel.

Rectangular Chambers

The rectangular Plexiglas chamber (94 × 41 × 53 cm [l × w × h]) has an interior volume of approximately 242 L (Figure 2). A small fan was used to ensure good mixing within the chamber. Tubing from the ozone generator was positioned immediately downwind of the fan. On one side of the chamber there was a sliding Plexiglas panel to allow access to adjust the tubing and fan and to position the samplers. Ports for the tubing and a relative humidity and temperature probe were drilled into other sides. Short lengths

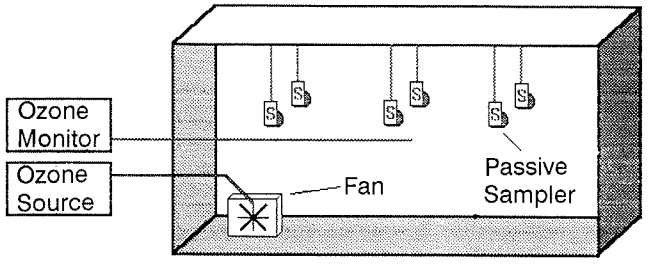

Figure 2. Plexiglas exposure chamber.

of string were affixed to the chamber ceiling, and the samplers were clipped to the strings during tests. The suspended samplers were 13 or 20 cm apart from each other, and at least 15 cm from the chamber walls. For a few tests, a smaller glass aquarium (48 × 25 × 30 cm [l × w × h]) was used as a chamber. The use of the aquarium was similar to that of the Plexiglas chamber, with the exception that the access was via its removable Plexiglas lid.

Before each test, the interior was allowed to condition and equilibrate to the target ozone concentration. Typically, this required three to four hours. At the beginning of each test, the sliding panel was moved just enough for a hand to reach into the chamber. The samplers were clipped onto the strings, and the panel was closed rapidly. The interior ozone concentration dropped, but then would usually re-equilibrate within three hours.

Polyethylene Container

The small cylindrical container (20 cm in diameter, 19 cm high) shown in Figure 3 was chosen for the temperature experiments because of the size limitations of the incubator. A single port was drilled into the container's side to accommodate the tubing, the relative humidity and temperature probe, and the fan's power cord. The mixing fan was run at a low speed to limit the turbulence within the small interior space. Tubing from the ozone generator was positioned immediately downwind of the fan. Before entering the container, this tubing was coiled within the incubator to equilibrate the ozonated air with the temperature of the container. The temperature was monitored using the relative humidity and temperature probe, not the incubator sensor system. The samplers were suspended from a framework made of metal wire and were nominally equidistant from each other and from the container walls.

Before each test, the container was conditioned and equilibrated with respect to target ozone concentration and temperature for three to four hours. At the beginning of a test, the door to the incubator was opened quickly. The samplers were clipped into place, the container was resealed, and the door was closed. Because of the preheated coil,

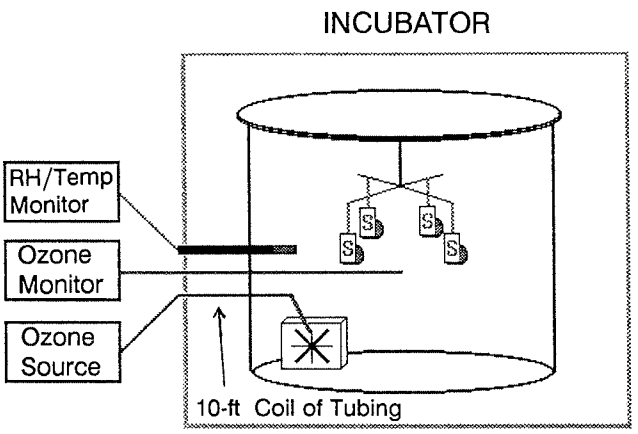

Figure 3. Polyethylene container used for temperature experiments.

there was little temperature fluctuation. The ozone concentration initially dropped, but achieved the target concentration within one to four hours.

Wind Tunnel

The wind tunnel consisted of two concentric Plexiglas cylinders, with the smaller cylinder nested within the larger (Figure 4). The smaller internal cylinder (21 cm in diameter × 1.52 m long) was exactly centered within the larger external cylinder (29 cm in diameter × 1.85 m long). The test section where the samplers were placed was upwind of the fan. The ends of the outer cylinder were closed, to allow recirculation. The ends of the inner cyliner were open. Ozone in a relatively low flow of air was fed into the system just upstream of the fan, so it was thoroughly mixed after passing through the inter-cylinder annulus and then into the inner cylinder. Individual probe ports were drilled through both cylinders for all tubing (except the water line), the relative humidity and temperature probe, and the anemometer. Maximum wind velocity for the wind tunnel was nominally 300 cm/sec (600 ft/min).

During the relative humidity tests, water vapor was added to the air in the return annulus. A syringe pump forced ultrapure water through fine tubing onto paper toweling that was taped to the internal cylinder. The toweling served as a wick to spread the water over a large area, which functioned as an evaporation surface. Excellent control of the test section's relative humidity was achieved.

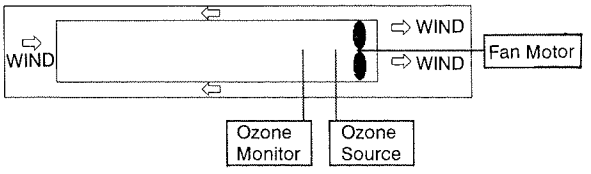

Figure 4. Plexiglas wind tunnel used for wind velocity experiments.

The end of the wind tunnel opposite the fan consisted of a removable plate. The plate provided access for sliding a sampling rack into the internal cylinder. The sampling rack was constructed of metal rods encased by Teflon tubing. In an orientation wind velocity test, four samplers were clipped to the rack to form a cross-sectional plane (top, bottom, left, and right). They were located 1 m downwind from the entrance edge of the internal cylinder. In a wind velocity test using protective cups, three cups were located downwind at distances of 0.52, 0.83, and 1.13 m.

Before each velocity test, the wind tunnel was conditioned and equilibrated with respect to a target ozone concentration for at least four hours. For relative humidity tests, the wind tunnel was given 12 hours to achieve a constant relative humidity. Equilibration was always conducted with the fan running. The samplers were placed on the sampling rack at the beginning of either type of test. The fan was turned off and the access plate was removed. The rack was slid into place quickly, the plate was replaced, and the fan was turned back on. After two to three hours, the target ozone and relative humidity levels were achieved.

Instrumentation

Temperature and relative humidity were measured with a Vaisala (Woburn, MA) model HMP 113Y combination humidity probe. Conditioning the exposure systems was sometimes assisted with a UV lamp (UV Products, Cambridge, England). We used a 4.5-in fan in the Plexiglas chamber. It was controlled with a variable autotransformer (Staco, Dayton, OH). A smaller fan (3-in diameter) was used in the aquarium and resealable container, and was similarly controlled. The incubator used in the temperature experiments (ProportioNull 1300 Series model, Tenney Engineering, Union, NJ) had a 25- × 25- × 36-cm interior chamber. The fan in the wind tunnel was controlled by a Stir-Pak mixer (model 4554–20, Cole-Parmer, Niles, IL). The syringe pump we used was a compact infusion pump (Harvard Apparatus, Natick, MA). Air velocity was monitored using a digital air velocity meter (model 1440, Kurz Instruments, Monterey, CA). Chart recorders (Esterline Angus Instrument Corp., Indianapolis, IN) were used to monitor ozone levels, relative humidity, and temperature.

A UV photometric ozone calibrator (model 49PS, Thermo Environmental Instruments, Franklin, MA) served as a calibrating unit and an ozone generator for the majority of laboratory experiments. The calibrator was periodically calibrated against a Dasibi model 1003PC ozone analyzer (Dasibi Environmental Corp., Glendale, CA). The Dasibi model 1003PC is a UV monitor configured by the manufacturer to be used as a continuous ambient air monitor for ozone. This monitor has been modified to be used as a primary standard UV photometer to calibrate continuous ozone monitors and "transfer standard" ozone calibrators, following the procedures described by the U.S. Environmental Protection Agency (1979). Immediately before and after each test, the ozone analyzer that was used underwent an abbreviated multipoint calibration. Analyzer accuracy was approximately 2%. Before room air was ozonated by the calibrator, it was pumped through a clean air system containing potassium permanganate–coated alumina and activated charcoal. For the tests performed at less than 30% relative humidity, silica gel was also used as part of the cleaning system.

Two types of continuous ozone monitoring instruments were used during different phases of the laboratory testing: an ozone analyzer (model 8410, Monitor Labs, San Diego, CA) using a chemiluminescent method, and a UV photometric ozone analyzer (model 49, Thermo Environmental Instruments). Fluorinated ethylene propylene (FEP) Teflon tubing was used throughout the exposure systems. In addition, polytetrafluorethylene Teflon (PTFE) filters were placed in line with the sample input of the ozone monitors. Calibrations were performed with the filters in place.

The output flow from the 49PS ozone generator was set between 1.5 and 4.2 L/min in order to maintain a low positive pressure within the exposure systems and to maintain a target ozone concentration. The flow rated depended on the type of continuous ozone monitor being used and the demand of the exposure system to be conditioned.

Ozone concentration in the exposure systems was always monitored on a strip chart recorder. In addition, the velocity and relative humidity tests were run with a data acquisition system supported on a personal computer. The software, ACQUIRE and PROCESS (Commonwealth Environmental), collected voltage outputs from the ozone monitor and the relative humidity probe and converted them into hourly averages. The true mean ozone concentration and the mean relative humidity values were the averages of the hourly values associated with a given exposure period. For all other tests, the true mean ozone concentration was calculated manually using the chart recorder trace for the exposure period. Ozone concentrations were assigned for half-hour or one-hour intervals, then averaged. The mean concentration included the ozone level recovery time occurring at the beginning of each test. Relative to the total exposure time, the recovery time was short and consequently did not have a large impact on the mean concentration.

SAMPLING AND ANALYSIS

During exposure, a sampler was removed from its bottle and resealable plastic bag and then exposed for a measured

period of time. After sample collection, the passive sampler was returned to the laboratory and disassembled in the clean-air glove box. The sampler's two coated filters were transferred to an 8-mL polyethylene bottle containing 5 mL of ultrapure water. The sample next was sonicated for 15 minutes in an ultrasonic bath. After preparation, sample extracts were stored at 5°C (typically for less than a week) and later analyzed for nitrate concentration by ion chromatography, using a chromatograph (model 2000i, Dionex Corp., Sunnyvale, CA) equipped with a conductivity detector. The anion separator column (4 mm, model AS4A) had a guard column (4 mm, model AG4A). The eluent was 1.26 mM sodium carbonate, 1.19 mM sodium bicarbonate, with a flow of 1.7 mL/min. The regenerant was 0.04 M sulfuric acid, and the detector range was 0 to 10 μS. It took approximately 12 minutes to produce a typical chromatograph (see Appendix B).

The concentration of nitrate in the extracts was determined by comparing sample peak heights with calibration standards in a regression equation. Because the number of moles of ozone collected on the filter medium was equal to the number of moles of nitrate formed, the average ozone concentration can be calculated easily for the exposure period.

At least three blank samplers were prepared for each test. They were assembled at the same time as the test samplers but were not removed from their polystyrene bottles for exposure. They were stored at room temperature conditions until after the test, when they were disassembled with the exposed test samplers. Their filters were prepared and analyzed in the same method as the test sampler filters. For each test, the mean nitrate concentration of the blank samplers was subtracted from the exposed sample value to obtain the net nitrate concentration.

DATA ANALYSIS

COLLECTION RATE

The sampling mechanism in passive devices is diffusion of the gaseous pollutant through some barrier (in this case, the end cap) to the collection medium. The theoretical collection rate for passive devices, defined by (DA/L), is given by Fick's First Law of Diffusion:

$$J \times A = \frac{D \times A}{L} C \qquad (1)$$

where J is the mass flux of ozone (μg/cm^2/sec); D is the diffusion coefficient (cm^2/sec); A is the cross-sectional area of the diffusion zone (cm^2); L is the length of the diffusion zone (cm); and C is the ambient ozone concentration (μg/cc).

For the Ogawa passive sampler, the diffusion zone was defined as the volume of the holes drilled into both diffusion end caps. Thus, the theoretical collection rate was 24.5 cc/min. This value was a point of reference for comparison with the collection rates observed in the validation tests.

The average ozone concentration to which the sampler was exposed can be determined using the following equation:

$$C_{PASS} = \frac{M \times V \times \dfrac{MW_{O_3}}{MW_{NO_3^-}}}{S \times K \times MW_{O_3} \times T} \qquad (2)$$

where C_{PASS} is the average ozone concentration determined by the passive monitor (ppb); M is the net NO_3^- concentration (μg/mL); V is the extraction volume (5 mL); MW_x is the molecular weight (μg/μmol); S is the reference collection rate ([cc/min] × [m^3/10^6 cc]); K is the constant 0.0409 (μmol/[ppb × m^3]; this constant refers to 1 atm of pressure and 25°C); T is the sampling time (min); and where the numerator represents the mass of ozone collected, and the denominator represents the "volume" of the sampled air. The denominator also includes K and MW_{O_3} for unit conversion purposes. For each sample, all quantities were known, except for the reference collection rate, S, which was calculated as the mean of all experimental collection rates (see S_E below).

Recognizing that most scientific methods experience some departure from theoretical behavior, we chose to determine the collection rate for the passive monitor empirically. The experimental collection rate, S_E, can be determined using the following formula:

$$S_E = \frac{M \times V \times \dfrac{MW_{O_3}}{MW_{NO_3^-}}}{C_{TRUE} \times T} \qquad (3)$$

where S_E is the experimental collection rate (cc/min); and C_{TRUE} is the true mean ozone concentration determined by the continuous analyzer (μg/cc), where the true mean ozone concentration was determined by averaging the data from the standard ozone continuous monitor over the exposure period. Actual collection rates were determined for all exposed samples using Equation 3. A mean collection rate was calculated for each group of samplers located in the same place (samplers from the same test run). By averaging the mean collection rates from all test runs, a reference collection rate, S_R, was obtained.

The average ozone concentration for each sampler was calculated from Equation 2 using the reference collection rate. To assess sampler performance, the ozone concentration measured by each passive sampler was compared with

the true mean ozone concentrations to which it was exposed.

PRECISION

The coefficient of variation (CV) was estimated by dividing the standard deviation (unbiased) by the mean value of the measured parameter. It was applied to a group of samplers from the same test run to assess precision within a test run.

RESULTS AND DISCUSSION

OVERVIEW

Laboratory validation tests of the passive sampler proceeded in two phases. The priority for the first phase was to understand better the collection rate, with varying ozone concentrations and exposure times. This was done by performing a series of tests in the rectangular exposure chambers.

The passive monitor was calibrated effectively by defining its collection rate under specific test conditions. We expected that the collection rate would be a constant value and that with further investigation, this test collection rate would be applicable to sampling conditions found in the field.

Coupled with these tests was the need to investigate analytical chemistry parameters, including limit of detection, collection capacity of the filter, and storage life of the filter extract.

Under EPA sponsorship, a field exposure study of weekly sampling began concurrently with this first phase. To compare outdoor tests carefully with laboratory tests, coated filters prepared at a given time were tested in both places. The individual sampler collection rates (from Equation 3) from the early outdoor data were reviewed with the corresponding laboratory results as they became available. The precision for each set of weekly tests was good, but the collection rates for outdoor tests were markedly higher than the rates for laboratory chamber tests.

Laboratory chamber studies were completed when the sampler had performed satisfactorily at the combinations of exposure times (24 hours and greater) and concentrations (20 to 60 ppb) that would most likely be encountered during initial ambient use. Because the sampler was an integrated monitor, it was also necessary to observe sampler performance over a dynamic range of total exposures (ppb•hour). Combining the laboratory chamber study and field study data sets filled a range from 400 ppb•hour to 12,000 ppb•hour, so further chamber tests at higher concentrations were not needed.

We began the second phase of validation tests to identify possible causes for the differences between outdoor and laboratory collection rates. These tests focused on temperature, wind velocity, and relative humidity. They were conducted at ozone levels ranging from 40 to 100 ppb, again in the range of typical ambient concentrations. Also, we wanted to have a similar amount of nitrite ion converted for each test, nominally equivalent to 50 ppb ozone for 40 hours (2,000 ppb•hour).

Each experiment focused on one variable, holding the others constant, i.e., the relative humidity experiment was performed in the wind tunnel at a given constant velocity. Because the laboratory chamber tests had already established stable collection rate behavior with varying ozone concentration, there was no need to perform each experiment over a range of ozone concentrations. Furthermore, the focus of these tests was not calculating some new reference collection rate, but rather observing what effect the varying parameter had upon collection rate behavior.

LABORATORY CHAMBER TESTING

Passive samplers were suspended in the Plexiglas or aquarium exposure chambers. The controlled fan speeds for each exposure chamber were chosen so that the test atmosphere would be adequately mixed when ozone was introduced. After a fan speed was set, the setting remained constant for all subsequent experiments.

A subset of samplers also was exposed by a team at Los Amigos Research and Education Institute (Downey, CA) and analyzed in a blinded manner at the HSPH laboratory. This exposure chamber was fabricated from stainless steel. Its volume was 93 m^3 (3,300 ft^3), and it was operated with 10 air changes per hour.

Data from the laboratory chamber experiments is presented in Table C.1. This table has been organized by exposure times. Filter identification codes beginning with "LA" are from Los Amigos tests; the remainder are tests at HSPH. Identification codes with "T" are from the temperature test series and were included with the chamber test data for analysis.

The HSPH laboratory test exposures ranged from 17 to 62 ppb ozone for 24 to 167 hours. Experiments at much higher concentrations, approximately 250 ppb ozone, with sampling times between 11 and 48 hours, were performed at the Los Amigos laboratory. The mean collection rate from Equation 3 was calculated for each laboratory test run of colocated samplers. The average of the colocated means was 18.1 ± 1.9 cc/min (± 10.5%). (Throughout this manuscript, values are given as means ± SD with the SD in percent following in parentheses.) This reference collection rate then

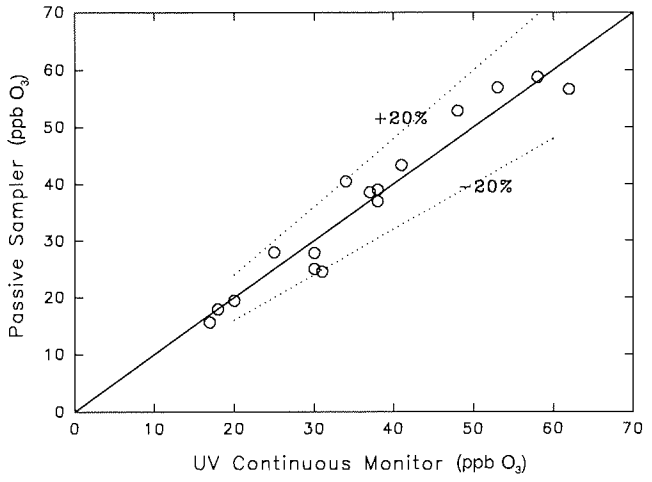

Figure 5. Laboratory exposure chamber tests: Comparison of passive samplers to a standard continuous monitor. Each data point is the mean of a chamber test, with ± 20% lines indicating the limits for a difference between the two measurements. See Table C.1 for the number of samplers included in each chamber test.

was used in Equation 2 to calculate the ozone concentrations for both sets of laboratory chamber experiments.

Figure 5 compares the passive monitor ozone concentration (Equation 2) and the standard continuous monitor concentration for the HSPH laboratory chamber tests. The relative error of the HSPH chamber data is ± 9.8%. As a visual assessment of the accuracy of the data, Figure 5 is shown with error bounds of ± 20%. For the HSPH laboratory tests, 15 out of 16 sampler groups predicted ozone levels within 20% of the actual concentrations. For the Los Amigos laboratory tests at higher concentrations, the three sampler groups predicted ozone within 7% of the actual concentrations.

For each colocated sampler group, the CV value for the collection rate was calculated. The highest CV values, 7.6%, 10.3%, and 14.3%, were associated respectively with the lowest ozone concentrations, 20, 18, and 17 ppb. Too few laboratory tests were performed in this low concentration range to understand conclusively the passive monitor's performance. There may have been conditioning problems within the chamber at low ozone concentrations. The remaining 17 sampler groups had an average CV value of 3.4%, indicating excellent precision for the majority of the HSPH and Los Amigos laboratory tests.

FIELD EXPOSURE TESTING

Field testing was performed in cooperation with the EPA's Environmental Monitoring and Assessment Program (EMAP), and with financial support from the EPA. The test site, located at Prince Edward, VA, is an active site of the National Dry Deposition Network, an ambient air monitoring program of the U.S. EPA at a number of locations throughout the United States. A UV photometric ozone analyzer (model 49–103, Thermo Environmental Instruments) was used at the site for continuous measurement. Precision checks were performed every two to three days at the site. Multipoint calibrations against an audit model 49–103 were performed quarterly. Instrument accuracy was maintained to within 5%. Final one-hour integrated ozone concentrations were provided by the EPA.

Two passive ozone samplers were housed under each of three A-frame shelters on top of a "tip" tower, a field-site structure designed to elevate atmospheric samplers to 10 m above the ground but also allow easy access by the operator. Each group of samplers was exposed for a period of seven days and then returned, with field log, to HSPH for laboratory analysis. Data presented here were collected during the period from November 13, 1990 to October 15, 1991.

The passive sampler data is displayed in Table C.2. As with the laboratory experiments, individual collection rates determined from Equation 3 were averaged for each sampling week to determine the colocated mean. The colocated means were averaged to find the reference collection rate for the field tests, 29.0 ± 2.7 cc/min (± 9.3%). (The field data reference collection rate was significantly higher than that calculated for the laboratory tests.) The reference collection rate was used in Equation 2 to determine average ozone concentrations for each sampling period. These concentrations are compared with the continuous ozone monitor results in Figures 6 and 7.

The variation in weekly average ozone concentrations over time at the field site is shown in Figure 6. This figure plots a chronological comparison of the passive samplers and continuous monitor for the EMAP field study, representing 44 sampling weeks across four seasons of the year.

For the period between March 31, 1991 and April 10, 1991, the continuous ozone monitor did not operate. Therefore, collection rates for the sampling weeks starting March 26 and April 9 could only be based on continuous monitor data from 75% and 86%, respectively, of the passive monitor exposure time. No mean collection rate could be calculated for the April 2 sampling week.

For the sampling week starting February 12, 1991, the passive ozone samplers measured an average ozone concentration unusually higher than that for the continuous monitor. The site operator noted in the field log the sampling equipment for that week was installed during a period of heavy rain. This suggests that extreme humidity may have affected the chemistry of the sampler, or that the samplers became wet during deployment, producing adverse effects. Because this was not the only week with high humidity, it is un-

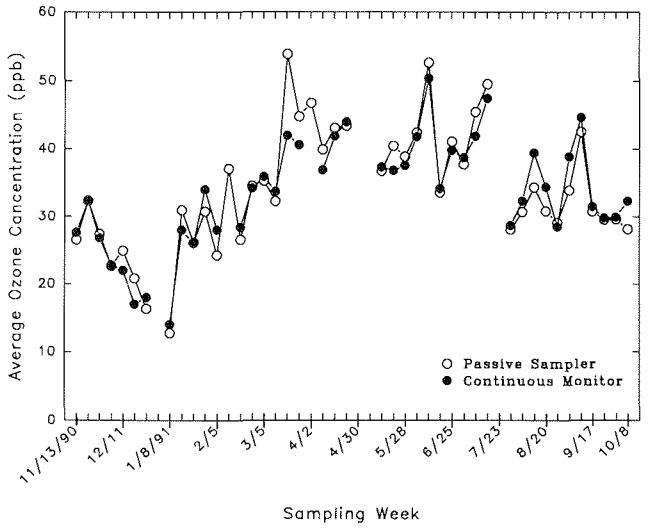

Figure 6. EMAP field tests comparing passive samplers to a standard continuous monitor for 11 months of sampling. Each data point is the mean of three colocated samplers.

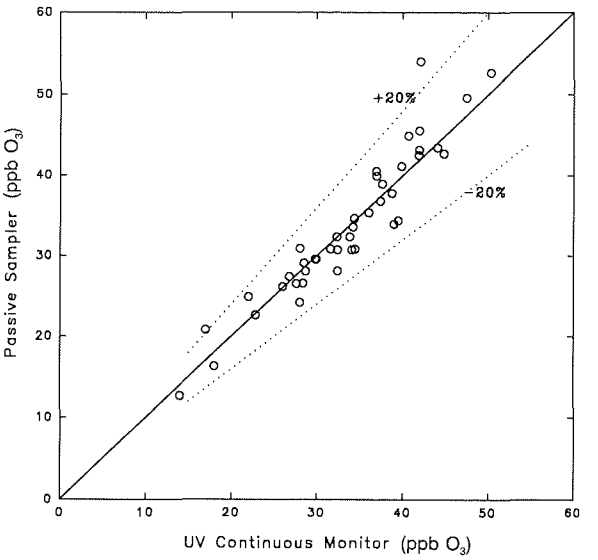

Figure 7. EMAP field tests comparing passive samplers to a standard continuous monitor. Each data point is the mean of three colocated samplers; dotted lines indicate ± 20% error bounds.

likely that the former hypothesis explains this discrepancy. (Later laboratory tests also showed that sampler performance was unaffected by humidity.) Data from the March 19 sampling week showed similar results, but with no probable explanation from the field log.

Because of the close agreement between the majority of the field sampler data and the continuous monitor, and because the field log gives reason to believe that certain conditions experienced during ambient monitoring could void a sample, the data from the February 12 sampling week were considered outliers. They were not averaged into the reference collection rate. Furthermore, a 90% data capture from the continuous monitor was required before a mean collection rate could be averaged into the reference collection rate. Therefore, collection rates from sampling weeks that were not included in the reference collection rate calculation are indicated by footnote c in Table C.2.

Figure 7 illustrates close agreement between the passive sampler response and that of the standard continuous ozone monitor. The relative error of the EMAP field data is ± 8.86%. This demonstrates excellent linearity of the sampling technique and suggests that after establishing a collection rate for the sampler under given exposure conditions, reasonable accuracy can be expected from the analytical technique. Predicted ozone levels were within 20% of the actual concentrations for 40 out of 43, or 93%, of the sampling weeks.

The majority of the weekly calculated CV values were low, indicating good precision in the method used. Three nonconsecutive weeks did display CV values greater than 10%, i.e., 10.6% at 28 ppb, 12.3% at 27 ppb, and 15.8% at 17 ppb. In the laboratory chamber tests, high CV values were associated with low concentrations. However, in the field tests, this trend did not occur. In fact, most of the low concentration sampling weeks at the EMAP site produced low CV values, i.e., 4.1% at 14 ppb, 5.2% at 18 ppb, and 4.7% and 6.7% at nominally 22 ppb. Because this is the first test of this sampler with outdoor extremes and minimal protection, the results can be considered quite good.

COLLECTION RATES FOR LABORATORY AND FIELD EXPERIMENTS

The reference collection rates for the laboratory and field experiments were 18.1 ± 1.9 cc/min (20 observations, HSPH and Los Amigos data combined) and 29.0 ± 2.7 cc/min (37 observations), respectively. These figures demonstrate a 60% difference. Figure 8 compares the two reference collection rates averaged from the colocated means.

The independent experiments performed by the Los Amigos laboratory show close correlation with the HSPH laboratory experiments. The higher Los Amigos ozone concentrations extended the range of exposures for which sampler performance has been accurate and precise for controlled laboratory conditions.

The low standard deviations demonstrated excellent agreement within each test series. However, the large difference between reference collection rates for the laboratory and field experiments suggested the possibility of interfer-

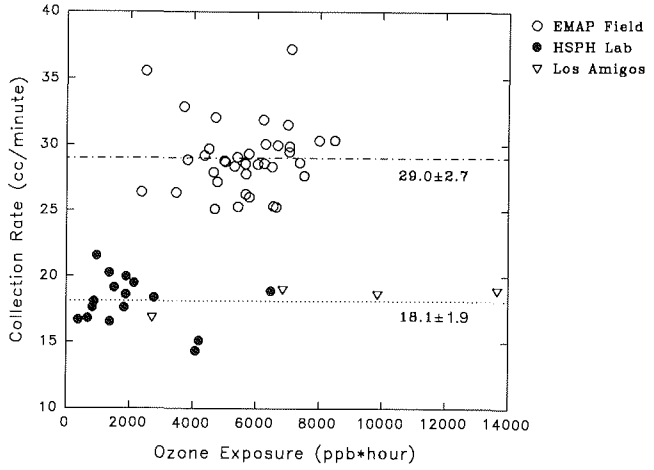

Figure 8. Comparison of passive sampler collection rates from laboratory and field exposure tests.

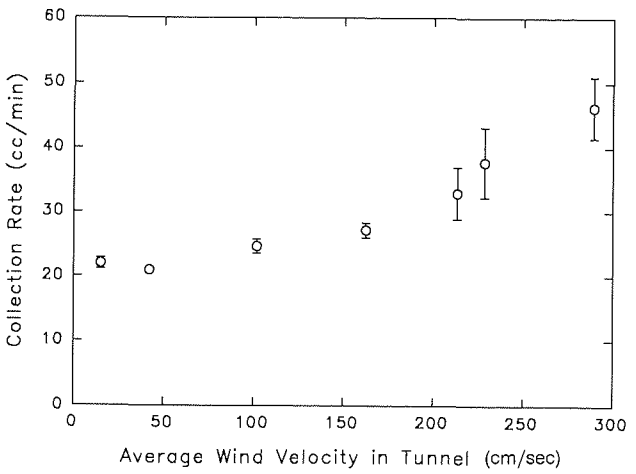

Figure 9. Wind tunnel velocity experiments: Collection rates for passive samples oriented at a 0° angle to the airstream. Each data point is the mean of one test run; the vertical bar shows ± 1 SD.

ing factors such as temperature, relative humidity, wind velocity, and copollutants. The reference collection rate from the laboratory chamber tests could not be applied to the monitor during field use, as had been intended originally. It was necessary to determine whether one of the interference factors mentioned above or some other unknown factor, which would perhaps discriminate between indoor and outdoor applications, was affecting the sampling characteristics. To understand the discrepancy in collection rates, further experiments were required.

EFFECTS OF FACE VELOCITY

Our results indicate that the passive sampler was affected by changes in wind velocity. The collection rate was dependent upon wind velocity and orientation of the sampler face to the wind (Figure 9).

The first set of experiments was performed with the diffusion end caps of the passive samplers oriented at a 0° angle to the direction of the wind. In other words, the wind was blown over the surface of the end caps, and the plane of the flat plastic holder was perpendicular to the direction of the wind. In this orientation, the mean collection rates from colocated passive samplers increased exponentially through the velocity range of 18 to 270 cm/sec (35 to 525 standard ft/min).

The data from the series of 0° experiments are listed in Table C.3. The mean collection rates range from 21 to 46 cc/min, increasing with velocity. At the three highest velocities tested, the standard deviations increased dramatically, with CV values greater than 10%. The mathematical relationship between wind speed and collection rate at this orientation was not determined because it would be impractical to apply it to the sampler's actual field use. Issues such as prevailing wind direction with respect to the sampler and prevailing wind speed would further complicate the use of the sampler.

However, to understand the essence of these results, consider that the boundary layer over the end caps will be part of the length of diffusion zone, L. Therefore, with increasing wind speeds, L decreases, and as seen in Equation 1, the collection rate increases.

Before attempting to modify the sampler geometry or its method of use to minimize the effect of wind speed on the collection rate, we decided to run a single test series at the opposite orientation, i.e., with wind blowing directly into one diffusion end cap. The purpose was to understand the wind speed effects at two extremes of orientation. Due to the conclusive results of the 0° orientation tests, we decided that performing wind speed tests through a range of orientations was unnecessary.

With the wind blowing directly into the diffusion end caps of a sampler group, i.e., 90° orientation, a lower and more stable collection rate was exhibited than that found with the 0° orientation. The collection rates from the test data given in Table C.4 are plotted in Figure 10. For comparison purposes, a reference collection rate for the 90° tests was calculated as 23.5 ± 2.4 cc/min (10.2%), which was similar to the 0° orientation collection rates at lower wind speeds.

For some of these 90° tests, the front and back filters were analyzed separately for each sampler; the two collection rates were added in order to make comparisons with the previous experiments. There was a slight difference (nominally 2 cc/min) in the collection rates of the upwind and downwind filters, but this difference was not as large as might have been expected for this orientation. Similar up-

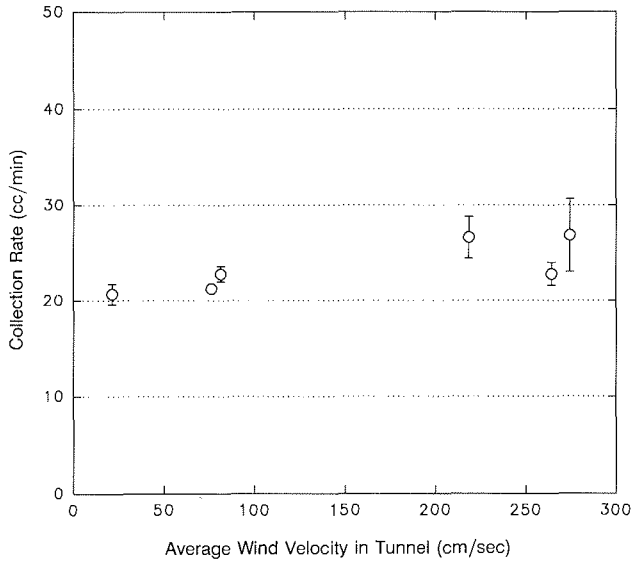

Figure 10. Wind tunnel velocity experiments: Collection rates for passive samplers oriented at a 90° angle to the airstream. Each data point is the mean of one test run; the vertical bar shows ± 1 SD.

wind and downwind collection rates, as well as only a slight increase in collection rate with wind speed (albeit with high variation), indicate that convective transport of air into the upwind diffusion barrier was minimal, if it indeed occurred.

A possible explanation for the collection rate stability shown in the 90° tests, given that the 0° tests display the influence of wind speed, is that a stagnation point existed at the upwind end of the sampler, a blunt body in the windstream. The velocity at a stagnation point is zero. Furthermore, it is possible that the turbulent eddies in the wake directly adjacent to the downwind end caps did not change dramatically within the range of wind speeds tested.

The face velocity and orientation experiments suggest that, barring the influence from other unknown interferences, the dramatic difference in collection rates observed between laboratory and EMAP field testing is largely due to differences in mean wind velocities. Because the field samples are protected only by a simple A-frame shelter, they are exposed directly to the relatively high wind velocities typically encountered outdoors. Also, wind direction with respect to the sampler will vary throughout an exposure period. Tower height (10 m) elevates the samplers to a location of greater wind speeds, away from ground-level obstructions that decrease wind speed.

Laboratory samples were exposed in test chambers where air mixing was conducted primarily to reduce the concentration gradients and effects of insufficient air entering the sampler. Measuring a mean wind velocity for these tests was not feasible because of the air flow patterns that developed as a result of the rectangular chamber shapes. (Wind speed at the chamber fan was believed to be nominally 20 cm/sec [40 standard ft/min]; thus, individual samplers likely would experience wind speeds less than this.) However, it is unlikely that the mean wind velocities in the laboratory experiments greatly exceeded those commonly found outdoors at ground level.

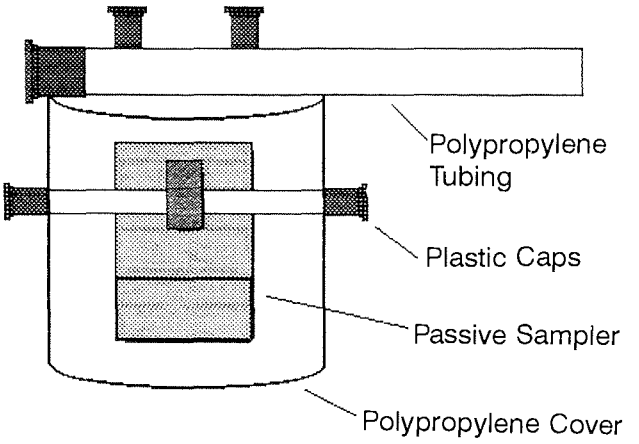

Figure 11. Passive sampler clipped inside a protective cup.

In order to reduce the effects of face velocity on the sampler, we developed a dual-purpose rain cover and windscreen to enclose an individual sampler (Figure 11). We used a commercially available polypropylene jar as an inverted cup. The jar has an 8-cm diameter at the mouth, and the center of the hanging sampler barrel is 4 cm above its edge. A metal cross rod inside the jar is encased in Teflon tubing except for a small central section where the sampler is attached to it with a clip.

The results shown in Figure 12 demonstrate that this protective cup is effective in attenuating the effects of high wind velocities on the passive sampler. The nominal relative humidity for these tests was 50%, within an ozone concentration range from 40 to 90 ppb. The data from each test with the cups are presented in Table C.5. The reference collection rate for wind speeds ranging from 25 to 295 cm/sec (50 to 580 standard ft/min) was 21.1 ± 1.9 cc/min (± 9%), based on the mean of the colocated averages. The reference collection rate was used in Equation 2 to calculate the ozone concentrations for the protected samplers. Although these bounds suggest a minimum wind speed of 25 cm/sec (50 standard ft/min) in order to avoid effects from insufficient air entering the sampler, using this protective cup effectively stabilized the collection rate throughout the test range. The cup geometry makes wind direction relatively independent of sampler placement within it.

Figure 13 provides a visual comparison of the sampler response to the standard ozone monitoring technique. For the

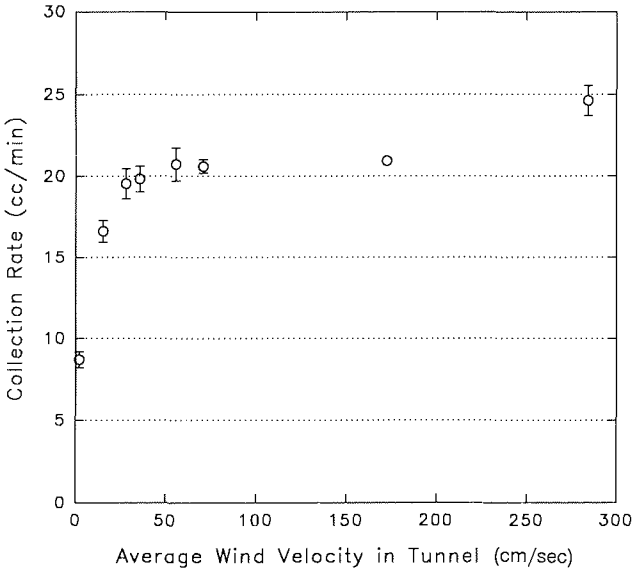

Figure 12. Wind tunnel velocity experiments: Collection rates for passive samplers that were clipped into protective cups. Each data point is the mean of one test run; the vertical bar shows ± 1 SD.

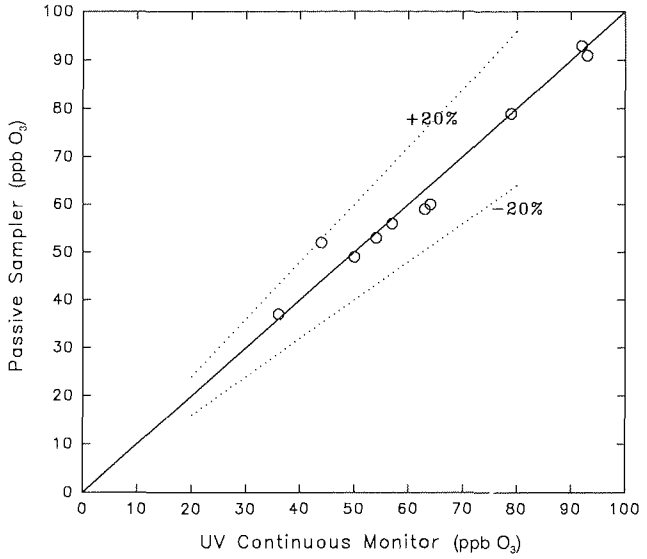

Figure 13. Wind tunnel velocity experiments: Comparison of passive samplers to a standard continuous monitor for samplers that were clipped into protective cups at velocities greater than 25 cm/sec, and between 10% and 80% relative humidity. Each data point is the mean of each wind tunnel test; dotted lines indicate ± 20% error bounds.

data from protected samplers experiencing a range of face velocities, all sampler groups predicted ozone levels within 20% of the actual concentrations.

Unfortunately, using the polypropylene cups for outdoor passive monitoring has been unsuccessful. In an ozone monitoring study in State College, PA, during the summer of 1991, monitors clipped into the cups demonstrated a high and variable positive interference. The cause for this interference is undetermined, but because the cup is translucent, the samplers may have overheated during exposure to the sun. Side-by-side monitoring was conducted with a second passive ozone monitor protected under opaque white polyvinyl chloride caps, which provided successful State College results (Liu et al. 1992). Current outdoor monitoring conducted by HSPH uses polyvinyl chloride covers with geometry similar to that of the wind tunnel–tested polypropylene jar.

LIMIT OF DETECTION AND SAMPLER CAPACITY

The sampling technique's limit of detection was defined as three times the standard deviation of the blanks in a batch of filters. Using the most conservative estimate, i.e., the lowest average collection rate of 18.1 cc/min, we calculated a limit of detection of about 201 ppb•hour, or 25 ppb at 8 hours, 8 ppb at 24 hours, and 4 ppb at 48 hours.

The sample capacity was defined as the conversion of 5% of the total nitrite ion on the coated filters to nitrate ion, using the higher reference collection rate of 29.0 cc/min. The capacity was approximately 19,865 ppb•hour, i.e., 2,483 ppb at 8 hours, 828 ppb at 24 hours, and 414 ppb at 48 hours. This capacity is a conservative estimate.

STORAGE STABILITY

After exposure, the passive samplers were returned to the laboratory, and the filters were extracted as soon as possible. Reanalysis of some EMAP field samples showed a maximum change of ± 0.5 parts per million nitrate concentration approximately 10 weeks after filter extraction (Figure 14). For these samples, the change in nitrate concentration corresponds to a maximum change of approximately ± 4 ppb ozone 10 weeks after extraction (Figure 15). These results suggest that the samples were reasonably stable in solution.

EFFECTS OF TEMPERATURE

The sampling method exhibited no significant change in collection rate due to temperature variability for the range from 0°C to 40°C (Figure 16). To maintain constant humidity within the exposure chamber for the series of temperature experiments, silica gel cartridges were added to the clean air system to remove moisture.

Table C.6 contains the data from the three temperature tests. Test exposures lasted for approximately 36 hours, with an average of 41 to 53 ppb ozone and approximately 10% to 25% relative humidity. For comparison purposes, a reference collection rate of 19.5 ± 0.85 cc/min (± 4.3%) was calculated. This reference collection rate agrees, within ex-

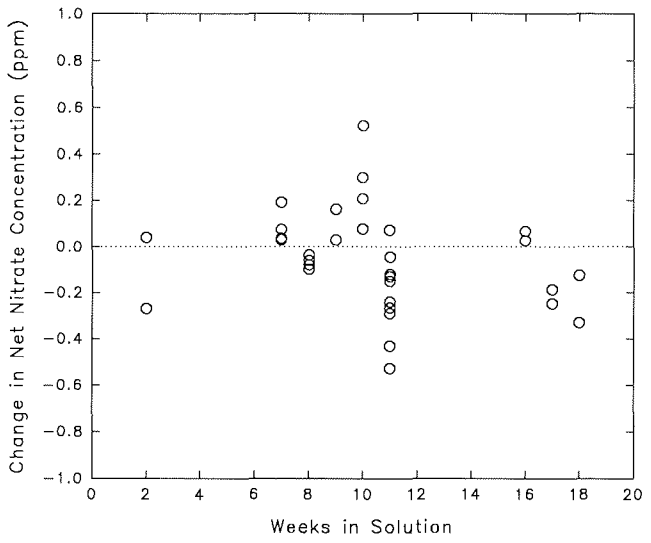

Figure 14. Sample stability after extraction, expressed as the change in nitrate concentration in the extract. Each data point represents one test extract.

perimental error, with the mean colocated collection rates reported above for room temperature laboratory tests in rectangular chambers. Therefore, the temperature test data were included with the HSPH and Los Amigos laboratory chamber test results.

We did not attempt tests at lower temperatures because they were beyond the range at which typical ambient ozone exposures were expected and use of this sampling device was anticipated.

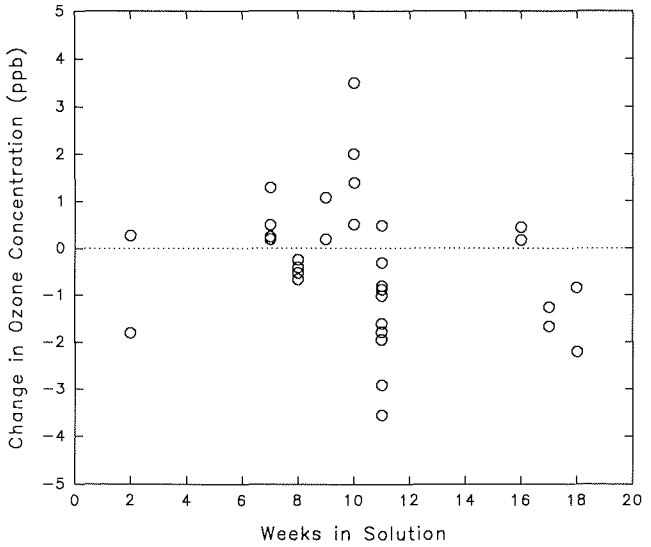

Figure 15. Sample stability after extraction, expressed as the change in ozone concentration. Each data point represents one test extract.

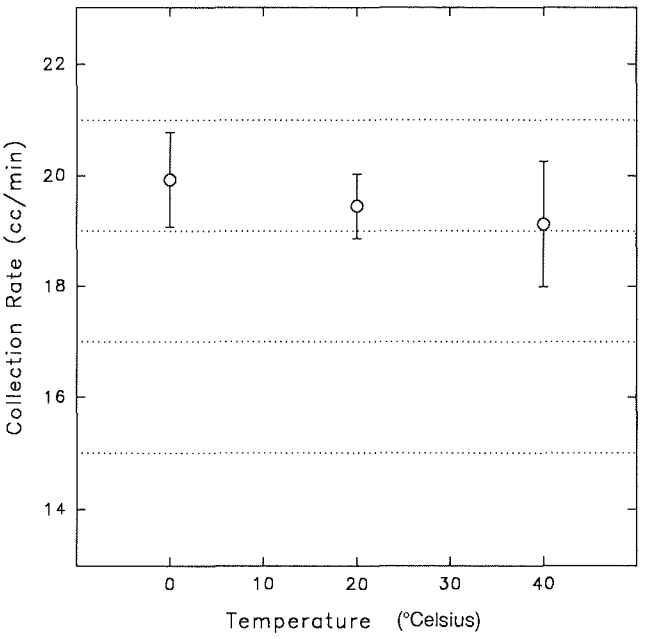

Figure 16. The effect of temperature on the passive sampler collection rate. Each data point is the mean of one test run ± 1 SD. The vertical bar on each data point represents the SD. See Table C.6 for the number of samplers in each test run.

EFFECTS OF HUMIDITY

After completing the wind speed tests with protective cups, we performed the relative humidity tests in the wind tunnel at a fixed wind speed. The samplers were clipped into the cups for these tests. The chosen wind speed was 170 cm/sec (340 standard ft/min) so that a test from the wind speed series could be included in the humidity effects data. Two tests were performed at low relative humidities (10% to 20%), and two were performed at high relative humidities (70% to 80%). The test from the wind speed series was in the middle of the total relative humidity range, at 48%.

The resulting collection rates, plotted on the same scale as the wind speed tests (Figure 17), showed no effects due to relative humidity. For comparison purposes, a reference collection rate of 20.9 ± 0.4 cc/min (± 1.9%) was calculated from the data (Table C.7). Test-to-test precision was good, as demonstrated by the individual CV values. Because the samplers were exposed to a range of ozone concentrations (36 to 92 ppb), these data have been included in the wind speed linearity plot in Figure 13.

COPOLLUTANT INTERFERENCES

Other pollutants in the environment may adversely affect the performance of this sampling technique. For example, nitric acid gas is collected simultaneously on the alkaline

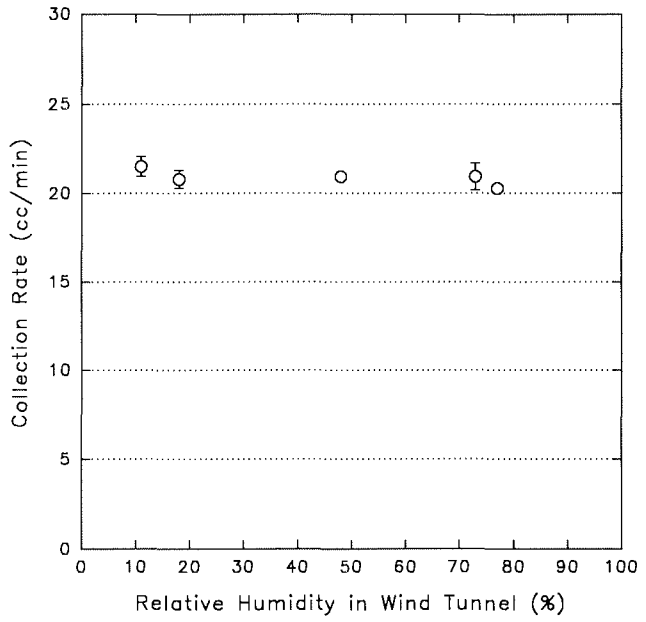

Figure 17. Passive sampler collection rates from relative humidity tests in the wind tunnel. Wind speed was kept constant at 173 cm/sec. Each data point is the mean of one test run ± 1 SD. The vertical bar on each data point represents the SD. See Table C.7 for the number of samplers in each test run.

filters during sampling. This could contribute to an overestimate of the ozone concentration. However, under typical ambient conditions, this positive interference probably represents less than 5% of the nitrate formed during the nitrite and ozone reaction (Koutrakis and Mueller 1989).

The possible reaction of ozone with organic aerosols collected on the coated filters may result in an underestimate of the ozone concentration. However, due to the amount of nitrite on the coated filters relative to the probable amount of organic aerosols collected, this interference is probably insignificant. Also, because particles have diffusion coefficients that are orders of magnitude less than gases, one would expect negligible amounts of particles to be deposited on the filter.

Prior to the validation tests, in establishing the potential for the coating chemistry, UV light exposure tests were conducted with ozone-exposed filters. There were no differences between these filters and those not exposed to UV light.

Interference from sulfur dioxide was not expected because this gas is not a strong oxidant. Any effects from oxygen, a weak oxidant, were accounted for when samples were corrected for those obtained with blank samplers that had not been exposed to ozone. The conversion of nitrite to nitrate, due to the aging of blank filters, was negligible over several days.

Nitrogen Dioxide

We believe that NO_2 does not affect ozone measurements using this passive device because preliminary results using active samplers showed no interferences. During development of the coating solution at HSPH, 100 ppb NO_2 in ozone-free air was forced through a filter pack prepared with the nitrite-based coating solution and through a filter pack prepared with a sodium carbonate and glycerol coating solution. The slight reductions in NO_2 downstream from each filter pack were quantitatively identical, indicating no reaction of NO_2 with nitrite on the filter medium. In separate evaluation tests of the active sampler (J.D. Mulik, U.S. Environmental Protection Agency, Atmospheric Research and Exposure Assessment Laboratory, Research Triangle Park, NC, unpublished results), no difference was seen between the active sampler and a continuous analyzer when sampling 30 ppb ozone in the presence of 76 ppb NO_2 in a test chamber. In both of these cases, the amount of NO_2 contacting the actively sampled coated filter was orders of magnitude greater than that expected for the filter in a passive device.

Peroxyacetyl Nitrate

Peroxyacetyl nitrate (PAN), as a strong oxidant, can oxidize nitrite to nitrate. Because ambient concentrations of PAN are typically 10 to 20 times smaller than ozone concentrations, they are not considered to cause significant interference in most locations (Finlayson-Pitts and Pitts 1986).

Peroxyacetyl nitrate exposure tests were performed by DGA Inc. (Ventura, CA) as part of the validation tests. The study design consisted of five tests: exposure to ozone alone, exposure to PAN alone, and exposure to three mixtures of PAN and ozone in varying proportions. The ozone concentrations were 41 and 80 ppb, similar to expected ambient levels. The results are presented in Table C.8.

Unfortunately, these data are not usable in assessing PAN's effect on the sampler. This is indicated by the test in which only ozone exposure occurred. This test served as the control for the experiment and allowed us to assess how comparable the PAN data are to the rest of the laboratory data, with respect to the collection rate. The collection rate for this test was only 4.4 cc/min, far below the rates for the experiments performed at HSPH. Such a collection rate indicates probable effects from insufficient air movement dominating the sampler response to ozone. Because of this, it is not possible to assess the effect of PAN on ozone collection when sampler response to ozone has been compromised.

In reviewing the exposure chamber design used by DGA and the results of our wind speed tests conducted after the

PAN experiments, we concluded that for the ozone levels of the current experiments, the air velocity inside DGA's exposure chamber was much lower than the levels observed with the monitors during the HSPH laboratory tests. No mixing fan was used in DGA's PAN exposure chamber, which depended upon the total air flow rate to ensure air velocity over the passive samplers. The chamber had only one inlet and one outlet port. Air flow ranged from 2 to 6 L/min. In the experiment with ozone only, the flow rate was 3.4 L/min. Thus, for the cubic exposure chamber (45-L capacity), the samplers experienced a velocity of about 0.051 cm/sec (0.1 standard ft/min).

Unfortunately, our understanding of wind speed with respect to this sampler's performance was incomplete when the PAN tests were scheduled. At that time, the promising HSPH and Los Amigos laboratory results, coupled with the initial months of EMAP field data, gave us confidence that the DGA exposure chamber would be satisfactory for this sampler's PAN tests.

CONCLUSIONS

This work has shown through laboratory and field testing that a nitrite ion–coated glass fiber filter can be used to collect ambient ozone with good precision. Sampler collection rates in well-mixed laboratory exposure chambers and unprotected field experiments were 18.1 and 29.0 cc/min, respectively. Using separate collection rates, excellent agreement was demonstrated between the sampler response and a standard ozone analyzer.

The large difference in collection rates observed with laboratory chamber tests and field tests appears to have been due primarily to face velocity effects. Laboratory experiments indicated that an increase in the mean wind velocity increases the collection rate nearly exponentially. However, a modified rain cover and wind screen attenuated these effects and stabilized the collection rate nominally to 21 cc/min, through a wind speed range from 25 to 295 cm/sec (50 to 580 standard ft/min). The HSPH is continuing its field efforts to determine whether this wind tunnel collection rate can be applied to outdoor monitoring using a polyvinyl chloride version of the protective cover. Because EMAP measurements of outdoor ozone with the passive sampler agree within ± 20% of the results from the continuous UV photometric method, these samplers are well suited for determining mean outdoor ozone concentrations for durations of one day or longer.

Because the Ogawa passive ozone sampler is influenced by face velocity, there are concerns about its use in indoor monitoring, which frequently involves still air. It is possible that the reference collection rate derived from the chamber tests could be applied to indoor monitoring, but further experimental work should first be done indoors (in locations with significant ozone levels), or in large exposure chambers where side-by-side monitoring can be performed with a standard continuous ozone monitor, or both. Alternatively, the passive monitor could be used indoors, provided it was placed in the windstream of a small fan so that the face velocity could be measured. Then, a collection rate could be estimated using the wind tunnel test for unprotected samplers at 0° orientation (Figure 9).

The application of this new collection technique to a passive sampler design has shown promising results. Without protection, the sampler collection rate is dependent on wind direction and velocity; however, the collection rate is independent of temperature and humidity over the ranges expected for typical outdoor sampling. Because of concern that direct moisture may affect performance, future studies should include investigating the stability of the collection rate in foggy or misty conditions. With respect to copollutants, tests to investigate the interference of PAN should be undertaken.

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APPENDIX A. Calculation of Relative Error

Relative error is defined as the square root of the mean of the squared difference between the true mean ozone concentration (C_{TRUE}) and the average ozone concentration measured by the passive monitor (C_{PASS}), divided by the mean of the true mean ozone concentrations from a test series. It is calculated by the following equation:

$$\frac{\sqrt{\dfrac{\sum_{i=1}^{n} (C_{TRUE_i} - C_{PASS_i})^2}{n}}}{\dfrac{\sum_{i=1}^{n} C_{TRUE_i}}{n}}$$

APPENDIX B. Typical Chromatograph of Ozone Analysis

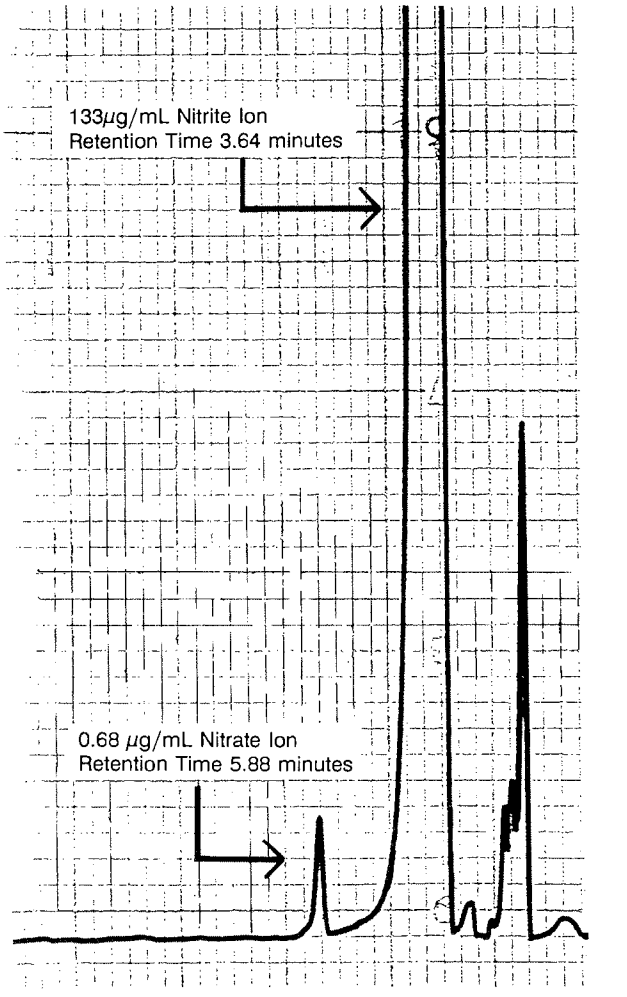

Figure B.1. Typical chromatograph of the separation of nitrate and nitrite.

APPENDIX C. Tables of Data Used for Figures

Table C.1. Laboratory Chamber Test Data

Sample ID	Exposure Time (hours)	Ion Chromatography Results		True Ozone (ppb)	Collection Rate (cc/min)			Concentration from Passive Monitor[b]		
		Nitrate (μg)	Ozone (μg)		S_E[a]	Mean	SD	Ozone (ppb)	Mean	SD
LA-E	11.70	7.80	6.04	249	17.60	16.87	0.70	242.04	231.96	9.65
LA-H	11.70	7.18	5.56		16.20			222.82		
LA-P	11.70	7.45	5.76		16.80			231.02		
EM2-01-P	24.12	0.95	0.74	17	15.26	16.65	2.38	14.33	15.63	2.23
EM2-02-P	24.12	1.13	0.87		18.10			17.00		
EM2-03-P	24.12	1.01	0.78		16.13			15.14		
EM3-01-P	24.12	0.83	0.64		13.28			12.47		
EM3-02-P	24.12	1.26	0.97		20.18			18.95		
EM3-03-P	24.12	1.06	0.82		16.94			15.91		
EM2-1-1/7	24.15	1.92	1.49	30	17.41	16.78	1.04	28.85	27.80	1.73
EM2-2-1/7	24.15	1.78	1.38		16.14			26.75		
EM2-3-1/7	24.15	1.94	1.50		17.60			29.17		
EM3-1-1/7	24.15	1.76	1.36		15.93			26.40		
EM3-2-1/7	24.15	1.99	1.54		18.06			29.92		
EM3-3-1/7	24.15	1.71	1.32		15.51			25.70		
EM3-01-2/28	23.68	2.66	2.06	34	21.71	21.53	0.24	40.76	40.44	0.44
EM3-02-2/28	23.68	2.60	2.02		21.26			39.93		
EM3-03-2/28	23.68	2.65	2.05		21.63			40.62		
EM3-04-P0116	24.25	3.74	2.90	62	16.36	16.53	0.23	56.02	56.60	0.78
EM3-05-P0116	24.25	3.76	2.91		16.44			56.30		
EM3-06-P0116	24.25	3.84	2.97		16.79			57.49		
LA-D	24.00	18.15	14.05	272	18.28	18.98	0.80	274.56	285.16	12.01
LA-I	24.00	19.71	15.26		19.85			298.20		
LA-L	24.00	18.69	14.47		18.82			282.72		
EM5-T09-P0401	35.73	5.00	3.87	48	19.16	19.93	0.85	50.81	52.84	2.26
EM5-T10-P0401	35.73	5.49	4.25		21.06			55.83		
EM5-T11-P0401	35.73	5.06	3.92		19.39			51.41		
EM5-T12-P0401	35.73	5.25	4.06		20.12			53.33		
EM5-T01-P0323	37.55	5.99	4.64	53	19.79	19.45	0.58	57.93	56.94	1.70
EM5-T02-P0323	37.55	6.08	4.71		20.08			58.78		
EM5-T03-P0323	37.55	5.79	4.48		19.12			55.96		
EM5-T04-P0323	37.55	5.70	4.41		18.82			55.10		
EM5-T05-P0329	34.90	4.35	3.37	41	19.97	19.12	1.13	45.23	43.30	2.57
EM5-T06-P0329	34.90	4.40	3.41		20.22			45.79		
EM5-T07-P0329	34.90	3.94	3.05		18.11			41.01		
EM5-T08-P0329	34.90	3.96	3.06		18.18			41.16		
LA-F	35.22	27.15	21.02	272	18.63	18.65	1.18	279.85	280.17	17.76
LA-N	35.22	25.47	19.72		17.48			262.75		
LA-O	35.22	28.92	22.39		19.84			298.08		
EM3-01-1/17	42.23	2.07	1.60	20	16.08	17.60	1.35	17.76	19.44	1.49
EM3-02-1/17	42.23	2.32	1.80		18.07			19.96		
EM3-03-1/17	42.23	2.40	1.86		18.65			20.60		
BL-07-2611	48.75	2.12	1.64	18	15.90	18.05	1.86	15.81	17.95	1.85
BL-08-2611	48.75	2.56	1.98		19.14			19.03		
BL-09-2611	48.75	2.55	1.98		19.12			19.01		
EM3-1-1/8	48.53	3.53	2.74	25	19.15	20.22	0.82	26.44	27.93	1.14
EM3-2-1/8	48.53	3.70	2.86		20.04			27.67		
EM3-3-1/8	48.53	3.75	2.90		20.32			28.06		
EM3-4-1/8	48.53	3.91	3.02		21.16			29.22		
EM3-5-1/8	48.53	3.61	2.79		19.54			26.98		
EM3-6-1/8	48.53	3.90	3.02		21.14			29.19		
BL-01-P	48.05	5.11	3.96	38	18.40	18.58	0.72	38.62	39.00	1.38
BL-02-P	48.05	5.08	3.94		18.30			38.41		

(*Table continues next page.*)

Table C.1. (*continued*)

Sample ID	Exposure Time (hours)	Ion Chromatography Results: Nitrate (µg)	Ion Chromatography Results: Ozone (µg)	True Ozone (ppb)	Collection Rate (cc/min): S_E[a]	Collection Rate (cc/min): Mean	Collection Rate (cc/min): SD	Concentration from Passive Monitor[b]: Ozone (ppb)	Concentration from Passive Monitor[b]: Mean	Concentration from Passive Monitor[b]: SD
BL-03-P	48.05	5.48	4.24		19.72			41.38		
BL-04-P	48.05	4.87	3.77		17.53			36.79		
BL-05-P	48.05	5.21	4.03		18.76			39.37		
BL-06-P	48.05	5.22	4.04		18.78			39.41		
EM3-04-P	49.35	4.75	3.68	38	16.65	17.59	0.97	34.96	36.92	2.03
EM3-05-P	49.35	5.00	3.87		17.53			36.80		
EM3-06-P	49.35	5.30	4.11		18.59			39.01		
BL-10-P	47.30	7.37	5.71	58	17.67	18.34	0.62	56.60	58.74	1.99
BL-11-P	47.30	7.70	5.96		18.45			59.10		
BL-12-P	47.30	7.89	6.11		18.90			60.53		
LA-A	46.92	37.69	29.18	278	18.99	18.97	0.10	291.63	291.31	1.59
LA-B	46.92	37.83	29.29		19.06			292.71		
LA-K	46.92	37.42	28.97		18.86			289.58		
LB-01-P	167.77	17.83	13.81	37	18.88	18.85	0.18	38.59	38.53	0.36
LB-02-P	167.77	17.91	13.86		18.96			38.74		
LB-03-P	167.77	17.56	13.60		18.60			38.00		
LB-04-P	167.77	17.92	13.87		18.97			38.78		
EM3-1-1/4	168.02	11.53	8.93	30	15.03	15.09	0.23	24.91	25.01	0.38
EM3-2-1/4	168.02	11.43	8.85		14.90			24.69		
EM3-3-1/4	168.02	11.51	8.91		15.01			24.87		
EM3-4-1/4	168.02	11.83	9.16		15.42			25.56		
EM3-1-1/17	166.58	11.30	8.75	31	14.38	14.32	0.29	24.62	24.51	0.49
EM3-2-1/17	166.58	11.00	8.52		14.00			23.97		
EM3-3-1/17	166.58	11.45	8.86		14.57			24.95		

[a] Calculated using Equation 3.

[b] Calculated using Equation 2 with a reference collection rate (S) of 18.1 cc/min.

Table C.2. Field Test Data from the Environmental Monitoring and Assessment Program Site

EMAP Week	Sample ID	Exposure Time (hours)	Ion Chromatography Results: Nitrate (µg)	Ion Chromatography Results: Ozone (µg)	True Ozone (ppb)	Collection Rate (cc/min): S_E[a]	Collection Rate (cc/min): Mean	Collection Rate (cc/min): SD	Concentration from Passive Monitor[b]: Ozone (ppb)	Concentration from Passive Monitor[b]: Mean	Concentration from Passive Monitor[b]: SD
11/13/90	AEM-001-P	168.50	20.09	15.55	28	28.39	27.91	0.53	27.01	26.55	0.50
	BEM-001-P	168.50	19.81	15.34		27.99			26.63		
	CEM-001-P	168.50	19.35	14.98		27.35			26.02		
11/20	AEM-002-P	167.25	23.62	18.29	32	28.74	29.05	1.08	32.00	32.35	1.21
	BEM-002-P	167.25	24.87	19.25		30.26			33.69		
	CEM-002-P	167.25	23.15	17.92		28.16			31.35		
11/27	BEM-003-P	167.83	18.27	14.15	27	26.70	29.68	2.41	24.67	27.42	2.22
	CEM-003-P	167.83	19.32	14.96		28.23			26.08		
	AEM-004-P	167.83	22.36	17.31		32.67			30.18		
	BEM-004-P	167.83	20.08	15.55		29.35			27.11		
	CEM-004-P	167.83	21.53	16.67		31.45			29.06		
12/04	AEM-005-P	167.33	16.12	12.48	23	27.78	28.84	1.35	21.83	22.67	1.06
	BEM-005-P	167.33	16.86	13.06		29.05			22.83		
	AEM-006-P	167.33	15.94	12.34		27.47			21.58		
	BEM-006-P	167.33	17.93	13.88		30.89			24.27		
	CEM-006-P	167.33	16.85	13.04		29.03			22.81		

(*Table continues next page.*)

Table C.2. Field Test Data from the Environmental Monitoring and Assessment Program Site (*continued*)

EMAP Week	Sample ID	Exposure Time (hours)	Ion Chromatography Results		True Ozone (ppb)	Collection Rate (cc/min)			Concentration from Passive Monitor[b]		
			Nitrate (μg)	Ozone (μg)		S_E[a]	Mean	SD	Ozone (ppb)	Mean	SD
12/11	AEM-007-P	167.83	20.44	15.82	22	36.38	32.87	2.19	27.58	24.93	1.66
	BEM-007-P	167.83	17.65	13.67		31.42			23.83		
	CEM-007-P	167.83	18.75	14.52		33.38			25.31		
	AEM-008-P	167.83	18.76	14.53		33.40			25.33		
	BEM-008-P	167.83	18.43	14.27		32.81			24.88		
	CEM-008-P	167.83	16.77	12.98		29.85			22.64		
12/18	AEM-009-P	146.17	13.52	10.47	17	35.76	35.57	5.62	20.96	20.85	3.29
	BEM-009-P	146.17	11.79	9.13		31.18			18.27		
	CEM-009-P	146.17	17.50	13.55		46.29			27.12		
	AEM-010-P	146.17	12.22	9.46		32.31			18.94		
	BEM-011-P	146.17	12.08	9.35		31.96			18.72		
	CEM-010-P	146.17	13.59	10.52		35.94			21.06		
12/24	AEM-011-P	191.83	13.78	10.67	18	26.22	26.34	1.37	16.27	16.34	0.85
	BEM-011-P	191.83	12.72	9.85		24.22			15.03		
	CEM-011-P	191.83	14.23	11.02		27.09			16.81		
	AEM-012-P	191.83	14.88	11.52		28.33			17.57		
	BEM-012-P	191.83	13.53	10.47		25.75			15.97		
	CEM-012-P	191.83	13.88	10.74		26.41			16.39		
01/01/91	No sampling this week.										
01/08	AEM-013-P	168.50	9.32	7.21	14	25.96	26.39	1.09	12.53	12.74	0.53
	BEM-013-P	168.50	10.07	7.79		28.04			13.53		
	CEM-013-P	168.50	8.93	6.91		24.87			12.00		
	AEM-014-P	168.50	9.32	7.22		25.97			12.53		
	BEM-014-P	168.50	9.47	7.33		26.39			12.73		
	CEM-014-P	168.50	9.74	7.54		27.14			13.10		
01/15	AEM-015-P	168.25	26.78	20.73	28	37.36	32.07	3.39	36.05	30.95	3.28
	BEM-015-P	168.25	23.87	18.48		33.30			32.14		
	CEM-015-P	168.25	19.81	15.33		27.63			26.67		
	AEM-016-P	168.25	22.15	17.15		30.91			29.83		
	BEM-016-P	168.25	21.35	16.53		29.79			28.75		
	CEM-016-P	168.25	23.97	18.56		33.44			32.27		
01/22	AEM-017-P	167.73	18.77	14.53	26	28.28	29.18	2.64	25.35	26.15	2.38
	BEM-017-P	167.73	19.62	15.19		29.57			26.50		
	CEM-017-P	167.73	18.68	14.46		28.16			25.23		
	AEM-018-P	167.73	17.25	13.36		26.00			23.30		
	BEM-018-P	167.73	19.29	14.94		29.08			26.06		
	CEM-018-P	167.73	22.55	17.46		33.98			30.45		
01/29	AEM-019-P	166.50	22.90	17.73	34	26.59	26.24	2.05	31.16	30.75	2.40
	BEM-019-P	166.50	21.30	16.49		24.73			28.99		
	CEM-019-P	166.50	24.86	19.25		28.86			33.82		
	AEM-020-P	166.50	22.57	17.48		26.21			30.71		
	BEM-020-P	166.50	23.98	18.57		27.85			32.63		
	CEM-020-P	166.50	19.99	15.47		23.21			27.20		
02/05	AEM-021-P	167.58	17.02	13.18	28	23.84	25.14	1.53	23.01	24.26	1.48
	BEM-021-P	167.58	17.83	13.81		24.98			24.11		
	CEM-021-P	167.58	16.92	13.10		23.70			22.87		
	AEM-022-P	167.58	19.96	15.45		27.95			26.98		
	BEM-022-P	167.58	18.05	13.98		25.29			24.40		
	CEM-022-P	167.58	17.90	13.86		25.08			24.20		

(*Table continues next page.*)

Table C.2. Field Test Data from the Environmental Monitoring and Assessment Program Site (*continued*)

EMAP Week	Sample ID	Exposure Time (hours)	Ion Chromatography Results		True Ozone (ppb)	Collection Rate (cc/min)			Concentration from Passive Monitor[b]		
			Nitrate (μg)	Ozone (μg)		S_E[a]	Mean	SD	Ozone (ppb)	Mean	SD
02/12[c]	AEM-023-P	167.92	32.42	25.10	27	47.00	39.86	4.91	43.74	37.10	4.57
	BEM-023-P	167.92	23.21	17.97		33.65			31.31		
	CEM-023-P	167.92	24.64	19.08		35.72			33.25		
	AEM-024-P	167.92	28.85	22.34		41.82			38.92		
	BEM-024-P	167.92	29.43	22.78		42.66			39.71		
	CEM-024-P	167.92	26.44	20.47		38.33			35.67		
02/19	AEM-25-P	168.02	20.54	15.90	28	28.29	27.17	2.38	27.69	26.59	2.33
	BEM-25-P	168.02	17.80	13.78		24.52			24.01		
	CEM-25-P	168.02	19.09	14.78		26.29			25.74		
	AEM-26-P	168.02	18.08	14.00		24.91			24.38		
	BEM-26-P	168.02	22.36	17.31		30.79			30.14		
	CEM-26-P	168.02	20.47	15.85		28.20			27.60		
02/26	AEM-27-P	167.92	24.56	19.01	34	28.03	29.31	2.08	33.13	34.65	2.46
	BEM-27-P	167.92	26.50	20.52		30.24			35.76		
	CEM-27-P	167.92	25.19	19.50		28.75			33.98		
	AEM-28-P	167.92	23.65	18.31		26.98			31.90		
	BEM-28-P	167.92	23.35	19.63		28.93			34.20		
	CEM-28-P	167.92	28.87	22.35		32.94			38.94		
03/05	AEM-29-P	167.83	25.49	19.73	36	27.72	28.50	0.76	34.40	35.37	0.94
	BEM-29-P	167.83	25.77	19.95		28.03			34.78		
	CEM-29-P	167.83	25.54	19.78		27.79			34.48		
	AEM-30-P	167.83	27.04	20.93		29.41			36.50		
	BEM-30-P	167.83	26.94	20.86		29.31			36.37		
	CEM-30-P	167.83	26.45	20.48		28.77			35.70		
03/12	AEM-31-P	167.91	25.40	19.67	34	29.42	27.78	1.83	34.27	32.37	2.13
	BEM-31-P	167.91	24.33	18.83		28.17			32.82		
	CEM-31-P	167.91	22.26	17.23		25.78			30.03		
	AEM-32-P	167.91	23.34	18.07		27.03			31.49		
	BEM-32-P	167.91	26.14	20.24		30.27			35.27		
	CEM-32-P	167.91	22.47	17.40		26.02			30.32		
03/19	AEM-033-PAS	168.17	40.62	31.45	42	37.71	37.22	3.09	54.72	54.01	4.48
	BEM-033-PAS	168.17	39.04	30.22		36.24			52.59		
	CEM-033-PAS	168.17	42.77	33.11		39.70			57.61		
	AEM-034-PAS	168.17	33.94	26.28		31.51			45.73		
	BEM-034-PAS	168.17	41.41	32.06		38.44			55.78		
	CEM-034-PAS	168.17	42.78	33.12		39.71			57.63		
03/26[c]	AEM-035-PAS	167.08	32.13	24.88	41	31.13	32.08	2.05	43.57	44.89	2.86
	BEM-035-PAS	167.08	33.18	25.69		32.15			44.99		
	CEM-035-PAS	167.08	30.26	23.43		29.32			41.03		
	AEM-036-PAS	167.08	36.74	28.44		35.60			49.82		
	BEM-036-PAS	167.08	33.25	25.74		32.21			45.08		
	CEM-036-PAS	167.08	33.09	25.62		32.06			44.87		
04/02[c]	AEM-037-PAS	168.42	34.83	26.96					46.85	46.80	2.06
	BEM-037-PAS	168.42	37.21	28.80					50.05		
	CEM-037-PAS	168.42	33.08	25.61					44.50		
	AEM-038-PAS	168.42	35.87	27.77					48.25		
	BEM-038-PAS	168.42	34.14	26.43					45.92		
	CEM-038-PAS	168.42	33.61	26.02					45.20		

(*Table continues next page.*)

Table C.2. Field Test Data from the Environmental Monitoring and Assessment Program Site (*continued*)

EMAP Week	Sample ID	Exposure Time (hours)	Ion Chromatography Results		True Ozone (ppb)	Collection Rate (cc/min)			Concentration from Passive Monitor[b]		
			Nitrate (μg)	Ozone (μg)		S_E[a]	Mean	SD	Ozone (ppb)	Mean	SD
04/09[c]	AEM-039-PAS	167.17	30.11	23.31	37	32.08	31.09	0.83	40.81	39.92	1.06
	BEM-039-PAS	167.17	28.92	22.39		30.82			39.19		
	CEM-039-PAS	167.17	30.64	23.72		32.65			41.52		
	AEM-040-PAS	167.17	29.16	22.57		31.07			39.51		
	BEM-040-PAS	167.17	29.38	22.75		31.31			39.82		
	CEM-040-PAS	167.17	28.53	22.09		30.40			38.66		
04/16	AEM-041-PAS	168.08	31.12	24.09	42	29.04	29.87	0.88	41.94	43.14	1.26
	BEM-041-PAS	168.08	33.76	26.13		31.50			45.50		
	CEM-041-PAS	168.08	32.10	24.85		29.96			43.27		
	AEM-042-PAS	168.08	31.37	24.29		29.28			42.29		
	BEM-042-PAS	168.08	32.06	24.82		29.92			43.21		
	CEM-042-PAS	168.08	31.64	24.50		29.53			42.65		
04/23	AEM-043-PAS	167.50	33.99	26.31	44	30.31	28.64	1.06	45.97	43.43	1.61
	BEM-043-PAS	167.50	30.80	23.85		27.47			41.66		
	CEM-043-PAS	167.50	31.24	24.19		27.86			42.25		
	AEM-044-PAS	167.50	32.59	25.23		29.06			44.08		
	BEM-044-PAS	167.50	32.66	25.29		29.13			44.17		
	CEM-PRR-PAS	167.50	31.38	24.29		27.98			42.44		
04/30	No sampling this week.										
05/07	No sampling this week.										
05/14	AEM-049-PAS	167.28	26.17	20.26	37	27.55	28.58	1.31	35.44	36.77	1.68
	BEM-049-PAS	167.28	28.07	21.73		29.54			38.02		
	CEM-049-PAS	167.28	29.07	22.50		30.59			39.37		
	AEM-050-PAS	167.28	25.68	19.88		27.03			34.78		
	BEM-050-PAS	167.28	26.95	20.86		28.37			36.50		
	CEM-050-PAS	167.28	26.97	20.88		28.39			36.53		
05/21	AEM-051-PAS	168.70	29.43	22.78	37	31.11	31.88	0.64	39.52	40.50	0.81
	BEM-051-PAS	168.70	30.21	23.39		31.93			40.57		
	CEM-051-PAS	168.70	30.60	23.69		32.35			41.09		
	AEM-052-PAS	168.70	30.95	23.96		32.72			41.56		
	BEM-052-PAS	168.70	30.29	23.45		32.02			40.67		
	CEM-052-PAS	168.70	29.49	22.83		31.17			39.60		
05/28	AEM-053-PAS	167.33	28.02	21.69	38	29.29	30.04	1.16	37.94	38.90	1.50
	BEM-053-PAS	167.33	29.32	22.70		30.65			39.70		
	CEM-053-PAS	167.33	30.56	23.66		31.95			41.37		
	AEM-054-PAS	167.33	28.81	22.31		30.12			39.01		
	BEM-054-PAS	167.33	28.26	21.88		29.54			38.26		
	CEM-054-PAS	167.33	27.43	21.24		28.68			37.14		
06/04	AEM-055-PAS	168.25	31.79	24.61	42	29.68	29.45	1.80	42.80	42.47	2.60
	BEM-055-PAS	168.25	31.41	24.32		29.33			42.29		
	CEM-055-PAS	168.25	29.71	23.00		27.74			40.00		
	AEM-056-PAS	168.25	29.42	22.78		27.47			39.62		
	BEM-056-PAS	168.25	34.76	26.91		32.46			46.81		
	CEM-056-PAS	168.25	32.14	24.88		30.01			43.27		
06/11	AEM-057-PAS	168.33	40.69	31.50	50	31.53	30.34	0.88	54.76	52.68	1.54
	CEM-057-PAS	168.33	38.75	30.00		30.03			52.15		
	AEM-058-PAS	168.33	37.56	29.08		29.11			50.54		
	BEM-058-PAS	168.33	39.55	30.62		30.65			53.22		
	CEM-058-PAS	168.33	39.17	30.33		30.36			52.72		

(*Table continues next page.*)

Table C.2. Field Test Data from the Environmental Monitoring and Assessment Program Site (*continued*)

EMAP Week	Sample ID	Exposure Time (hours)	Ion Chromatography Results		True Ozone (ppb)	Collection Rate (cc/min)			Concentration from Passive Monitor[b]		
			Nitrate (μg)	Ozone (μg)		S_E[a]	Mean	SD	Ozone (ppb)	Mean	SD
06/18	AEM-059-PAS	165.50	25.73	19.92	34	29.92	28.54	1.07	35.22	33.59	1.26
	BEM-059-PAS	165.50	23.79	18.42		27.66			32.56		
	CEM-059-PAS	165.50	25.26	19.55		29.37			34.57		
	AEM-060-PAS	165.50	23.62	18.29		27.47			32.34		
	BEM-060-PAS	165.50	23.75	18.39		27.62			32.52		
	CEM-060-PAS	165.50	25.09	19.42		29.18			34.34		
06/25	AEM-061-PAS	167.67	34.19	26.47	40	33.68	29.97	2.23	46.20	41.12	3.06
	BEM-061-PAS	167.67	29.27	22.66		28.82			39.54		
	CEM-061-PAS	167.67	29.44	22.79		28.99			39.77		
	AEM-062-PAS	167.67	27.63	21.39		27.21			37.33		
	BEM-062-PAS	167.67	30.48	23.60		30.02			41.19		
	CEM-062-PAS	167.67	31.57	24.44		31.10			42.66		
07/02	AEM-063-PAS	167.83	26.60	20.59	39	26.91	28.32	1.19	35.90	37.77	1.59
	BEM-063-PAS	167.83	28.64	22.17		28.98			38.66		
	CEM-063-PAS	167.83	29.60	22.91		29.95			39.95		
	AEM-064-PAS	167.83	27.61	21.37		27.94			37.27		
	BEM-064-PAS	167.83	26.81	20.76		27.13			36.19		
	CEM-064-PAS	167.83	28.64	22.18		28.98			38.66		
07/09	AEM-065-PAS	166.92	31.92	24.72	42	30.00	31.51	2.75	43.33	45.51	3.98
	BEM-065-PAS	166.92	33.57	25.99		31.55			45.57		
	CEM-065-PAS	166.92	31.78	24.60		29.86			43.13		
	AEM-066-PAS	166.92	32.47	25.14		30.52			44.08		
	BEM-066-PAS	166.92	32.08	24.84		30.15			43.54		
	CEM-066-PAS	166.92	39.37	30.48		37.00			53.43		
07/16	AEM-067-PAS	168.42	38.28	29.64	47	31.49	30.30	1.48	51.50	49.56	2.42
	BEM-067-PAS	168.42	38.41	29.73		31.59			51.66		
	CEM-067-PAS	168.42	34.51	26.71		28.38			46.42		
	AEM-068-PAS	168.42	34.71	26.87		28.55			46.69		
	BEM-068-PAS	168.42	37.08	28.71		30.49			49.87		
	CEM-068-PAS	168.42	38.09	29.49		31.33			51.24		
07/23	No sampling this week.										
07/30[c]	AEM-071-PAS	167.75	21.24	16.45	29	28.99	28.41	2.03	28.69	28.11	2.01
	BEM-071-PAS	167.75	18.11	14.02		24.71			24.45		
	CEM-071-PAS	167.75	21.06	16.30		28.74			28.44		
	AEM-072-PAS	167.75	20.58	15.93		28.08			27.79		
	BEM-072-PAS	167.75	21.34	16.52		29.13			28.82		
	CEM-072-PAS	167.75	22.58	17.48		30.81			30.49		
08/06[c]	AEM-073-PAS	168.00	22.80	17.65	32	27.57	27.55	1.33	30.74	30.72	1.48
	BEM-073-PAS	168.00	23.03	17.83		27.85			31.06		
	CEM-073-PAS	168.00	24.56	19.02		29.71			33.12		
	AEM-074-PAS	168.00	21.31	16.50		25.78			28.74		
	BEM-074-PAS	168.00	22.99	17.80		27.80			31.00		
	CEM-074-PAS	168.00	22.00	17.03		26.61			29.67		
08/13	AEM-075-PAS	167.95	26.18	20.27	39	25.97	25.26	1.32	35.32	34.36	1.80
	CEM-075-PAS	167.95	23.50	18.19		23.30			31.70		
	AEM-076-PAS	167.95	25.13	19.45		24.92			33.89		
	BEM-076-PAS	167.95	25.49	19.73		25.28			34.38		
	CEM-076-PAS	167.95	27.08	20.96		26.86			36.53		

(*Table continues next page.*)

Table C.2. Field Test Data from the Environmental Monitoring and Assessment Program Site (*continued*)

EMAP Week	Sample ID	Exposure Time (hours)	Ion Chromatography Results		True Ozone (ppb)	Collection Rate (cc/min)			Concentration from Passive Monitor[b]		
			Nitrate (μg)	Ozone (μg)		S_E[a]	Mean	SD	Ozone (ppb)	Mean	SD
08/20	AEM-077-PAS	167.92	21.90	16.95	34	24.93	26.01	1.92	29.54	30.83	2.28
	CEM-077-PAS	167.92	22.10	17.11		25.16			29.82		
	AEM-078-PAS	167.92	20.99	16.25		23.89			28.31		
	BEM-078-PAS	167.92	24.41	18.90		27.79			32.93		
	CEM-078-PAS	167.92	24.86	19.24		28.30			33.54		
08/27[c]	AEM-079-PAS	167.77	21.09	16.33	29	28.99	29.66	1.23	28.48	29.14	1.21
	BEM-079-PAS	167.77	20.37	15.77		28.00			27.51		
	CEM-079a-PAS	167.77	21.67	16.77		29.78			29.26		
	AEM-080-PAS	167.77	21.17	16.39		29.10			28.58		
	BEM-080-PAS	167.77	22.38	17.32		30.76			30.22		
	CEM-079b-PAS	167.77	22.81	17.66		31.35			30.80		
09/03	AEM-081-PAS	168.00	22.63	17.52	39	22.76	25.32	1.50	30.52	33.95	2.02
	BEM-081-PAS	168.00	25.27	19.56		25.41			34.08		
	CEM-081-PAS	168.00	25.35	19.63		25.50			34.19		
	AEM-082-PAS	168.00	24.57	19.03		24.72			33.14		
	BEM-082-PAS	168.00	26.26	20.33		26.42			35.42		
	CEM-082-PAS	168.00	26.95	20.86		27.10			36.34		
09/10	AEM-083-PAS	167.90	28.42	22.00	45	24.86	27.65	1.86	38.34	42.65	2.87
	BEM-083-PAS	167.90	32.11	24.86		28.09			43.32		
	CEM-083-PAS	167.90	29.50	22.84		25.81			39.81		
	AEM-084-PAS	167.90	32.98	25.53		28.85			44.50		
	BEM-084-PAS	167.90	33.39	25.85		29.20			45.05		
	CEM-084-PAS	167.90	33.25	25.74		29.09			44.86		
09/17	AEM-085-PAS	168.42	21.36	16.54	32	26.41	28.37	1.49	28.74	30.87	1.62
	BEM-085-PAS	168.42	21.87	16.93		27.03			29.41		
	CEM-085-PAS	168.42	22.57	17.47		27.90			30.36		
	AEM-086-PAS	168.42	23.93	18.53		29.58			32.19		
	BEM-086-PAS	168.42	23.57	18.25		29.14			31.71		
	CEM-086-PAS	168.42	24.40	18.89		30.17			32.83		
09/24	AEM-087-PAS	167.47	20.64	15.98	30	27.17	28.79	2.25	27.91	29.58	2.31
	BEM-087-PAS	167.47	20.99	16.25		27.64			28.40		
	CEM-087-PAS	167.47	21.26	16.46		28.00			28.77		
	AEM-088-PAS	167.47	21.29	16.48		28.03			28.80		
	BEM-088-PAS	167.47	25.28	19.57		33.28			34.19		
	CEM-088-PAS	167.47	21.75	16.84		28.63			29.42		
10/01	AEM-089-PAS	167.78	20.63	15.97	30	26.99	28.70	1.41	27.86	29.61	1.46
	BEM-089-PAS	167.78	20.94	16.21		27.40			28.28		
	CEM-089-PAS	167.78	21.88	16.94		28.63			29.55		
	AEM-090-PAS	167.78	22.61	17.50		29.58			30.53		
	BEM-090-PAS	167.78	23.58	18.25		30.85			31.84		
	CEM-090-PAS	167.78	21.95	17.00		28.72			29.64		
10/08	AEM-091-PAS	168.08	19.81	15.34	32	23.98	25.27	1.96	26.71	28.14	2.18
	BEM-091-PAS	168.08	19.50	15.10		23.60			26.28		
	CEM-091-PAS	168.08	18.96	14.68		22.95			25.56		
	AEM-092-PAS	168.08	22.46	17.38		27.18			30.27		
	BEM-092-PAS	168.08	22.40	17.34		27.10			30.18		
	CEM-092-PAS	168.08	22.16	17.15		26.82			29.87		

[a] Calculated using Equation 3.

[b] Calculated using Equation 2 with a reference collection rate (S) of 29.0 cc/min.

[c] The mean experimental collection rates from these samples were not used to calculate the reference collection rate.

Table C.3. Data from Wind Velocity Tests at 0° Orientation

Wind Speed (cm/sec)	Sample ID	Exposure Time (hours)	Ion Chromatography Results		True Ozone (ppb)	Collection Rate (cc/min)		
			Nitrate (μg)	Ozone (μg)		S_E[a]	Mean	SD
15	EM5-01-P0506	36.92	5.62	4.35	44	22.72	21.95	0.88
	EM5-02-P0506		5.56	4.31		22.50		
	EM5-03-P0506		5.14	3.98		20.78		
	EM5-04-P0506		5.38	4.17		21.78		
42	EM5-01-P0508	39.00	6.00	4.64	49	20.63	20.94	0.28
	EM5-02-P0508		6.19	4.79		21.30		
	EM5-03-P0508		6.07	4.70		20.86		
	EM5-04-P0508		6.10	4.72		20.98		
102	EM5-01-P0513	43.50	7.96	6.16	47	25.47	24.66	1.12
	EM5-02-P0513		7.34	5.68		23.48		
	EM5-03-P0513		7.47	5.79		23.92		
	EM5-04-P0513		8.05	6.23		25.76		
163	EM5-01-P0521	13.00	9.80	7.59	55	27.40	27.15	1.16
	EM5-02-P0521		9.26	7.17		25.88		
	EM5-03-P0521		10.24	7.93		28.63		
	EM5-04-P0521		9.55	7.40		26.69		
212	EM5-01-P0515	40.80	7.76	6.01	43	29.36	33.00	4.08
	EM5-02-P0515		10.18	7.88		38.51		
	EM5-03-P0515		8.08	6.26		30.56		
	EM5-04-P0515		8.88	6.87		33.58		
229	LAB1-01-P0627	50.33	13.04	10.10	45	38.27	37.76	5.45
	LAB1-02-P0627		13.02	10.08		38.19		
	LAB1-03-P0627		10.45	8.09		30.65		
	LAB1-04-P0627		14.97	11.59		43.93		
290	EM5-01-P0518	39.92	12.11	9.38	48	41.46	46.27	4.76
	EM5-02-P0518		15.44	11.95		52.85		
	EM5-03-P0518		13.19	10.21		45.14		
	EM5-04-P0518		13.34	10.33		45.66		

[a] Calculated using Equation 3.

Table C.4. Data from Wind Velocity Tests at 90° Orientation

Wind Speed (cm/sec)	Sample ID	Exposure Time (hours)	Ion Chromatography Results		True Ozone (ppb)	Collection Rate (cc/min)			Concentration from Passive Monitor[b]		
			Nitrate (μg)	Ozone (μg)		S_E[a]	Mean	SD	Ozone (ppb)	Mean	SD
21	EM5-01F-P0530	46.00	2.91	2.25	40	10.52	20.68	1.06	17.71	34.82	1.78
	EM5-01B-P0530		2.44	1.89		8.80			14.82		
	EM5-02F-P0530		2.49	1.93		9.01			15.17		
	EM5-02B-P0530		3.08	2.38		11.11			18.71		
	EM5-03F-P0530		2.75	2.13		9.93			16.71		
	EM5-03B-P0530		3.11	2.41		11.23			18.91		
	EM5-04F-P0530		2.61	2.02		9.44			15.89		
	EM5-04B-P0530		3.51	2.72		12.68			21.35		
76	LAB1-01F-P0628	43.50	3.77	2.92	53	10.66	21.25	0.16	24.24	48.32	0.36
	LAB1-01B-P0628		3.77	2.92		10.65			24.22		
	LAB1-02F-P0628		3.67	2.84		10.37			23.59		
	LAB1-02B-P0628		3.76	2.91		10.62			24.15		
	LAB1-03F-P0628		3.65	2.83		10.33			23.49		
	LAB1-03B-P0628		3.92	3.04		11.09			25.23		
	LAB1-04F-P0628		3.55	2.75		10.02			22.80		
	LAB1-04B-P0628		3.98	3.08		11.24			25.57		
81	EM5-01-P0523	44.08	7.46	5.78	48	23.24	22.78	0.79	47.36	46.44	1.61
	EM5-02-P0523		7.45	5.77		23.19			47.27		
	EM5-03-P0523		7.42	5.75		23.11			47.11		
	EM5-04-P0523		6.94	5.37		21.60			44.02		
218	EM5-01-P0526	40.06	6.92	5.36	42	26.83	26.60	2.19	48.29	47.89	3.94
	EM5-02-P0526		6.25	4.84		24.26			43.66		
	EM5-03-P0526		6.67	5.16		25.85			46.53		
	EM5-04-P0526		7.60	5.88		29.48			53.06		
264	EM5-01F-P0619	19.00	2.88	2.23	107	9.29	22.78	1.20	42.36	103.84	5.48
	EM5-01B-P0619		4.11	3.18		13.28			60.53		
	EM5-02F-P0619		3.35	2.59		10.80			49.24		
	EM5-02B-P0619		3.82	2.96		12.34			56.28		
	EM5-03F-P0619		3.04	2.36		9.83			44.81		
	EM5-03B-P0619		4.50	3.49		14.54			66.29		
	EM5-04F-P0619		3.07	2.38		9.92			45.24		
	EM5-04B-P0619		3.44	2.66		11.10			50.61		
274	EM5-01F-P0621	48.00	2.80	2.17	44	8.70	26.84	3.81	16.34	50.44	7.16
	EM5-01B-P0621		7.71	5.97		23.89			44.90		
	EM5-02F-P0621		3.01	2.33		9.34			17.56		
	EM5-02B-P0621		6.01	4.65		18.63			35.01		
	EM5-03F-P0621		3.57	2.76		11.06			20.78		
	EM5-03B-P0621		3.90	3.02		12.09			22.72		
	EM5-04F-P0621		3.36	2.60		10.42			19.58		
	EM5-04B-P0621		4.27	3.31		13.24			24.88		

[a] Calculated using Equation 3.

[b] Calculated using Equation 2 with a reference collection rate (S) of 23.5 cc/min.

Table C.5. Data from Wind Velocity Tests Using Protective Cups[a]

Wind Speed (cm/sec)	Sample ID	Exposure Time (hours)	Ion Chromatography Results		True Ozone (ppb)	Collection Rate (cc/min)			Concentration from Passive Monitor[b]		
			Nitrate (µg)	Ozone (µg)		S_E[a]	Mean	SD	Ozone (ppb)	Mean	SD
2	LAB2-01-P0731	23.00	2.11	1.63	67	9.04	8.69	0.49	28.65	35.15	13.22
	LAB2-02-P0731		1.94	1.50		8.35			26.44		
	LAB2-03-P0731		3.70	2.87		15.89			50.36		
15	LAB1-01-P0723	23.00	4.10	3.17	69	17.06	16.60	0.67	55.78	54.27	2.19
	LAB1-02-P0723		4.06	3.15		16.91			55.28		
	LAB1-03-P0723		3.80	2.94		15.83			51.76		
28	LAB1-01-P0724	23.00	4.54	3.51	63	20.44	19.52	0.92	61.77	58.99	2.78
	LAB1-02-P0724		4.34	3.36		19.53			59.00		
	LAB1-03-P0724		4.13	3.20		18.60			56.20		
36	SC05-01-P0725	23.00	4.59	3.55	64	20.52	19.81	0.79	62.45	60.28	2.39
	SC05-02-P0725		4.46	3.45		19.94			60.67		
	SC05-03-P0725		4.24	3.28		18.97			57.72		
56	LAB2-01-P0726	65.67	11.59	8.97	54	21.38	20.72	1.00	55.25	53.54	2.59
	LAB2-02-P0726		11.50	8.91		21.21			54.82		
	LAB2-03-P0726		10.61	8.21		19.57			50.56		
71	LAB2-01-P0729	24.00	6.98	5.40	93	20.60	20.59	0.41	90.99	90.94	1.82
	LAB2-02-P0729		7.11	5.51		21.00			92.74		
	LAB2-03-P0729		6.83	5.29		20.17			89.10		
173	LAB2-01-P0730	24.25	6.05	4.68	79	20.67	20.94	0.25	78.03	79.07	0.95
	LAB2-02-P0730		6.19	4.79		21.16			79.90		
	LAB2-03-P0730		6.14	4.76		21.00			79.29		
284	LAB1-01-P0708	47.50	8.15	6.31	44	25.63	24.61	0.94	53.70	51.57	1.97
	LAB1-01-P0708		7.77	6.01		24.42			51.17		
	LAB1-03-P0708		7.56	5.85		23.78			49.82		

[a] Calculated using Equation 3.

[b] Calculated using Equation 2 with a reference collection rate (S) of 21.0 cc/min.

Table C.6. Temperature Test Data

Temperature[a] (°C)	Sample ID	Exposure Time (hours)	Ion Chromatography Results		True Ozone (ppb)	Collection Rate (cc/min)			Concentration from Passive Monitor		
			Nitrate (µg)	Ozone (µg)		S_E[b]	Mean	SD	Ozone (ppb)[c]	Mean	SD
20	EM5-T01-P0323	37.55	5.99	4.64	53	19.79	19.45	0.58	53.78	52.87	1.58
	EM5-T02-P0323		6.08	4.71		20.08			54.57		
	EM5-T03-P0323		5.79	4.48		19.12			51.95		
	EM5-T04-P0323		5.70	4.41		18.82			51.16		
40	EM5-T05-P0329	34.90	4.35	3.37	41	19.97	19.12	1.13	41.99	40.20	2.38
	EM5-T06-P0329		4.40	3.41		20.22			42.52		
	EM5-T07-P0329		3.94	3.05		18.11			38.08		
	EM5-T08-P0329		3.96	3.06		18.18			38.22		
0	EM5-T09-P0401	35.73	5.00	3.87	48	19.16	19.93	0.85	47.17	49.06	2.10
	EM5-T10-P0401		5.49	4.25		21.06			51.84		
	EM5-T11-P0401		5.06	3.92		19.39			47.73		
	EM5-T12-P0401		5.25	4.06		20.12			49.52		

[a] Relative humidity was 10% to 25%.

[b] Calculated using Equation 3.

[c] Calculated using Equation 2 with a reference collection rate (S) of 19.5 ± 4.3 cc/min.

Table C.7. Data from Relative Humidity Tests Performed in the Wind Tunnel

Relative Humidity (%)	Sample ID	Exposure Time (hours)	Ion Chromatography Results		True Ozone (ppb)	Collection Rate (cc/min)			Concentration from Passive Monitor[b]		
			Nitrate (μg)	Ozone (μg)		S_E[a]	Mean	SD	Ozone (ppb)	Mean	SD
11	LAB2-01-P0813	46.00	5.30	4.11	36	20.87	21.51	0.56	36.26	37.37	0.97
	LAB2-02-P0813		5.56	4.30		21.88			38.01		
	LAB2-03-P0813		5.54	4.29		21.79			37.85		
18	LAB2-01-P0904	45.00	8.22	6.37	57	21.16	20.79	0.50	57.46	56.47	1.36
	LAB2-02-P0904		8.16	6.32		21.00			57.02		
	LAB2-03-P0904		7.86	6.08		20.22			54.92		
48	LAB2-01-P0730	24.25	6.05	4.68	79	20.67	20.94	0.25	78.40	79.45	0.96
	LAB2-02-P0730		6.19	4.79		21.16			80.28		
	LAB2-03-P0730		6.14	4.76		21.00			79.67		
73	LAB2-01-P0912	23.00	7.05	5.46	92	21.82	20.94	0.76	96.45	92.57	3.37
	LAB2-02-P0912		6.64	5.14		20.54			90.77		
	LAB2-03-P0912		6.62	5.12		20.47			90.48		
77	LAB2-01-P0910	38.00	5.90	4.57	50	20.23	20.27	0.09	48.85	48.94	0.22
	LAB2-02-P0910		5.89	4.56		20.20			48.77		
	LAB2-03-P0910		5.94	4.60		20.37			49.18		

[a] Calculated using Equation 3.

[b] Calculated using Equation 2 with a reference collection rate (S) of 20.9 cc/min.

Table C.8. Data from the Peroxyacetyl Nitrate Tests

Sample ID	Exposure Time (hours)	Ion Chromatography Results		PAN (ppb)	True Ozone (ppb)	Collection Rate (cc/min)		
		Nitrate (μg)	Ozone (μg)			S_E[a]	Mean	SD
EM5–03P-P0319	47.00	2.99	2.32	19.90	41	10.20	9.76	0.27
EM5–19P-P0319		2.84	2.20			9.68		
EM5–24P-P0319		2.79	2.16			9.52		
EM5–41P-P0319		2.88	2.23			9.81		
EM5–45P-P0319		2.82	2.18			9.61		
EM5–01P-P0319	51.00	0.41	0.32	19.30	0	ND[b]		
EM5–06P-P0319		0.47	0.36					
EM5–07P-P0319		0.39	0.30					
EM5–25P-P0319		0.44	0.34					
EM5–39P-P0319		0.55	0.42					
EM5–10P-P0319	47.65	1.37	1.06	0.06	41	4.63	4.40	0.23
EM5–21P-P0319		1.23	0.95			4.14		
EM5–28P-P0319		1.29	1.00			4.35		
EM5–37P-P0319		1.26	0.98			4.24		
EM5–43P-P0319		1.38	1.07			4.64		
EM5–04P-P0319	48.07	4.49	3.48	10.50	41	14.98	15.04	0.53
EM5–09P-P0319		4.25	3.29			14.19		
EM5–11P-P0319		4.68	3.63			15.62		
EM5–22P-P0319		4.56	3.53			15.21		
EM5–31P-P0319		4.56	3.53			15.20		
EM5–05P-P0319	47.00	6.54	5.06	18.20	80	11.44	11.36	0.28
EM5–26P-P0319		6.22	4.82			10.87		
EM5–29P-P0319		6.60	5.11			11.54		
EM5–35P-P0319		6.60	5.11			11.53		
EM5–36P-P0319		6.54	5.06			11.43		

[a] Calculated using Equation 3.

[b] ND = not determined.

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Susan E. Froehlich provided engineering support in this study and designed and performed experimental trials for samplers. She was also the project manager for personal and fixed location monitoring studies. Ms. Froehlich received her M.S. in mechanical engineering from the University of Massachusetts.

PUBLICATIONS RESULTING FROM THIS RESEARCH

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ABBREVIATIONS

EMAP	Environmental Monitoring and Assessment Program
EPA	U.S. Environmental Protection Agency
HSPH	Harvard School of Public Health
NAAQS	National Ambient Air Quality Standard
NO_2	nitrogen dioxide
NO_2^-	nitrite ion
NO_3^-	nitrate ion
O_3	ozone
PAN	peroxyacetyl nitrate
ppb	parts per billion (in air)
ppm	parts per million (μg/mL in solution)
SD	standard deviation
standard ft/min	feet per minute under standard conditions of 1 atm and 25°C
UV	ultraviolet

A Passive Ozone Sampler Based on a Reaction with Iodide

Yukio Yanagisawa

ABSTRACT

A new passive sampler for ozone and its simple analytical system have been developed. Because it is small and sensitive, the sampler can be used for determining personal exposures to ozone and oxidants and for multilocation measurements. The sampler consists of an electrode, a spacer, and several layers of membrane filters and Teflon meshes. The electrode is a carbon paper disk coated with nylon-6 polymer and potassium iodide. The membrane filters are used to remove interferences. A sampling rate of ozone is controlled by the spacer and Teflon meshes. Iodine is liberated by an oxidation reaction of potassium iodide with ozone. The iodine is stabilized by forming a charge transfer complex with nylon-6 and is accumulated in the nylon-6 layer. The amount of iodine, which is proportional to the level of ozone exposure, is quantified by constant current coulometry. The discharge time of a galvanic battery is measured using the electrode as a positive electrode and a zinc plate as a counter electrode. A time-weighted average concentration of ozone is derived from the discharge time after exposing the electrode to ozone. The effects of various environmental conditions on the sampler's performance were investigated. The results indicated that the sampler showed a linear response to ozone exposure up to 1,450 parts per billion for every hour of use (ppb•hour)*. The minimum detectable exposure was about 400 ppb•hour. The effects of surface wind velocity, temperature, and humidity were small. However, a relative humidity below 20% resulted in an underestimation of the ozone concentration. Because the electrode requires no pretreatment and the analytical method is very simple, this method is suitable for large-scale studies of personal exposures to ozone and oxidants using multilocation measurements.

INTRODUCTION

Ambient air pollution from ozone (O_3) is a serious environmental problem in industrialized countries because of its adverse health effects. The ambient air quality standard for O_3 in the United States is 120 parts per billion (ppb) for a one-hour average. In Japan, the standard has been set at 60 ppb for a one-hour average, with 120 ppb for a one-hour average set as a warning level. These standards are often exceeded, particularly during the summer, when the O_3 formation rate is high due to strong sunlight. Despite these standards, peak ambient O_3 concentrations are still high enough to cause transient changes in lung function, respiratory symptoms, and airway inflammation in healthy people (reviewed by Lippman 1989). These transient effects are more closely related to cumulative daily exposure than one-hour peak concentrations of O_3. The effect of long-term chronic exposures to O_3 is not defined yet, but current levels are sufficient to cause premature aging of the lung. Even in the rural areas of Western Massachusetts, for example, hourly O_3 concentrations exceeded 100 ppb for more than six hours a day, whereas nitric oxide (NO) and nitrogen dioxide (NO_2) concentrations were below 20 ppb (Lioy and Dybar 1989). Personal exposure levels or doses of O_3, however, have not been clarified yet due to the lack of a suitable personal sampler.

Several types of analyzers are commercially available for measuring O_3 levels in air (Rice 1986). One of these is a photometer that measures ultraviolet absorption of O_3 at 250 to 260 nm. The second is a chemiluminescence detector that measures light produced by a reaction between O_3 and ethylene. The chemiluminescence method is specific to O_3 and suitable for ambient air monitoring. An analyzer based on amperometry is also available. With the neutral buffered potassium iodide (NBKI) method, a wet chemical is used to measure O_3 and oxidant levels in ambient air (Saltzman

* A list of abbreviations appears at the end of the Investigator's Report for your reference.

This Investigator's Report is one part of the Health Effects Institute Research Report Number 63, which also includes an Investigators' Report by Hackney and associates, an Investigators' Report by Koutrakis and colleagues, a Commentary by the Health Review Committee, and an HEI Statement about the research projects. Correspondence concerning the Investigator's Report by Dr. Yukio Yanagisawa may be addressed to Research Institute of Innovative Technology for the Earth, Headquarter Laboratories, 9-2, Kizugawadai, Kizucho, Sorakugan, Kyoto 619-02, Japan.

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and Gilbert 1959). The oxidants are defined as air pollutants that can oxidize the potassium iodide (KI) solution and liberate iodine (I_2). With the NBKI method, O_3 and oxidants in air are introduced into the neutral buffered KI solution and liberate I_2. The amount of I_2 is determined by measuring the ultraviolet absorbance of the solution at 365 nm.

In general, a passive sampler is simple in structure, reliable, and can be used easily by subjects, including children and the elderly, without any particular instruction. Passive samplers have become an important tool in air pollution studies. They can be used to measure personal exposures and multipoint stationary levels, thereby reliably determining temporal and spatial variabilities of air pollution. Monn and Hangartner (1990) used a passive sampler for O_3 that employed the reaction of O_3 and 1,2-dipyridylethylene, and spectrophotometric determination. Although the sampler they used is simple and specific to O_3, it is not applicable to personal monitoring because it requires shielding from ultraviolet radiation and wind.

In another study, investigators attempted to apply the NBKI method to the passive sampler using a filter paper impregnated with the NBKI solution (Suzuki et al. 1983). After exposing the filter paper to air, they extracted the I_2 on the filter paper and titrated it with sodium thiosulfate. This passive sampler suffered a loss of I_2 due to its sublimation during and after the sampling, and the result was low sensitivity. When applying the NBKI method to the personal exposure measurements, the vapor pressure of I_2 must be lowered to prevent its loss.

The sublimation of I_2 observed with the NBKI filter paper method can be avoided by absorbing I_2 on nylon-6, which is known to form a charge transfer complex (CTC) with I_2 (Hishinuma and Yamamoto 1984). This interaction can lower the vapor pressure of I_2. The liberation of I_2 followed by the formation of CTC can be regarded as the charge process of a positive electrode of a zinc|zinc iodide|I_2–nylon-6 battery (Yamamoto et al. 1985). This expression indicates that the battery cell consists of a zinc negative electrode, a zinc iodide electrolyte, and an I_2–nylon-6 positive electrode. Because CTC is an active material of the positive electrode of the zinc|zinc iodide|I_2–nylon-6 battery, the amount of I_2 absorbed by nylon-6, and therefore, the amount of O_3 and oxidant exposures, can be determined simply by discharging the battery.

Based upon this principle, we have developed a passive O_3 and oxidant sampler. The basic processes of O_3 and oxidant sampling consist of three steps:

1. Ozone diffuses from bulk air to the electrode surface, made from a carbon fiber disk coated with nylon-6 and KI, by molecular diffusion;
2. A chemical reaction occurs between O_3 and KI at the surface of the KI layer, where I_2 is liberated; and
3. The liberated I_2 is absorbed by the nylon-6 layer by forming a CTC.

A galvanic cell is made using the exposed electrode as a positive electrode and a zinc plate as a negative electrode. The CTC is electrochemically reduced by discharging the galvanic cell. Because the amount of CTC is proportional to the O_3 and oxidant exposures, the exposures can be determined by measuring the discharge time of the battery at a constant current.

The sampling and quantification processes consist of forming the CTC by the oxidation reaction and measuring the amount of CTC by discharging the galvanic cell at a constant current. We call this measuring system the "ozone battery."

The basic performances of the O_3 and oxidant electrode has been reported previously (Hishinuma et al. 1989). In the current project, we have developed an O_3 and oxidant sampler with an electrode and diffusion barrier to be used for actual O_3 exposure measurements. Excellent linear relationships were obtained between O_3 exposures and the discharge time. In addition to the good linear relationship, the major advantage of this method is its very simple analytical procedure; no preliminary treatment is required for sample analysis. We have conducted very intensive laboratory experiments to determine compositions, concentrations, amounts, and times for the ozone battery. Data presented here all were determined from laboratory experiments. To avoid redundancy, I describe the final configuration, composition, and operating conditions in the main text, and the selection processes in the Appendices.

EXPERIMENTAL METHODS

ELECTRODE PREPARATION

A carbon fiber disk (Kureha KG-200, 3-cm diameter; see Appendix A) was washed with 2 N hydrochloric acid, water, and methanol (MeOH), and dried under a vacuum using a rotary vacuum pump (Figure 1). Calcium chloride dihydrate ($CaCl_2 \cdot 2H_2O$; Aldrich Chemical Co., Aldrich, WI) was dehydrated by heating at 200°C under a vacuum for two hours (see Appendix B). A saturated solution of $CaCl_2$ was prepared by mixing 100 g of the dehydrated $CaCl_2$ with 200 mL MeOH. Eighty milligrams of nylon-6 (Aldrich) was dissolved in 8 mL of the $CaCl_2$-saturated MeOH solution and diluted with 5 mL MeOH. An aliquot of 200 μL of the nylon-6 solution was applied to the carbon disk using a micropipet. The MeOH was evaporated under a vacuum until

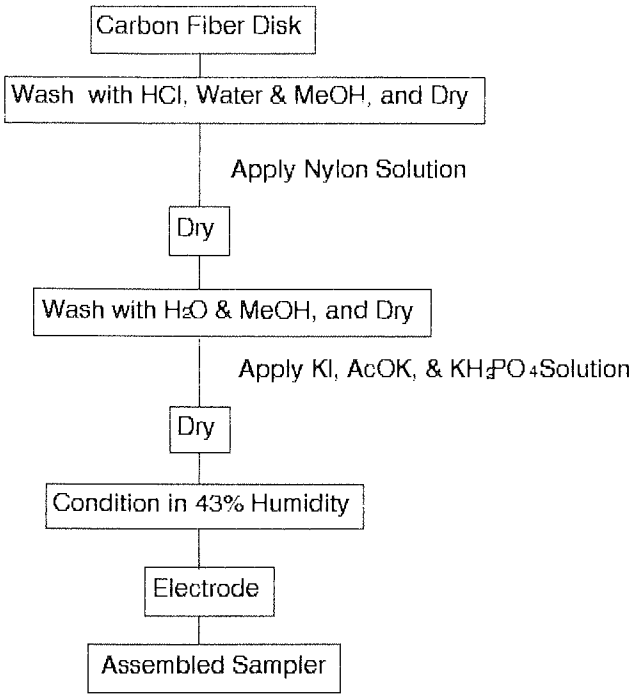

Figure 1. Procedures for electrode preparation.

$CaCl_2$ crystals became visible on the surface of the disk (approximately two hours). The crystallized $CaCl_2$ was washed with water and then with MeOH. After drying, the disk was coated with 150 µL of a mixed solution of 0.2 N KI, 0.2 N potassium acetate (AcOK), and 0.07 N potassium phosphate dibasic (KH_2PO_4) in MeOH and water (1:2 v:v). The disks, coated with the mixed solution, were dried under a vacuum. The prepared electrode was conditioned over a potassium carbonate–saturated solution (at 43% relative humidity) and stored in a sealed container for one day to absorb the water.

TEST SAMPLE

Test samples used for determining the optimal operating conditions of the coulometry and for storage tests were prepared by impregnating the electrodes with a dibenzoylperoxide ether solution, which caused many electrodes to have nearly identical discharge times. Iodine was liberated by the oxidation reaction of dibenzoylperoxide, instead of O_3.

POTASSIUM PERMANGANATE FILTER

A glass fiber filter impregnated with potassium permanganate ($KMnO_4$) (Aldrich) was used to remove sulfur dioxide (SO_2) interference. A glass fiber filter (47 mm, Whatman GF/C) was impregnated with 250 µL of a 0.5% aqueous solution of $KMnO_4$, using a micropipet. The filter was dried under a vacuum for two hours.

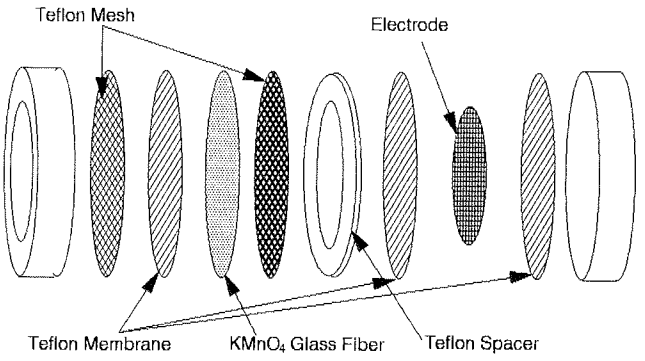

Figure 2. Sampler assembly.

SAMPLER ASSEMBLY

A polystyrene case (50-mm o.d. and 10-mm thickness; Petri dish No. 7232, Gelman Sciences, Ann Arbor, MI) was used as a case for the sampler (Figure 2). An opening of 31 mm in diameter was made on the cover. At the bottom of the case, a Teflon membrane (Mitex, pore size 5 µm, Millipore) and the conditioned electrode were placed, with the following filter layers on top of them: a Teflon membrane filter, a Teflon spacer, a coarse Teflon mesh (1,000 µm, Spectra/Mesh), the glass fiber filter containing $KMnO_4$, a Teflon membrane filter, and a fine Teflon mesh (macro filter, 150 µm, Spectra/Mesh). The cover was taped to the body of the case.

EXPOSURE EXPERIMENT

An exposure chamber was constructed using a No. 4 Pyrex flask with a lid having three holes for inserting wire, tubing, and a motor shaft (Aldrich) (Figure 3). The glass chamber was placed in an incubator (model 815, Precision) to control the temperature. Four samplers were mounted on a turntable rotated by a stirrer motor, thereby evenly exposing them to a test gas at various temperatures and relative humidity conditions. The samplers were mounted to stand on edge and perpendicular to the circumferential movement. The average wind velocity on the surface of the sampler was calculated to be 0.1 m/sec. Test air containing known concentrations of O_3, NO_2, NO, SO_2, or a mixture of O_3 and each other gas was fed to the exposure chamber at a flow rate of 2.8 L/min. Ozone was generated with an ozone calibrator (model 49PS, Thermo Electron Instru-

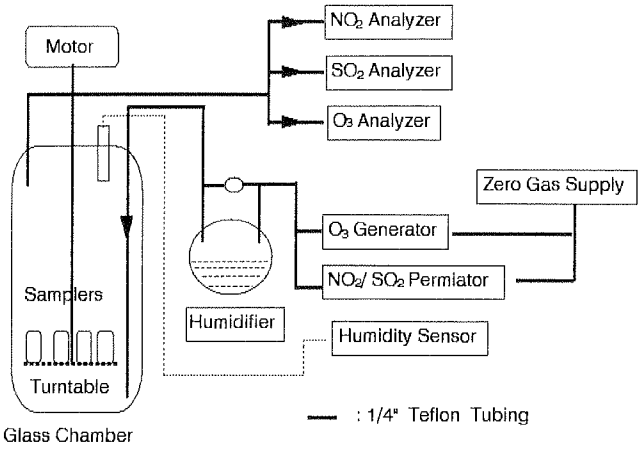

Figure 3. Exposure system (glass chamber).

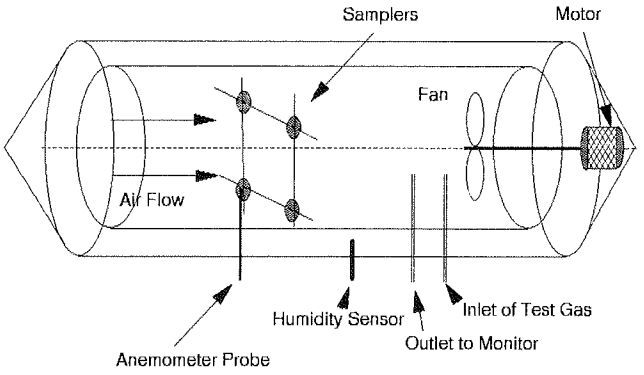

Figure 4. Wind tunnel.

ments), and NO_2 and SO_2 with a dynacalibrator (model 340, Metronics). A certified standard of NO in nitrogen (9 parts per million) (Medical-Technical Gas) was diluted with air and mixed with the test air. A fraction of the test air was passed over a distilled water surface contained in a humidifier flask to control relative humidity. Concentrations of O_3, NO_2, NO, and SO_2 in the exposure chamber effluent and humidity inside the chamber were continuously monitored with an ozone analyzer (model 8410E, Monitor Lab), a nitrogen oxides analyzer (model 14B/E, Thermo Electron Instruments), an SO_2 pulsed fluorescence analyzer (model 43, Thermo Electron Instruments), and a humidity sensor (HMP 113A, Vaisala).

The effects of temperature and humidity were examined using this system. The effect of temperature was examined at 50% relative humidity. The effect of humidity was examined at 25°C. Exposure periods were two hours.

WIND TUNNEL

A wind tunnel exposure system was used to evaluate wind effects on sampler performance and to examine NO_2 interference (Figure 4). The wind tunnel was made from two acrylic cylinders: an inner cylinder (21.9-cm i.d., 152-cm long) and an outer cylinder (29.5-cm i.d., 188-cm long). Test air was generated and monitored with the same instruments used for the glass chamber experiment. The test air introduced into the wind tunnel was circulated between the two cylinders with a fan to maintain the wind velocity at a specific level. The test air was drawn by the monitoring instruments from the center of the inner cylinder, where the test gas concentrations were confirmed to be the same as the exposure levels. Four samplers were placed 5 cm from the center of the inner tube, parallel with the wind direction. Wind speed at the surface of the sampler was monitored by a hot wire anemometer (model 415, Kurz). The temperature in the tunnel was not controlled and ranged from 25°C to 28°C. Humidity was controlled and ranged from 40% to 55%.

The effects of the velocity at the sampler face and NO_2 interference were examined using this system. To examine the face velocity effect, we exposed samplers to 200 ppb O_3 at the face velocity of 0.1, 0.3, or 1 m/sec for three to four hours. To examine NO_2 interference, we exposed samplers to NO_2, O_3, or a 1:1 mixture of NO_2 and O_3 for six hours. The face velocity was set at 0.3 m/sec.

STORAGE OF THE SAMPLER

It is not always possible to analyze samples immediately after sampling. Thus, it is important to ensure that storing the electrode after sampling does not degrade it. The stability of the CTC during a storage period was tested using the test samples and the exposed samples. The stability was evaluated by a recovery efficiency, which was a ratio of the discharge time after storage to the initial discharge time. Presence of the $KMnO_4$ filter, volume of a storage container, and temperature were considered potential factors affecting the stability of CTC during the storage period. As with the sampler, the electrode and filters were layered and sealed in polystyrene culture dishes with aluminum foil to shield them from light. They were stored under various combinations of these potentially influential factors. These included the presence and absence of the $KMnO_4$ filter, using 13 mL or 3 mL of the storage container volume, and using various storage temperatures.

COULOMETRIC DETERMINATION

A galvanic cell for the discharge was made of 200 mL of 0.1 N ammonium chloride electrolyte, a positive electrode of the O_3 electrode, and a counter electrode of a zinc plate

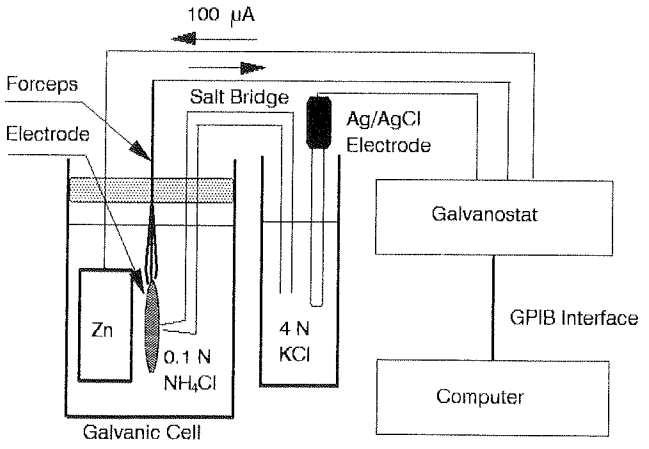

Figure 5. Discharge measurement system.

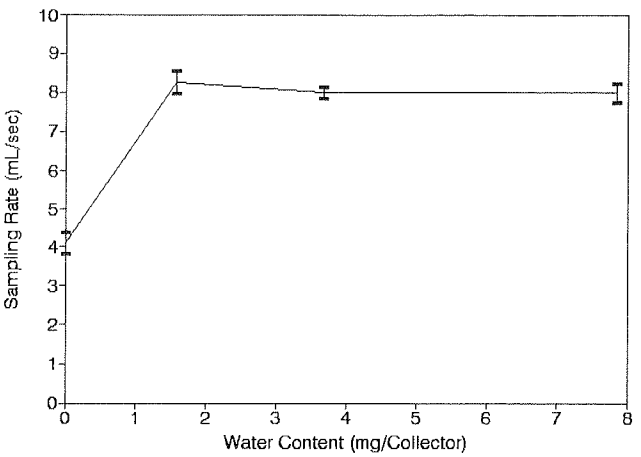

Figure 6. Water content and sampling rate. Electrodes with different water contents were exposed to 190 to 274 ppb of O_3 for 1.5 hours in the glass chamber without a diffusion barrier to O_3. Water content was controlled by adding $CaCl_2$. The temperature of the test gas was 25°C; humidity ranged from 46% to 48%. Each data point shows the mean ± SD of three determinations.

(0.025 cm × 7 cm × 10 cm) (Aldrich) (Figure 5). A 400-mL beaker was used to contain the electrolyte and electrodes. The O_3 electrode was clamped with a pair of platinum-tipped forceps. The cell was covered with polystyrene foam to prevent evaporation of the electrolyte solution. The electrode potential of the O_3 electrode was monitored via a salt bridge from the ammonium chloride solution into a 4 N KCl solution, where a silver/silver chloride reference electrode (Z11; 308–5, Aldrich), which could provide a standard electrode potential, was inserted and connected to the galvanostat. The discharge time was counted while the electrode potential was above −0.015 volts, compared with the reference electrode (see Figure 7 in the Results section).

A sequence of the discharge time measurement was automated by using a personal computer with a general purpose interface bus (see Appendix C). Once a sample identification code was entered, the computer was ready for the data acquisition. With the electrode immersed in the electrolyte, a microswitch, which triggered data acquisition, was pressed by an arm holding the forceps. The electrode potential and the elapsed time information were monitored by the computer every one second until the electrode potential reached −0.15 volts. After the discharge was completed, the electrode potential and discharge time data were entered onto a disk file.

In order to determine optimal conditions of the discharge time measurement, the effects of dissolved oxygen in the electrolyte and repeatability of the discharge were tested. The effects of dissolved oxygen in the electrolyte were tested by comparing the discharge time obtained from oxygen-free electrolyte with that from the air-saturated electrolyte. The oxygen-free electrolyte was prepared by purging it with nitrogen gas and the air-saturated electrolyte was produced by shaking the electrolyte vigorously.

RESULTS AND DISCUSSION

COMPOSITION OF THE ELECTRODE

The carbon disk was coated with nylon-6, KI, KH_2PO_4, and AcOK. Each component functions as follows: KI is a reactant of O_3; nylon-6 traps I_2 and is the interface between KI and the carbon fiber disk; a mixture of KH_2PO_4 and AcOK can function as a buffer and humectant.

Because of its hydrophobic nature, the carbon fiber could not be coated with KI without the nylon layer. When the CTC was formed by exposing the electrode to O_3, the nylon layer turned yellow, whereas the I_2 in the KI solution turned a dark brown. Thus, although no spectrum was measured, the formation of CTC was visually evident by its yellow color.

As shown in Figure 6, when the electrode was exposed to the test air with a 50% relative humidity, the O_3 sampling rate was dependent on the electrode's water content. The water content for the electrode, which was not treated with any humectant, was zero; the sampling rate was less than that of the electrode coated with a humectant. This suggests that a minimum amount of water was required for the reaction of O_3 with KI. At first, the electrode's water content was adjusted by adding $CaCl_2$, which is a well known humectant and was used in the electrode preparation. When the water content of the electrode was higher than 1.7 mg, the sampling rate of O_3 was independent of the water content. The reaction between O_3 and KI in a neutral solution is expressed as follows (Sullivan et al. 1986):

$$O_3 + 2I^- + H_2O \longrightarrow I_2 + O_2 + 2(OH)^-. \quad (1)$$

This shows that the reaction requires water, the stoichiometry between the O_3 and I_2 is unity, and the pH of the solution increases as the reaction proceeds.

In an alkaline solution, the stoichiometry becomes less than unity, due to partial hypoiodite $[(IO)^-]$ and iodate $[(IO_3)^-]$ formation (Sullivan et al. 1986):

$$3O_3 + I^- \longrightarrow 3O_2 + (IO_3)^- \quad (2)$$

$$O_3 + I_2 + 2(OH)^- \longrightarrow O_2 + 2(IO)^- + H_2O. \quad (3)$$

Therefore, constancy of the pH on the surface of the electrode for the entire sampling period is important for the reaction's consistent stoichiometry. To maintain a constant surface pH level and water content for the electrode, AcOK and KH_2PO_4 (pH 6.4) were used as a humectant and buffer. The relative humidities over the saturated solutions of AcOK and $CaCl_2$ are 20% and 32%, respectively, at 20°C (Weast 1990). These percentages indicate that AcOK acts as a humectant for a wider range of humidity than $CaCl_2$. The electrode contained 1.7 to 2.0 mg of water when the AcOK was used as a humectant. The sampling rate was consistent for exposures ranging from 400 to 1,450 ppb•hour (see Figure 8 in the Response to Ozone Exposure section and Appendix D).

COULOMETRY

Figure 7 shows discharge curves for the electrodes exposed to different amounts of O_3. The electrode potential is a function of a ratio of I_2:I^- ion and becomes higher when the ratio of I_2:I^- increases. For the electrode with the shortest discharge time, the electrode potential decreased gradually from the beginning of the discharge and then decreased quickly when its potential reached approximately 0 volts when measured against the electrode potential of the reference electrode. The rapid decrease of the electrode potential suggests that the residue of I_2 or CTC in the electrode was very small. The curve at approximately 0 volts did not have any shoulder, indicating that active materials for the discharge might be only I_2 and CTC. For the electrode with the longest discharge time, the electrode potential increased as a result of the higher concentration of I_2 on the surface of the electrode. For the highly exposed electrode, the concentration gradient of I_2 is so sharp from an air-monitor interface to the carbon fiber disk that the I_2 flux to the carbon disk surface is larger than the production rate of I^- by electrochemical reduction of I_2. Hence, the electrode potential initially increases for the electrodes with long discharge times. The discharge curve at 0 volts was similar to that of the electrode with the shortest discharge time. A blank electrode, which was not exposed to O_3, had a discharge time of less than one second.

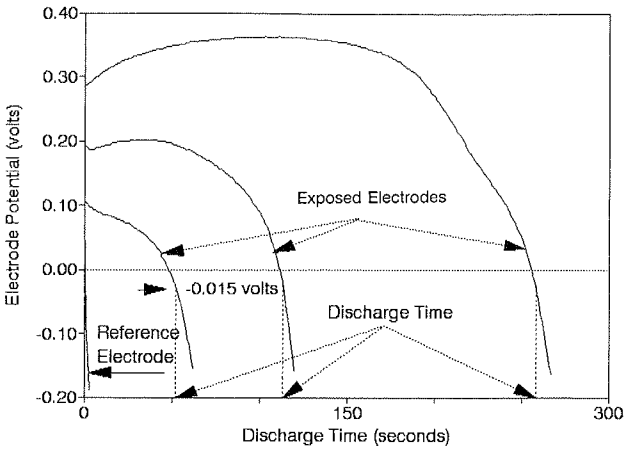

Figure 7. Discharge curves.

Dissolved oxygen in the electrolyte had no effect on the discharge time measurement. The average discharge time and standard deviation of the test samples (n = 5) in the oxygen-free and air-saturated electrolyte were 343.9 ± 2.9 seconds and 347.6 ± 4.7 seconds, respectively. When nitrogen gas was introduced to the electrolyte, the discharge time decreased by 94.7 seconds for the oxygen-free electrolyte and by 98.4 seconds for the air-saturated electrolyte. This suggests that disturbing the electrolyte may increase the dissolution of I_2 from the electrode surface, thereby shortening the discharge time. To avoid the excessive I_2 loss caused by this disturbance, no gases were introduced into the electrolyte. In addition, the discharge cell was covered with a lid to prevent convection flow due to evaporation of the electrolyte. The discharge was started immediately after immersion of the electrode into the electrolyte.

The repeatability of the discharge measurement was good. The coefficient of variation was 4% for 28 test sample measurements.

RESPONSE TO OZONE EXPOSURE

A linear relationship was obtained between the discharge time and the level of the O_3 exposure up to 1,450 ppb•hour (Figure 8). In these experiments, samplers were exposed to 30 to 300 ppb O_3 for six hours in the wind tunnel. Face velocity was 0.3 m/sec, and temperature and relative humidity ranged from 25°C to 28°C and 40% to 55%, respectively. Each data point shows the mean ± SD of four determinations. At 1,800 ppb•hour of exposure, a decrease in sensitivity was observed. This may have been due to the saturation

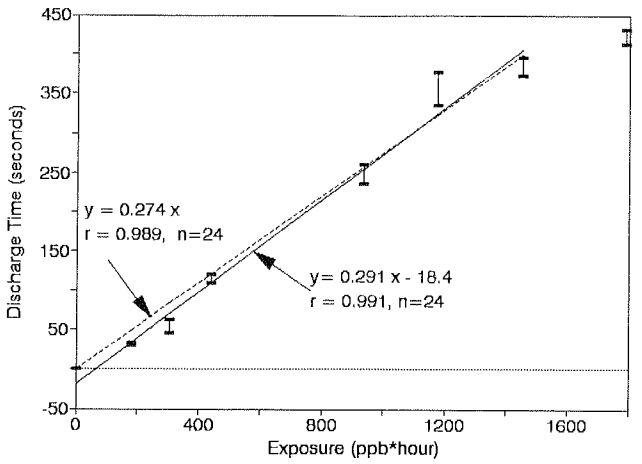

Figure 8. Calibration curve. Samplers were exposed to 30 to 300 ppb O_3 for six hours in the wind tunnel. Face velocity was 0.3 m/sec. The temperature of the test gas ranged from 25°C to 28°C; humidity ranged from 40% to 55%. Each data point shows the mean ± SD of four determinations. Data at 1,800 ppb•hour were excluded from the regression because of saturation of the nylon electrode.

of CTC, because the amount of KI present was sufficient to react with the amount of absorbed O_3. The CTC formation may become saturated at the surface of the gas-electrode interface.

Generally, any kind of sensor response is basically a sigmoidal curve. The response is lower than the expected linear line at the low end because of the sensor's inertia, and lower at the upper end because of saturation. If a dynamic range or linear region is wide enough, the lower and upper nonlinear regions are negligible. Unfortunately, however, the dynamic region of the monitor is relatively narrow so that we can see the sigmoidal curve. The monitor can be used in the linear region because the nonlinearity at the low end is always included for the linear region application.

Forced regression and normal regression lines were drawn on the figure using 24 data points. The data at 1,800 ppb•hour were excluded from the calculation because of the saturation. The slope of a normal regression line was 0.291 (sec/ppb•hour), with a 95% confidence interval of 0.273, 0.310. The slope of a forced regression line was 0.274 (sec/ppb•hour), which was included in the 95% confidence interval of the normal regression slope. A y intercept was statistically significant ($p<0.03$); the 95% confidence interval of the y intercept was −34.1, −1.8. The correlation coefficient (r) was 0.989 for the forced regression and 0.991 for the normal one.

A sampling rate was defined as

$$\text{Sampling rate (mL/sec)} = \frac{\text{Sampled amount of } O_3 \text{ (mol)}}{\text{Concentration (mol/mL)} \times \text{Time (sec)}}. \quad (4)$$

The sampled amount of O_3 was derived assuming 1:1 stoichiometry of the O_3 and I_2, as shown in equation 1:

$$\text{Sampled amount (mol)} = \frac{\text{Discharge time (sec)} \times \text{Current (A)}}{\text{F (coulomb/mol)}} \quad (5)$$

where F is the Faraday constant. By defining the current as 100 μA and the Faraday constant as 96,400 coulomb/mol, and converting the units of the denominator from mol/sec/mL to ppb•hour, the sampling rate at 25°C was calculated from the following equation:

$$\text{Sampling rate (mL/sec)} = 7.06 \times \frac{\text{Discharge time (sec)}}{\text{Exposure (ppb•hour)}}. \quad (6)$$

The sampling rates calculated from the slope of the forced and normal regression lines were 1.93 and 2.05 mL/sec, respectively.

The forced regression line was selected as a calibration line, to calculate O_3 exposure from the discharge time (although the y intercept was statistically significant at $p<0.03$ level), because the discharge times of the blanks were very close to zero. The discharge times for O_3 exposures below 400 ppb•hour were shorter than the expected time from the forced regression line. This may have been due to the decomposition of a specific amount of O_3 on the surface of filters used as the diffusion barrier. When the exposures were more than 400 ppb•hour, differences between the two regression lines were less than 10%.

When the sampling rate in Equation 6 is substituted by 1.93 mL/sec, Equation 6 can be rewritten as:

$$\text{Discharge time (sec)} = 0.27 \text{ (sec/ppb•hour)} \times O_3 \text{ Concentration (ppb)} \times \text{Time (hours)}. \quad (7)$$

INTERFERENCES

When the electrodes (with no diffusion barrier) were exposed to test gas containing NO_2 or SO_2, positive or negative interferences for the O_3 sampling were observed. To eliminate the negative interference by SO_2, a glass fiber filter containing $KMnO_4$ was used. After the $KMnO_4$ filter was installed, SO_2 showed practically no interference (Table 1). Sulfur dioxide seemed to be oxidized by $KMnO_4$ and retained in the glass fiber layer. Nitric oxide was expected to have a positive interference because $KMnO_4$ might oxidize NO to NO_2. But NO had no interfering effects.

Although several attempts were made to remove the NO_2 interference without affecting detection of O_3, no appropriate method was found (see Appendix E). In order to evaluate the interference of NO_2, the samplers were exposed to 45 or 95 ppb NO_2 for six hours. The sampling rate of NO_2, assuming that 1 mol NO_2 liberated 1 mol I_2, was 0.54 mL/sec,

Table 1. Response of the Sampler Containing Potassium Permanganate Filter[a]

Gas	Concentration (ppb)	Exposure Duration (hours)	Discharge Time Mean (seconds)	Discharge Time CV (%)	Sampling Rate (mL/sec)
SO_2	100	5	0.4	34	7.06×10^{-3}
NO	70	6	0.2	35	7.06×10^{-3}
O_3	180	4	190	4.8	1.84

[a] Three ozone samplers with $KMnO_4$ filters were exposed to the test gases containing O_3, NO, or SO_2 separately. Temperature was 25°C. Humidity ranged from 46% to 48%.

as shown in Figure 9, which also indicates the O_3 calibration line. The NO_2 sampling rate of 0.54 mL/sec was 28% of the O_3 sampling rate, which was 1.93 mL/sec. If the sensitivity to NO_2 is an additive process for the O_3 sampling, the discharge time for a mixture of O_3 and NO_2 gas should be a weighted sum of each concentration:

$$\text{Discharge time (sec)} = 0.27\ (\text{sec/ppb•hour}) \times [\text{O}_3\ \text{Concentration (ppb)} + 0.28 \times \text{NO}_2\ \text{Concentration (ppb)}] \times \text{Time (hour)}. \quad (8)$$

To confirm this assumption, the samplers were exposed to a mixture of 55 ppb NO_2 and 56 ppb O_3 or to a mixture of 105 ppb NO_2 and 111 ppb O_3 for six hours. In Figure 9, the discharge times of the samplers exposed to the O_3 and NO_2 mixture were plotted along with the samplers exposed to O_3 alone and NO_2 alone. The mean ± SD for each discharge time was 122.2 ± 9.1 seconds for the mixtures of 55 ppb NO_2 and 56 ppb O_3, and 242 ± 7.4 seconds for the mixtures of 105 ppb NO_2 and 111 ppb O_3. The discharge times, calculated with Equation 7, were 140 seconds for the 55-ppb NO_2 and 56-ppb O_3 exposure, and 228 seconds for the 105-ppb NO_2 and 111-ppb O_3 exposures. This good agreement supports the additive assumption. To simulate a typical environmental situation, the samplers were exposed to a mixture of 110 ppb O_3 and 45 ppb NO_2. As expected, the discharge time increased about 10% from the NO_2 interference. There are two possible ways to deal with the NO_2 interference: subtract the NO_2 interference by simultaneously measuring NO_2 concentration, or consider the O_3 concentrations measured by this method as total oxidant concentrations.

EFFECTS OF FACE VELOCITY

As shown in Figure 10, the sampling rates were consistent with the increase in face velocity from 0.1 to 1 m/sec. In our sampler configuration, the diffusion path length of O_3 from the surface of the sampler to the electrode was 4.1 mm. The dependence on wind velocity is small enough that this method can be applied to O_3 monitoring (see Appendix F).

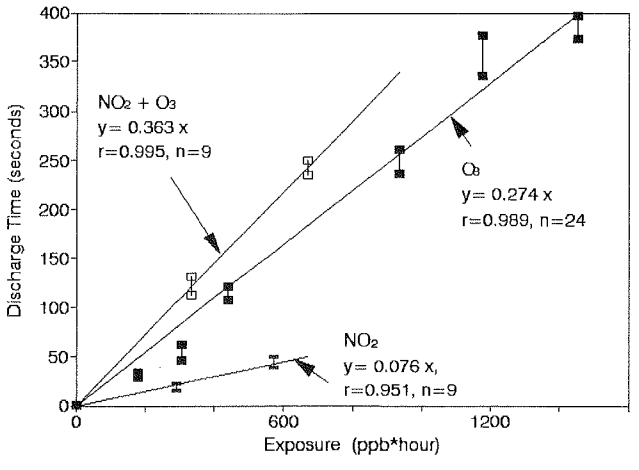

Figure 9. Interference of NO_2. The samplers were exposed to NO_2, O_3 or a 1:1 mixture of NO_2 and O_3 for six hours. The O_3-alone data are the same as that presented in Figure 8. The face velocity was set at 0.3 m/sec. The temperature of the test gas ranged from 25°C to 28°C; humidity ranged from 40% to 55%. Each data point shows the mean ± SD of four determinations.

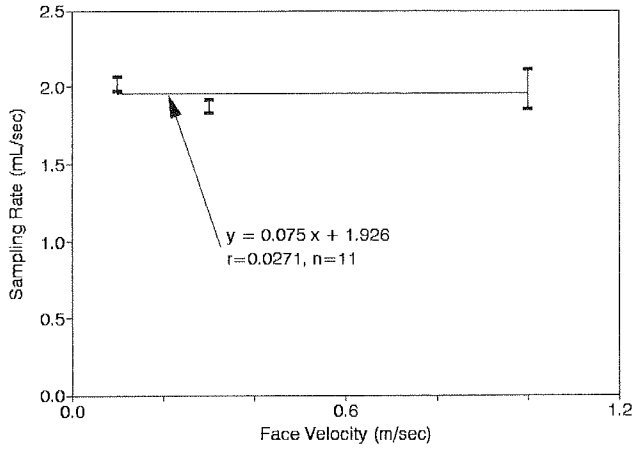

Figure 10. Face velocity and sampling rate. Samplers were exposed to 200 ppb O_3 in the wind tunnel for three to four hours. The temperature of the test gas ranged from 25°C to 28°C; humidity ranged from and 40% to 55%. Each data point shows the mean ± SD of four determinations.

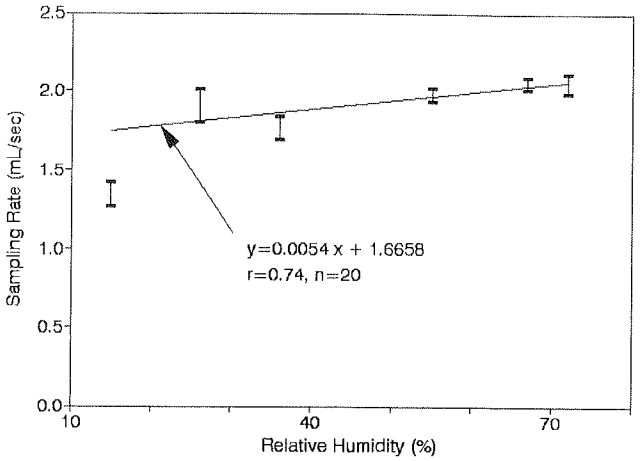

Figure 11. Effects of humidity. The samplers were exposed to 350 ppb O_3 in the glass chamber for two hours. The effect of humidity was examined at 25°C. The wind velocity on the surface of the sampler was calculated to be 0.1 m/sec. Each data point shows the mean ± SD of four determinations. The data at 16% relative humidity were not used to calculate the regression because they are beyond the sampler's application range.

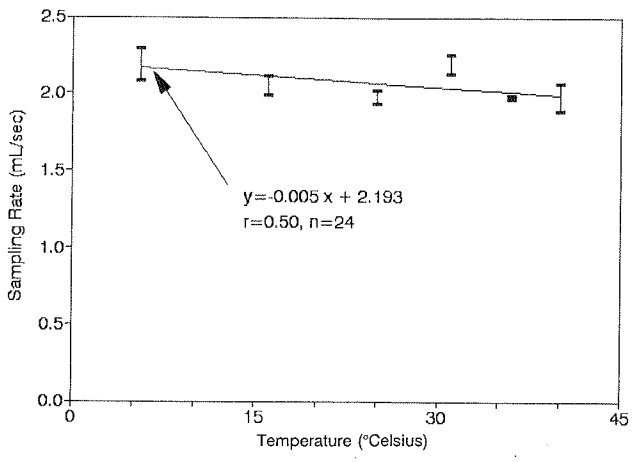

Figure 12. Effects of temperature. The samplers were exposed to 350 ppb O_3 in the glass chamber for two hours. The effect of temperature was examined at 50% relative humidity. The wind velocity on the surface of the sampler was calculated to be 0.1 m/sec. Each data point shows the mean ± SD of four determinations.

EFFECTS OF HUMIDITY

As shown in Figure 11, the sampling rate had a very weak positive correlation with relative humidity over ranges from 25% to 72%. However, the sampling rate was smaller when the relative humidity was 15% than when the relative humidity was higher. This corresponds to the fact that the saturated AcOK water solution releases water at relative humidities below 20% (at 25°C). The decrease of sampling rate at low humidity may be due to a decrease in water content during sampling. When the samplers are used in an area with a relative humidity of less than 20%, O_3 concentrations will be underestimated.

EFFECTS OF TEMPERATURE

As shown in Figure 12, the dependence of the sampling rate on temperature over a range of 5.6°C to 40°C was negligible. When the concentration is expressed by a dimensionless unit such as ppb, the sampling rate is a function of absolute temperature to the power of 0.5. Because the sampling rate is proportional to a molecular diffusion coefficient and gas density, their dependence on absolute temperature is to the power of 1.5 for the diffusion coefficient and the power of −1 for the gas density. The change of the sampling rate between 5.6°C and 40°C is calculated to be about 6% of the sampling rate at 25°C.

EFFECTS OF STORAGE

As shown in Figure 13, the exposed sampler stored in a refrigerator at 4°C for 28 days after the exposure (see Appendix G) retained 90% of the initial amount of I_2. However, when the samples were stored at room temperature, less than 90% of the initial I_2 was recovered after 14 days. The temperature was found to be the major factor for the stability of the CTC during storage, whereas the presence of a $KMnO_4$ filter made no difference in the recovery. The effect of storage was examined using the test samples, as shown in Figure 14. The test sample stored in a large volume dish showed larger losses of I_2. The dependency of the recovery on the volume of the dish and the storage temperature suggest that the loss was due to the slow evaporation of I_2.

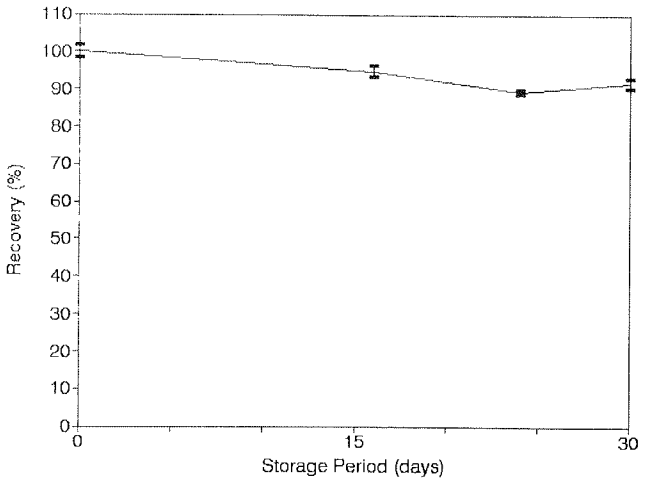

Figure 13. Storage of exposed samples. Twelve samplers were exposed to 350 ppb O_3 for three hours in the glass chamber. Three were analyzed immediately after the exposure. The rest of the samplers with a $KMnO_4$ filter were stored in a refrigerator and analyzed later. Each data point shows the mean ± SD of four determinations.

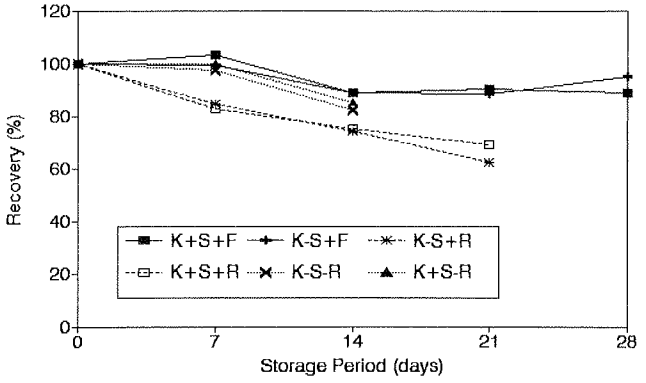

Figure 14. Storage of test samples. The test samples were placed in polystyrene culture dishes, with aluminum foil to shield them from light, and then stored. Storage conditions were a combination of three factors: (1) with (K+) or without (K−) a $KMnO_4$ filter; (2) using 13 mL (S+) or 3 mL (S−) of the storage container volume; and (3) storing samples at room temperature (R) or in a refrigerator (F). The stability of the CTC was evaluated by a recovery efficiency, which was a ratio of the mean discharge time of three test samples after the storage at various conditions to the discharge time immediately after exposure.

Because oxygen in the air was considered as a potential oxidizer for the KI solution, the storage experiments for unexposed blank electrodes were conducted as well (a small amount of I_2 was added to clarify positive or negative changes). No change was observed in the discharge time of the blank electrode, which was stored in a sealed dish containing the $KMnO_4$ filter for 20 days in the refrigerator. Discharge times (mean ± SD) of the blanks before and after the storage were 16.3 ± 5.3 and 13.4 ± 6.2 (n = 3). This indicates that oxygen in the air did not produce I_2 on the electrode.

SUMMARY AND CONCLUSION

A new passive sampler for O_3 has been developed. The basic performances were examined by exposing samplers to the test air. The sampler showed a linear response to O_3 exposure at levels up to 1,450 ppb•hour. The minimum detectable exposure was about 400 ppb•hour. Changes in the sensitivity caused by temperature and humidity were negligible. The effect of face velocity was very small. The sampler showed no response to coexisting SO_2 or NO. The interference of NO_2 was additive and the sampling rate of NO_2 was 28% of the rate for O_3. The exposed samples could be stored in a refrigerator for four weeks.

The sampler is small, light-weight, accurate, and very easy to analyze. Thus, it will be a suitable method for large-scale personal exposure and multilocation measurements.

ACKNOWLEDGMENTS

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APPENDIX A. Selection of Electrode Base

Because the electrode was actually used to determine the O_3 exposure, it had to have good electric conductivity as well as high purity. Graphite is known to be a good electrode material, and several carbon (graphite) fiber papers were commercially available.

We tested several kinds of carbon fiber plates as an electrode base material, examining electrical conductivity, mechanical strength, flexibility, and impurity. The carbon fiber plates V-105E, P-200, B-300, and S-300 (Kureha) were rejected because of their high resistance to conductivity. The KGF-200 plate and the graphite plate G-2080 (Kureha) had high electrical conductivity, moderate mechanical strength, and flexibility. These carbon fiber plates can be used as the base of the electrode. We chose the type KGF-200 model E-704 for further experiments because it was more flexible than the G-2080 model.

APPENDIX B. Preparation of Calcium Chloride Solution

Nylon must be dissolved in a solvent in order to coat a carbon fiber disk with it. Some organic acids are known to dissolve nylon, but it was very difficult to remove acid from the nylon coated on the carbon. A mixture of $CaCl_2$ and MeOH was used as a solvent for nylon, because both MeOH and $CaCl_2$ were easily removed from the nylon layer.

Initially, we tried to use a commercially available anhydrous $CaCl_2$ to make a saturated solution of $CaCl_2$ and MeOH to dissolve nylon-6. The anhydrous $CaCl_2$ was required because the solubility of nylon-6 in a saturated solution of $CaCl_2$ and MeOH was greatly reduced when the solution contained water, because of the crystal water of $CaCl_2 \cdot nH_2O$. However, when the commercially available highest grade of anhydrous $CaCl_2$ (97% purity) was used without any pretreatment to prepare the saturated $CaCl_2$ and MeOH solution, the KI solution was oxidized with the impurity in the anhydrous $CaCl_2$ and liberated the I_2 on a carbon fiber disk. The discharge time of a blank electrode, which was not exposed to O_3, exceeded 60 seconds. To keep this discharge period short, tedious reduction steps were used to purify the $CaCl_2$, using zinc powder and hydrogen chloride. These reduction steps could be eliminated by using $CaCl_2 \cdot 2H_2O$ (purity greater than 98%; Aldrich), which had a purity higher than that of the anhydrous solution. By heating $CaCl_2 \cdot 2H_2O$ at 200°C for two hours under vacuum, we easily obtained sufficiently pure $CaCl_2$. The discharge time of the blank electrode using this $CaCl_2$ solution was less than one second.

APPENDIX C. Automation of the Analysis

To process a large number of samples and maintain the quality of the analysis at a sufficient level, we used semiautomated procedures for the discharge time measurement. As shown in Figure C.1, the semiautomated system consisted of a galvanic cell, galvanostat (model HA-501G, Hokuto), and a personal computer (APCIV, NEC Corp.) with a general purpose interface bus (model MBC-488, Metrabyte) and digital input/output port (model DT 2801, Data Translation). The galvanostat has a general purpose interface bus.

The procedures for determining the discharge time were as follows:

1. Supply 200 mL of electrolyte solution to the galvanic cell.
2. Turn on the galvanostat.
3. Turn on the personal computer. The program starts automatically.
4. Input sample identity to personal computer.
5. Set the galvanostat to galvanostat mode.
6. Set current at 100 μA.
7. Set a new electrode to galvanic cell.
8. Turn on the microswitch lever on the lid of the galvanic cell. This supports the electrode and the discharge measurement starts.
9. Record the potential and current data every one second.
10. Stop the discharge measurement when the potential is less than −0.15 volts.
11. Set the galvanostat to clear mode.
12. Record the discharge time of the electrode and the sample identity on a disk file.
13. Repeat, starting at step 4, or stop measurement.

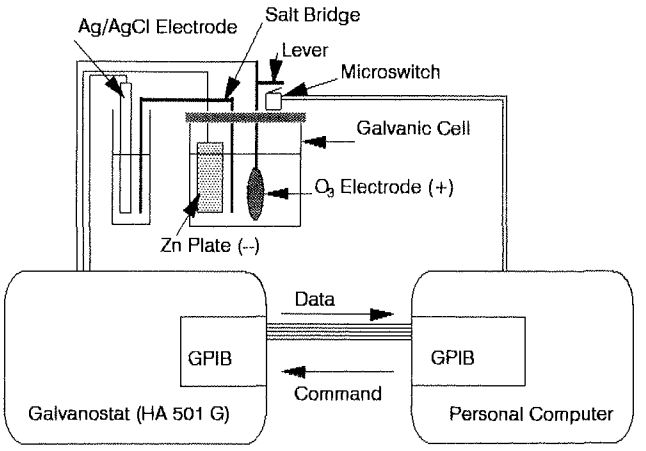

Figure C.1. Discharge time measurement system.

Steps 5 through 13 were automated. The measurement was initiated by a microswitch that was pressed when the electrode was dipped into the electrolyte in step 7. The potential of the electrode and current data were taken every one second, using the timer interrupt feature of the BASIC program. The potential was shown on the display as a discharge curve graph. When the potential was below −0.15 V, the measurement was stopped. Each potential retrieved was compared to the preset end potential (−0.015 V) during measurement, and the discharge time was calculated and shown on the display at the end of each measurement. Results of the analyses (date and time of the measurement, sample identity, discharge time) were recorded in a disk file. The discharge curve data also were stored in a separate file. The program used for this measurement is given in Appendix I.

APPENDIX D. Water Content and pH of the Electrode

At the initial stage of this project, we used a dry electrode, which contained no humectant or buffer. However, we found a positive correlation between relative humidity and the sampling rate (Figure D.1) and no response when the dry electrodes were exposed to the dry test air (less than 10% relative humidity). Also, the interbatch variability of the sampling rates was relatively high. These experimental results suggest that the water content of the electrode played an important role in the O_3 sampling.

To control the water content of the electrode, $CaCl_2$ dissolved in MeOH was used as a humectant for the electrode. The $CaCl_2$ was applied to the electrode as a mixture of KI and $CaCl_2$. The water content of the electrode that contains the $CaCl_2$ humectant (CC electrode) was proportional to the amount of $CaCl_2$ in the electrode (Table D.1). As shown in Figure 6, the CC electrode containing more than 1.7 mg of water showed a constant sampling rate. The CC electrode containing 1.7 to 2.0 mg of water had better reproducibility and sensitivity than the electrode that contained no humectant (NC, or no-calcium, electrode). The coefficient of variation of the sampling rates was less than 5% for different batches of the electrode (Table D.2). The enhanced response rate of the CC electrode may have been due to a wider wet surface area of the electrode and an increased yield of the CTC.

The O_3 absorption rates of the dry and wet electrode were similar, that is, the O_3 concentration decrease was the same whether a dry or wet sampler was used in the glass chamber. The reaction between KI and O_3 continued regardless of the water content. The I_2 was transported to the nylon layer to form the CTC. Iodine diffuses much more slowly in solid KI than in an aqueous solution. Thus, when the electrode's water content was very low, formation of the CTC was probably less favorable than vaporization of I_2. When the water content was insufficient to form CTC in a portion of a sampler, the I_2 formed by the oxidation of O_3 was lost via vaporization. Formation of CTC would proceed in the portions of the sampler with sufficient water. A water content of 1.7 mg/electrode seemed to be sufficient to cover the surface of the electrode. The water content of the NC electrode was much less than 1 mg. The weight of the wet NC electrode, was the same as that of the dry NC electrode. A small water content change affected the sampling rate significantly, especially when the water content was near zero. Therefore, the water content had to be controlled. However, when more than 1.7 mg of water was retained in the electrode, the sampling rate did not change with water content variation.

We found that it was necessary to control the surface pH levels to maintain a constant sampling rate for O_3 for the entire sampling period. Because the electrode's initial pH ranged from 6.4 to 6.7, a mixture of KH_2PO_4 and sodium phosphate was used as a buffer to maintain this pH value, along with $CaCl_2$ as a humectant. However, the solubility of

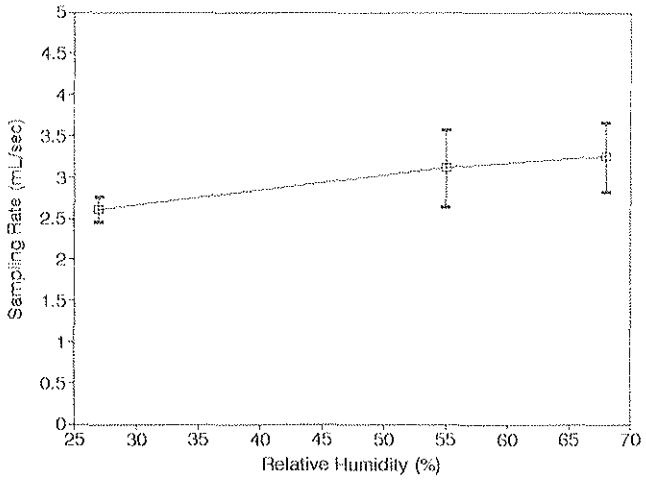

Figure D.1. Effect of humidity on sampling rate.

Table D.1. Water Content of the Electrode Impregnated with Calcium Chloride

Applied Amount of $CaCl_2$ (mg)	Water Content[a]	
	Mean (mg)	CV (%)
0.0	0.0	1.3
1.17	1.58	2.3
3.50	3.67	3.7
7.00	7.84	1.6

[a] Mean and CV were calculated from three replicate samples.

Table D.2. Interbatch and Intrabatch Variability of Electrode Containing the $CaCl_2$ Humectant

Batch Number	Sampling Rate for Each Sampler (mL/sec) 1	2	3	4	Mean	SD	CV (%)
1	0.925	1.250	1.327		1.165	0.177	15.1
2	1.172	1.137	1.052		1.123	0.049	4.5
3	1.236	1.172	1.123	1.186	1.179	0.042	3.3
4	1.123	1.165	1.130		1.144	0.035	1.7
5	1.094	1.158	1.172		1.144	0.035	2.9
Overall					1.151	0.056	4.9

the calcium phosphate, formed by a chemical reaction between $CaCl_2$ and buffer, was not high. We found that AcOK could be used as a humectant for a wider range of relative humidities (20% to 100%) than $CaCl_2$ (31% to 100%); and the problem of solubility was solved because the KH_2PO_4 was soluble (KH_2PO_4 is a reaction product of AcOK). We used KH_2PO_4 and AcOK as a buffer and humectant.

The amount of the AcOK applied to an electrode was determined so that the water content of the electrode was the same as that of the CC electrode. The sampling rates of the electrodes were almost the same, regardless of the humectant used.

APPENDIX E. Interference of Nitrogen Dioxide

Nitrogen dioxide has a positive interference in this O_3 measurement method. The sampling rate for NO_2 was 0.54 mL/sec, which is 28% of the rate for O_3. We tested several methods for stopping this interference, such as a neutralization reaction with an alkali-soaked filter, an anion exchange filter, an esterification reaction with glycerol, and reduction with sodium sulfite. None of the methods was successful, presumably because O_3 is far more reactive than NO_2. All chemicals were tested with the pre-filter method discussed below, and glycerol also was tested by directly impregnating it into the electrode. The sodium sulfite was found to be unsuitable in preliminary tests, so further tests were abandoned.

We intended to absorb NO_2 gas with a glass-fiber filter layer installed as a diffusion barrier for the O_3 electrode. A nylon membrane filter impregnated with a solution of potassium carbonate, sodium hydroxide, and glycerol dissolved in MeOH and water, or an anion-exchange membrane was used as a diffusion barrier. A Teflon membrane filter was inserted between the electrode and the diffusion barrier to avoid contact between the chemicals. Results are shown in Table E.1. The nylon and Teflon filters without the alkali treatment were not reactive to O_3, whereas the alkali-treated filter papers seemed to react with O_3. The filter pa-

Table E.1. Sampling Rate of Electrode with Specific Diffusion Barrier Materials

Materials	Sampling Rate[a] (mL/sec) Ozone Mean	Ozone CV (%)	NO_2 Mean	NO_2 CV (%)	Ratio
Teflon	0.614	1.52	0.219	6.31	0.36
Nylon + Teflon	0.522	2.35	0.184	10.1	0.35
Anion exchange filter	0.056	101.1	ND[b]	ND	ND
Anion exchange filter + glycerol	0.021	19.87	ND	ND	ND
Teflon + nylon + K_2CO_3 + $CaCl_2$	0.353	6.30	0.134	5.39	0.38
Teflon + nylon + NaOH	0.282	9.44	0.169	7.74	0.60
Teflon + nylon + glycerol + K_2CO_3	0.339	10.17	0.205	13.66	0.61

[a] Mean and CV of the responses were calculated from four replicate samples.

[b] ND = not done.

per impregnated with the alkali solution could not absorb NO_2 efficiently. The anion exchange filter absorbed or decomposed ozone almost completely. Therefore, none of the methods mentioned above could remove NO_2.

For the glycerol-impregnated electrode, we tried to inactivate NO_2 for O_3 monitoring by forming a nitro-ester, instead of absorbing NO_2 with the alkali filter paper. Nitrogen dioxide is known to react with water to form nitric and nitrous acids. Nitric acid can react with glycerol and forms esters. Glycerol was substituted for $CaCl_2$ to control the water content of the electrode. The electrode impregnated with glycerol had similar performance to the $CaCl_2$ electrode in terms of O_3 exposures. When the glycerol electrode was exposed to 100 ppb NO_2 for 16 hours, no I_2 was liberated. However, the glycerol electrode did not liberate I_2 when exposed to O_3 if the exposure concentration was lower than 200 ppb. The reason for this is unclear; we suspect that glycerol contained some reducing agents. Because the glycerol electrode did not liberate I_2 in the presence of O_3, it could not be used to remove NO_2 interference.

For the pre-filter method using sodium sulfite, we used glass fiber filters impregnated with 250 µL of a solution of 0.2 M sodium sulfite and 0.2 M sodium hydroxide, which is known to absorb NO_2. These filters were tested for NO_2 removal using the glass chamber. The O_3 concentration in the effluent air was 330 ppb when no sampler was in the glass chamber. Ten minutes after four filters were placed on the turntable, the O_3 concentration in effluent air was 103 ppb, and reached the equilibrium concentration. This experiment indicated that sodium sulfite reacted with the O_3 in the glass fiber filter and reduced the amount of O_3 available to react with KI. Because of its reaction with O_3, we concluded that sodium sulfite was not suitable for eliminating NO_2 interference.

None of the methods examined could reduce the interference of NO_2.

APPENDIX F. Wind Tunnel Experiment

The wind tunnel was designed and constructed to examine wind effects on the sampling rate and to determine the optimum thickness of the O_3 diffusion barrier. Two factors are important with regard to wind effects: wind speed and the orientation of the sampler to wind flow. Our experiments indicated that the sampling rate was affected by wind velocity, but not by the orientation of the sampler. Therefore, we increased the diffusion barrier by inserting fine Teflon mesh and a Teflon spacer (1.7-mm thick) in the sampler to decrease the sampling rate's dependency on wind velocity.

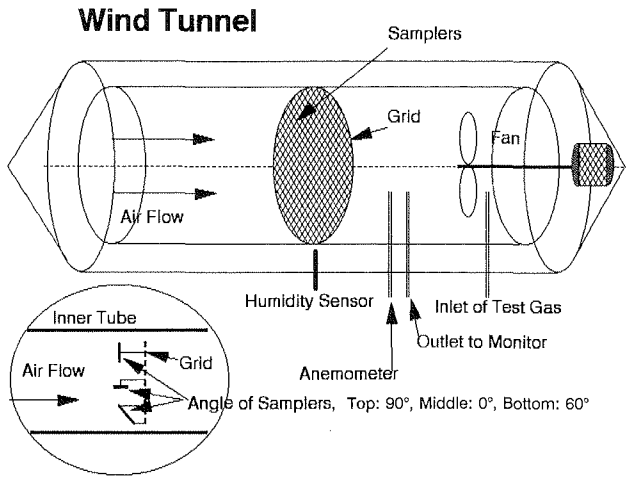

Figure F.1. Schematic diagram of the wind tunnel and the orientation of the samplers relative to air flow.

We tried two compositions of diffusion barriers in these experiments. One was made of Teflon mesh (1-mm thick), two Teflon membrane filters, and a $KMnO_4$ filter; the other was made of two Teflon membrane filters and a $KMnO_4$ filter. We compared the sampling rates of samplers at different orientations and exposed to different wind velocities (Figure F.1). Four samplers were hung in three orientations on a grid at the center of the inner tube of the wind tunnel (Figure F.1, inset). Two samplers were set perpendicular to the wind stream (angle 90°), one sampler was placed parallel to the wind direction (angle 0°), and the fourth sampler was oriented at 60° to the air flow (angle 60°). Four experiments were conducted at wind velocities of 0.6 m/sec and 1.3 m/sec, with different sampler configurations, and with and without Teflon mesh.

The sampling rates of the samplers placed perpendicular to the wind (angle 90°) for each condition (Figure F.2) were as follows: for samplers with Teflon mesh, 1.97 mL/sec for wind velocity of 0.6 m/sec, and 2.76 mL/sec for wind velocity of 1.3 m/sec; for samplers without Teflon mesh, 3.22 mL/sec for wind velocity of 0.6 m/sec, and 3.58 mL/sec for wind velocity of 1.3 m/sec.

The variation of the sampling rates among various orientations was small, except for the experiment at the wind velocity of 1.3 m/sec, using samplers without Teflon mesh. The sampling rate at different wind velocities differed by about 25% for the samplers without Teflon mesh and about 10% for those with Teflon mesh. Although the samplers without Teflon mesh had a higher sensitivity than those with Teflon mesh, because of the shorter diffusion path length, the sampling rates of the samplers with Teflon mesh were high enough to measure time-weighted averages of O_3

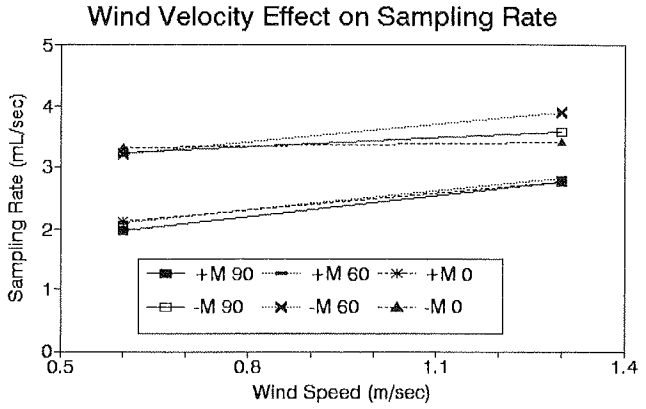

Figure F.2. The effect of the orientation of the sampler on sampling rate. +M = with Teflon mesh; −M = without Teflon mesh; 0, 60, and 90 refer to angle of orientation as shown in Figure F.1.

concentrations for six hours. We used the Teflon mesh to protect the Teflon membrane surface, which is very fragile.

When we increased the diffusion path length, the sampling rates and its dependence on wind velocity decreased. Because the sampling rate was high enough to apply the O_3 sampler to personal exposure measurements, we used a coarse Teflon mesh and fine Teflon mesh as support for the Teflon membrane and spacer to minimize the sampling rate's dependence on wind velocity. As explained in the main text in the Effect of Face Velocity section, the sampling rate of the O_3 sampler was independent of wind velocity.

APPENDIX G. Storage of the Sampler

We conducted several tests of the sampler's storage capability. Included here is a summary of those tests not discussed in the main text of this report. The results indicate that the nylon membrane filter, used in a previous version of the sampler as a diffusion barrier material, absorbs I_2 during storage. The results also indicate that the electrode's pH may affect storage. When the electrode's pH was higher than neutral, the recovery decreased; when the electrode's pH was neutral or slightly acidic, the recovery was good. We modified the electrode composition and removed the nylon membrane from the diffusion barrier.

We tested the stability of I_2's CTC by comparing two sets of electrodes simultaneously exposed to the test air. One set was analyzed immediately after exposure, and the other was analyzed after being stored at room temperature for varying lengths of time. Five storage experiments were performed (Table G.1). In the first experiment, 12 electrodes using $CaCl_2$ as the humectant were directly exposed to 150 ppb O_3 for 2.5 hours. Four electrodes analyzed immediately after the exposure showed a discharge time of 361 seconds, whereas the electrodes stored in a glass bottle for 4 days and 10 days had discharge times of 430 seconds and 445 seconds, respectively. These discharge times were 119% (4-day storage) and 123% (10-day storage) of the value for the electrodes analyzed immediately. This indicates that the CTC is stable for 10 days of storage.

When the electrodes with the AcOK humectant were stored in a sampler case with the $KMnO_4$ glass fiber filter and nylon-coated filter, which was the same filter used in Appendix E (experiment 2), only 28% of the discharge time of the samples analyzed immediately was obtained after seven days of exposure. By turning yellow, the nylon filter indicated that it had absorbed I_2. When the exposed electrodes were stored with a $KMnO_4$ glass fiber filter and no nylon filter (experiment 3), 59% to 68% of the CTC was recovered, based upon the initial discharge time. When the exposed electrodes inserted between two Teflon membrane layers were stored in the sampler case (experiment 4), about 90% of the CTC was recovered after seven days of storage. However, the discharge time decreased with increases in the storage periods and became almost half of the initial value after 22 days of storage.

Similar storage methods were used for experiments 1 and 4, but the stability of the CTC differed. The differences in experimental conditions between the two experiments were: (1) the storage media; (2) the kinds of humectant; and (3) the presence or absence of Teflon membrane layers. Because Teflon membrane layers are considered to be inactive, we conducted the storage experiments to examine the first two factors. Because the $CaCl_2$ solution lacked the buffering capacity to maintain the pH at a constant level, it was replaced with the AcOK solution. The $CaCl_2$ solution's pH was neutral, whereas the AcOK solution was alkaline, with a pH of 8.4. Adding acetic acid (AcOH) to the AcOK solutions produced pHs of 6 for the $CaCl_2$ solution, and 5 for the AcOK solution. In experiment 5, the exposed electrodes were stored in the glass bottle or styrol sampler case. During six to seven days of storage, no significant loss of the CTCs was observed.

APPENDIX H. Field Experiments

Field tests were conducted in August of 1990 to test the performance of our sampler, although it was still in the developmental stages. The composition of this sampler's diffusion barrier was different from that of the final sampler. The barrier was made of a coarse Teflon mesh, a Teflon

Table G.1. Results of Storage Experiments

Recovery Experiment Number	n[a]	Humectant and Additive	Sampler[b] Composition	Exposure (ppb•hour)	Storage Method[c]	Storage Period (days)	Discharge Time Mean (seconds)	Discharge Time SD	Discharge Time Relative to Immediate Analysis (%)
1	4	$CaCl_2$	E	425	Glass bottle	0	361	(18)	
	4					4	430	(22)	119
	4					10	445	(28)	123
2	2	AcOK	T + $KMnO_4$ + T	720	Sampler	0	160	(2.5)	
	2		+ N + T + E + T		(with N + $KMnO_4$)	7	44	(0.8)	28
	2			840		0	140	(0.8)	
	2					7	36	(4.0)	26
3	1	AcOK	T + $KMnO_4$ + T	420	Sampler	0	143	(NA)	
	2		+ E + T		(with $KMnO_4$)	9	84	(4.8)	59
	1			435		0	138	(NA)	
	2					9	81	(11)	59
4	3	AcOK	T + $KMnO_4$ + T	560	Sampler	0	218	(8.3)	
	3		+ E + T		(with N)	7	197	(7.6)	90
	3					14	139	(7.2)	63
	3					22	113	(22)	52
	1			520	Sampler	0	161	(NA)	
	2				(with N)	7	147	(4.3)	91
	1			510	Glass bottle	0	157	(NA)	
	2					7	147	(10)	93
5		AcOK + AcOH							
	1	pH 6	T + $KMnO_4$ + T	430	Sampler	0	132	(NA)	
	2		+ E + T		(with N)	7	122	(14)	92
	1	pH 6		470	Glass bottle	0	147	(NA)	
	2					6	143	(12)	97
	1	pH 5	540	Sampler	0	141	(NA)		
	2				(with N)	6	135	(5.8)	96
	1	pH 5		580	Glass bottle	0	150	(NA)	
	1					6	160	(11)	106

[a] Number of samples.

[b] E = electrode; T = Teflon membrane; N = nylon membrane; $KMnO_4$ = $KMnO_4$-impregnated glass fiber.

[c] Sampler = Gelman petri dish; Glass bottle = Wheaton 30-mL bottle with polyethylene cap.

membrane, a $KMnO_4$ filter, and a Teflon membrane. The sampling rate was higher and more dependent on the wind velocity than that of the final sampler.

Field test results were compared with those from the chemiluminescence monitor (Table H.1). Except for the test on August 13, the ambient O_3 concentrations were less than 50 ppb, which was lower than we had expected. The NO_2, NO, and SO_2 concentrations were in expected ranges. The O_3 concentrations measured by the two methods were in close agreement, as indicated by the correlation coefficient of 0.87 (Figure H.1). The O_3 concentration measured by the O_3 sampler on August 31 was 13 ppb, although the ambient level indicated by the chemiluminescent analyzer was 33 ppb. This discrepancy between the two methods can be explained partially by a contamination of the glassware used to store the AcOK by some reducing reagents. This was confirmed by the fact that the I_2 color disappeared when we added I_2 to the potassium solution.

Further field tests have not been conducted yet because the ambient O_3 concentrations are low at present. We are planning to perform field tests in a high ozone concentration area.

Table H.1. Result of the Field Experiments

	Average Concentration of Pollutants (ppb)				
	Ozone Sampler	Monitors[a]			
Date	O_3	O_3	NO_2	NO	SO_2
8/09	24	37	32	10	15
8/10	16	10	19	31	8
8/13	84	83	9	< 1	10
8/14	24	37	12	3	9
8/31	13	33	41	17	13

[a] See the Exposure Experiment section in Methods for identification of the monitors.

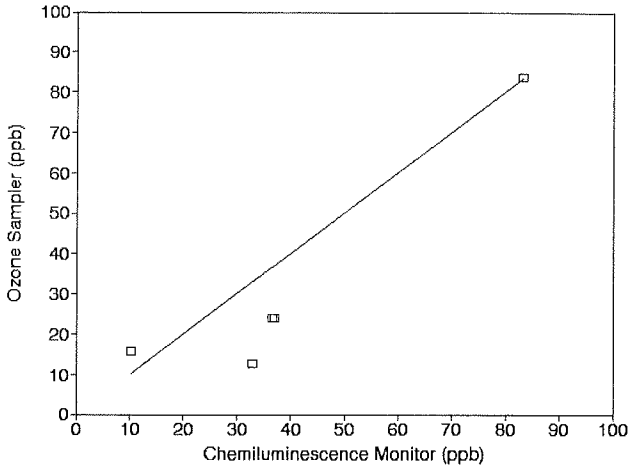

Figure H.1. Correlation of O_3 concentrations between personal ozone sampler and chemiluminescence monitor.

APPENDIX I. Composition of the BASIC Program Used to Measure the Discharge Time of the Electrode

This computer program is available on request from the Health Effects Institute, 141 Portland Street, Suite 7300, Cambridge, MA 02139 (Telephone: 617-621-0266; fax: 617-621-0267).

ABOUT THE AUTHOR

Dr. Yukio Yanagisawa is an Associate Professor of Environmental Health in the Department of Environmental Sciences and Engineering, Harvard School of Public Health. He received a Bachelor of Engineering, Master of Engineering, and Doctor of Engineering in Chemical Engineering from the University of Tokyo. He has been studying indoor air pollution and the relationships between personal exposures to air pollutants and adverse health effects. He developed personal monitors for NO_2, NO, and carbon monoxide. The ozone battery is his fourth invention. Recently, he has been studying air pollution problems on the global scale. Currently, he has a joint appointment as a chief researcher at the Research Institute of Innovative Technology for the Earth in Japan and as director of a research group of System Analysis for Global Environment.

PUBLICATIONS RESULTING FROM THIS RESEARCH

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Hishinuma M, Yanagisawa Y. 1992. U.S. Patent No. 5128268 (USA). Halogen/charge-transfer gas monitor. U.S. Patent Office, Washington, DC.

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ABBREVIATIONS

AcOK	potassium acetate
AcOH	acetic acid
Ag/AgCl	silver/silver chloride
$CaCl_2$	calcium chloride
CTC	charge transfer complex
CV	coefficient of variation
GPIB	general purpose interface bus
HCl	hydrochloric acid
I_2	iodine
$(IO)^-$	hypoiodite
$(IO_3)^-$	iodate
K_2CO_3	potassium carbonate

KH_2PO_4	potassium phosphate dibasic
KI	potassium iodide
$KMnO_4$	potassium permanganate
MeOH	methanol
NaOH	sodium hydroxide
$NaHPO_4$	sodium phosphate
NBKI	neutral buffered potassium iodide
NH_4Cl	ammonium chloride
NO	nitric oxide
O_3	ozone
NO_2	nitrogen dioxide
ppb	parts per billion
r	correlation coefficient
SO_2	sulfur dioxide
Zn	zinc

INTRODUCTION

In the summer of 1988, the Health Effects Institute (HEI) issued RFA 88–1, "Ozone and Carbon Monoxide: Assessment of Population Exposure and Dose." A specific objective of the RFA was to support studies on the development and testing of personal exposure samplers or monitors for ozone. Two projects funded under this RFA are discussed in this report. One was based on an application by Dr. Jack Hackney and colleagues, of the Los Amigos Research and Education Institute, Inc., in which they proposed to continue developing both active and passive ozone samplers based on ozone's reaction with a binary reagent. Their two-year study began on May 1, 1989. A draft final report was received on October 1, 1991, and a revised report was received on July 22, 1992. The study's total costs were $128,600.

The second proposal funded under RFA 88–1 was that of Dr. Yukio Yanagisawa, of the Harvard School of Public Health. Dr. Yanagisawa proposed to design and test a passive ozone sampler based on ozone's reaction with iodide ion. Dr. Yanagisawa's two-year study began on July 1, 1989. His draft final report was received on September 4, 1991, and a revised report was received on September 30, 1992. The total costs for the study were $285,020.

Dr. Petros Koutrakis submitted an application under one of HEI's Requests for Preliminary Applications (RFPA 89–3). Together with colleagues at the Harvard School of Public Health, the United States Environmental Protection Agency, and NSI Technology Services, Dr. Koutrakis had designed both active and passive ozone samplers. Because Dr. Koutrakis' project was complementary to the two ozone sampler studies already funded, HEI initiated a six-month study, which began on January 1, 1991, to evaluate his passive sampler. His draft final report was received on October 17, 1991, and a revised report was received on September 10, 1992. The total costs for the study were $17,560.

The three Investigators' Reports were reviewed by HEI's Health Review Committee at the same time, and the revised reports were accepted for publication by the Committee in November 1992. During the review of the Investigators' Reports, the Review Committee and the investigators had the opportunity to exchange comments and to clarify issues in the Investigators' Reports and in the Review Committee's Commentary. The Health Review Committee's Commentary is intended to place the three Investigators' Reports in perspective, and to compare their results with other developments in this field, as an aid to the sponsors of HEI and to the public.

Because sensitive and reliable personal samplers for ozone are critical for epidemiological studies, HEI is publishing the three reports under one cover, together with a short description of the characteristics of other ozone samplers, in order to communicate the state-of-the-art in this important area to the scientific and regulatory communities.

REGULATORY BACKGROUND

The U.S. Environmental Protection Agency (EPA)* sets standards for oxidants (and other pollutants) under Section 202 of the Clean Air Act, as amended in 1990. Section 202(a)(1) directs the Administrator to "prescribe (and from time to time revise) . . . standards applicable to the emission of any air pollutant from any class or classes of new motor vehicles or new motor vehicle engines, which in his judgment cause, or contribute to, air pollution which may reasonably be anticipated to endanger public health or welfare." Sections 202(a), (b)(1), (g), and (h) and Sections 207(c)(4), (5), and (6) impose specific requirements for reductions in motor vehicle emissions of certain oxidants (and other pollutants) and, in some cases, provide the U.S. Environmental Protection Agency with limited discretion to modify those requirements.

In addition, Section 109 of the Clean Air Act provides for the establishment of National Ambient Air Quality Standards (NAAQS) to protect the public health. The current primary and secondary NAAQS standard for ozone is 120 parts per billion (ppb). This standard is met when the number of days per year with maximum hourly average concentrations above 120 ppb is one or less. Section 181 of the Act classifies the 1989 nonattainment areas according to the degree that they exceed the NAAQS and assigns a primary standard attainment date for each classification.

The determination of the appropriate emissions of oxidants and their precursors depends, in part, on an assessment of the risks to health that they present. Risk assessment is a process that characterizes and quantifies the potential detrimental effects that may result from exposures to harmful agents in the environment. One phase of the risk assessment process is exposure assessment, which estimates the magnitude, frequency, duration, and route of exposure to a pollutant. For ozone and many other air pollutants, exposure assessment is the weakest link in the risk assessment process. Personal samplers that can increase the accuracy of determining the ozone levels to which humans are exposed can improve estimates provided by risk assessment procedures.

* A list of abbreviations appears at the end of the Investigators' Reports.

SCIENTIFIC BACKGROUND

Ozone plays a protective role in the upper layers of the atmosphere, shielding the earth from the sun's harmful ultraviolet radiation. In contrast, ozone in the lower atmosphere is a pollutant; it is the major component of photochemical smog. Ozone forms in the atmosphere by complex photochemical reactions between nitrogen dioxide (NO_2) and certain species of hydrocarbons, termed volatile organic compounds, in the presence of sunlight. In the atmosphere, NO_2 is formed from the nitric oxide (NO) found in motor vehicle and industrial emissions (Finlayson-Pitts and Pitts Jr. 1993). Volatile organic compounds are present in motor vehicle and industrial emissions (U.S. Environmental Protection Agency 1992), and in evaporative emissions from automobile fuel lines and gasoline tanks. Because of their role in producing volatile organic compounds and NO, motor vehicles are major targets of efforts to control ozone levels.

Epidemiological studies are of central importance in assessing the risks to humans from air pollution. This implies the need for methods of exposure assessment that are well suited to epidemiological applications (Michaud and Quackenboss 1991). Because people are exposed to different levels of ozone and other pollutants in different settings, both indoors and outdoors, assessing the risk of adverse health effects from exposure to air pollutants requires field data on the actual concentrations that humans experience (Ott et al. 1986).

Representative ozone data cannot always be obtained from fixed-site monitors placed at a few locations in a metropolitan area. For example, in the vicinity of heavy vehicular traffic, local concentrations of ozone are often reduced because, under certain conditions, additional NO from tailpipe emissions destroys ozone, rather than contributes to its formation (Wolff and Korsog 1992). In contrast, less trafficked areas downwind of a fixed monitor may have higher ozone concentrations, because the air mass can be enriched in ozone when sunlight reacts with plumes of motor vehicle exhaust containing precursor chemicals. A practical example of these effects may be reflected by the results of Liu and colleagues (1993). These investigators used the nitrite-based sampler (described by Dr. Koutrakis and colleagues in their Investigators' Report) to measure microenvironmental ozone concentrations in the area of State College, PA. Their results showed that a significant spatial variation in outdoor ozone concentrations existed; densely populated regions had lower ozone concentrations than rural regions. The investigators proposed that the spatial variation might have resulted from differences in housing or population density, traffic intensity, and the availability of NO sources. They suggested that ignoring the spatial variation and using fixed-site monitors alone to estimate personal exposures to ozone could result in significant error in estimating exposures. Thus, actual ozone concentrations at outdoor microenvironments can be higher or lower than those measured at relatively widely spaced fixed-monitoring sites.

Outdoor ozone concentrations are almost always higher than those indoors because there are few indoor sources of ozone, and because indoor surfaces efficiently scavenge ozone from the air (Lippmann 1992). Nevertheless, accumulating evidence (reviewed by Weschler et al. 1989) suggests that indoor ozone concentrations can reach levels of more than 50% of those found outdoors. During periods of high ozone pollution, indoor levels can equal or approach the current standard (Weschler et al. 1989). Because people spend more than 90% of their time indoors, Weschler and colleagues (1989) concluded that total indoor exposure to ozone (measured as pollutant concentration × time) can be greater than outdoor exposures, even when indoor concentrations are less than those outdoors.

Because pollutant concentrations differ from site to site, small personal samplers worn by subjects are needed to measure the time-weighted average exposure to ambient levels of pollutants as people move from one environmental setting to another.

OZONE'S REACTIVITY AS AN OXIDANT

The personal ozone samplers developed by Dr. Koutrakis and colleagues and by Dr. Yanagisawa are based on ozone's ability to oxidize certain chemicals to products that can be quantified and reflect the amount of ozone present. The purpose of this section is to discuss briefly how knowledge of ozone's capacity to act as an oxidant can be used to design personal exposure samplers and to evaluate their potential usefulness in the presence of contaminating pollutants.

An oxidant is an ion, atom, or molecule that readily accepts electrons from another ion, atom, or molecule. One molecule of ozone, which contains three oxygen atoms, can shift among four different structures. Of these, the two structures that predominate have one oxygen atom with fewer electrons than the other two; the electron-deficient oxygen atom allows ozone to accept electrons from another agent.

In contrast to oxidants, a reducing agent is an ion, atom, or molecule that readily adds electrons to another ion, atom, or molecule. When oxidation and reduction reactions occur in pairs, these couplings are termed "redox" reactions. The degree to which a chemical species may undergo oxidation or reduction is termed its redox potential, which is expressed in volts. Redox potentials can be either positive

or negative, with a higher positive potential indicating a stronger oxidant. For example, compare the redox potentials produced when ozone or oxygen dissolves in water:

$$O_3 + H_2O + 2 \text{ electrons} \rightarrow O_2 + 2OH^-$$

For this reaction, the redox potential is +1.24 volts.

$$O_2 + H_2O + 2 \text{ electrons} \rightarrow HO_2^- + OH^-$$

For this reaction, the redox potential is −0.076 volts. The larger redox potential for the first reaction indicates that ozone is a stronger oxidant than oxygen.

A second example of the value of comparing redox potentials is that they allow an investigator to determine the degree of interference to be expected from a potentially competing reaction. For example, if the redox potential for ozone's reaction with a compound of interest is close to that of ozone's reaction with another common atmospheric pollutant, an investigator could expect that the secondary reaction might interfere substantially with the desired reaction by depleting the ozone and decreasing the extent of the desired reaction. Alternatively, if another pollutant's reaction with ozone yielded the same product as the desired reaction, ozone levels would be overestimated.

DETERMINING AMBIENT OZONE LEVELS

The levels of ozone to which humans are exposed can be estimated in two ways: time-weighted measurements derived from relatively widely spaced outdoor fixed-site monitors, or by smaller devices that measure personal exposure.

Fixed-Site Monitors

Prior to 1971, the most commonly used procedure for routinely measuring ozone levels was based on the oxidation of iodide ion (I^-) to iodine, which was measured photometrically by ultraviolet absorption. Because other air pollutants, such as NO_2, peroxides, and peroxyacetylnitrate (PAN) also contribute to iodine formation, the term "total oxidants" was used to characterize these measurements. In contrast to the positive interference caused by oxidants other than ozone, reducing agents such as sulfur dioxide cause a negative interference by consuming the iodine produced (U.S. Environmental Protection Agency 1986). As detection methods specific for ozone became available, the U.S. EPA changed its NAAQS from total oxidants to a standard for ozone. Monitors that measure ozone-induced chemiluminescence were designated as the reference method for ozone detection. In the gas-phase chemiluminescence method, light is produced when ozone present in ambient air is drawn into a monitor and reacts with ethylene. The response is a linear function of ozone concentrations ranging from 1 ppb to more than 1,000 ppb. Improved ultraviolet monitors that allow specific detection of ozone have been designated as equivalent methods for monitoring ambient ozone levels. (U.S. EPA 1986).

Although fixed-site monitors provide accurate measurements of the ozone concentration in ambient air, they are too large and expensive to use for measuring individual exposures of large numbers of human subjects, and their readings may not accurately reflect pollutant levels in different microenvironments. Therefore, there is a need for small, inexpensive, devices to measure personal exposures to pollutants.

Personal Exposure Devices

Measuring personal exposures to pollutants is a direct approach to exposure assessment. Such information can be obtained using two types of instruments. Integrated samplers collect a pollutant over a specified time period and the collection medium is analyzed at a later time. These samplers provide average concentration levels for discrete time intervals. In contrast, continuous ("real time") monitors use a self-contained analytical system to measure and record pollutant concentrations immediately. It is possible, in general, to have any combination of either integrated or continuous passive or active devices. The main difference between active and passive modes is the mechanism by which pollutants are transferred from the atmosphere to the collecting material (Yanagisawa 1989). In the active mode, air is drawn to the collecting material by a pump. Passive devices depend on molecular diffusion of air to the collection medium, or sorbent.

Yanagisawa (1989) noted that there are three air layers through which a gaseous pollutant must diffuse before being collected by the sorbent in a passive device. First, pollutant-containing air passes through a boundary layer at the area where ambient air first contacts the passive device. Because these samplers and monitors contain barriers to control diffusion, there is a second, stagnant region through which the pollutant must diffuse. Finally, there is a boundary layer of air at the sorbent. Because passive devices depend on molecular diffusion, their rates of collecting an air pollutant are affected by atmospheric conditions more than those for pump-driven samplers, which draw a known amount of air to the sorbent and overcome the problems inherent in passive diffusion.

Wind velocity, temperature, and relative humidity are the three major environmental factors that introduce uncertainties into a passive device's ability to adequately measure pollutant levels (Yanagisawa 1989). Because wind velocity affects air diffusion through the first boundary layer, its effect on the collection of a pollutant must be examined experimentally. Temperature can affect the diffusion coefficient of a gas in air and the rate at which a desired chemical

reaction takes place on the sorbent. If relative humidity affects the water content of the sorbent, the diffusion coefficient of the pollutant in the sorbent's aqueous phase and the reaction rate between the pollutant and sorbent may be affected. Each of these factors are considered in the individual Investigators' Reports.

Active devices are often used to obtain integrated exposure measurements over an 8- to 24-hour period. In general, they are expensive, bulky, noisy, and require frequent maintenance and calibration to assure the accuracy of the data they collect. In contrast, passive devices are noiseless, and are simpler, smaller, less expensive, and easier to use than active devices. However, passive devices normally require a long time period (for example, one to two weeks) at ambient concentration levels to collect sufficient pollutant for detection, and they provide only time-weighted measurements. Because of these limitations, passive devices generally cannot be used to measure relatively short-term exposures (for example, minutes or hours). Passive devices are also usually less accurate than larger, continuous monitors. In spite of these drawbacks, the advantages mentioned above make passive devices useful in large surveys of population exposures where the accuracy obtainable with continuous monitors is not required, and in situations where cumulative exposures are of primary interest (Sexton and Ryan 1988).

Passive samplers for nitrogen dioxide have been designed by Palmes and colleagues (1976), Yanagisawa and Nishimura (1982), and Mulik and colleagues (1989). The passive sampler designed by Palmes and colleagues (1976) has proven useful in determining indoor levels of this pollutant (Bodian et al. 1989; Samet and Spengler 1989; Ryan and Lambert 1991; Samet et al. 1993b; Lambert et al. 1993). Indoor air quality can vary greatly from house to house and from room to room. For these reasons, studying indoor air quality requires collecting large amounts of data in order to obtain statistically reliable exposure estimates. The simplicity of passive NO_2 samplers make them well suited for large scale studies.

Studies of human exposures to ambient ozone levels have been hampered by the lack of a suitable device that conveniently allows large numbers of measurements to be taken. Stock and colleagues (1985) used a continuous monitor to measure indoor and outdoor levels of ozone in the homes of subjects with asthma. To estimate the subjects' personal exposure to ozone, a technician carrying a portable monitor followed each research subject. This cumbersome method limited the number of subjects that could reasonably be studied, and illustrates the need for personal samplers.

Advances have been made in the development of both passive samplers and an active monitor for measuring personal exposures to ozone. Monn and Hangartner (1990) designed a passive sampler based on the absorption of ozone by 1,2-di-(4-pyridyl)-ethylene coated onto glass fiber filters. The reactive intermediate produced decomposes spontaneously to yield an aldehyde, which is detected spectrophotometrically by forming a colored reaction product with methyl benzthioazolinone hydrazone. Penrose and colleagues (1990) designed an active, amperometric monitor containing a sensor that detects both ozone and NO_2. To measure either gas selectively requires filters that efficiently remove one of the gases, but not the other. Grosjean and Hisham (1992) described a passive sampler based on the disappearance of the color from indigo carmine in the presence of ozone. Indigo carmine was coated onto paper filters, and the extent of the reaction was measured directly, by reflectance spectroscopy, without eluting the compound from the filter paper. The sampler was tested in the field for periods ranging from 3 to 30 days at several California mountain forest locations (Grosjean and Williams 1992). The investigators reported that the loss of indigo carmine's color was closely related to the ozone concentrations measured by a continuous reference ozone monitor.

Appendix A of this Commentary summarizes the characteristics of these three devices, together with those described in this Research Report.

JUSTIFICATION FOR THE STUDIES

Determining the risk to public health posed by environmental pollutants requires a knowledge of five fundamental components: The sources of the pollutants; the transport of pollutants from their sources to humans; the actual human exposure to the pollutants; the actual dose received by those who are exposed; and the adverse health effects resulting from these doses (Ott 1985). Our knowledge of two components of this risk model, exposure and dose, are rudimentary for most pollutants of concern. Field studies carried out during the 1970s and 1980s demonstrated that the levels of carbon monoxide (another criteria pollutant for which there is a NAAQS) experienced by people engaged in normal daily activities did not correlate well with simultaneous readings detected by fixed monitoring networks (summarized by Ott 1985). The absence of reliable human exposure data for other pollutants, such as ozone, can hinder the adoption of sound regulatory policies designed to protect public health (Ott 1985).

Epidemiological studies to determine the causes of

asthma and other lung diseases, dose-response assessment of ozone's effects on humans, and studies that evaluate the impact of controlled exposures in ambient situations on the general population would all be advanced by the availability of a reliable personal ozone sampler. Such a sampler would also be invaluable in addressing issues related to ozone exposures that endure for many hours.

When it issued RFA 88–1, "Ozone and Carbon Monoxide: Assessment of Population Exposure and Dose," HEI had three objectives:

1. To develop and test exposure samplers for ozone;
2. To develop and test field methods for estimating physiological determinants of pollution dose to the lung; and
3. To characterize the carbon monoxide dose in human populations.

Under objective 1, developing a small device that continuously records pollutant exposure was the highest priority, although a sensitive diffusion-based sampler was also of interest. Field validation studies of existing or newly developed technology were also considered. The proposals of Drs. Hackney and Yanagisawa responded to the first objective of the RFA.

The Health Effects Institute also issues Requests for Preliminary Applications to solicit proposals for studies of the health effects of automotive emissions outside of those defined by the more targeted RFA's. Dr. Koutrakis initially applied to HEI for funding under RFPA 89–3. Following discussions with HEI staff, he requested funds for a six-month study to validate a passive sampler that had been developed in his laboratory with support from the EPA. Because Dr. Koutrakis' project complemented the two ozone sampler studies already in progress, the HEI Health Research Committee recommended the project for funding.

The importance of information concerning exposure and dose in evaluating the potential health risk of exposure to environmental pollutants has been well established. The studies funded under RFA 88–1 (or initiated in response to RFPA 89–3) deal with these two critical parameters. First, developing personal ozone samplers addressed the need to accurately measure ozone concentrations in human microenvironments. Second, Drs. Samet and McCool, responding to objective 2 in RFA 88–1, developed methods that may eventually be used to estimate the pollutant dose that humans actually receive at a given concentration level. The results of these studies are presented in HEI's Research Report Number 59 (Samet et al. 1993a; McCool and Paek 1993). The research needs of the third objective of RFA 88–1 remain unaddressed because none of the applications submitted in response to this objective were recommended for funding.

GENERAL PRINCIPLES OF SAMPLER VALIDATION

Before addressing the technical evaluation of each sampler, this section will discuss the general principles of sampler validation, and the methods used by each of the investigators to determine the accuracy of their samplers. Validation is the process of determining the suitability of a method to provide useful analytical data (Taylor 1983). Validation procedures establish that the performance characteristics of a method meet the requirements of the intended analytical applications (U.S. Pharmacopeial Convention 1988). The variety of parameters used to validate a method include precision, accuracy, limits of detection, limits of quantification, selectivity, linearity, range, and ruggedness (U.S. Pharmacopeial Convention 1988).

A validated method is necessary, but not sufficient, for producing reliable data. Most methods also require a degree of skill on the part of the analyst; this skill constitutes a critical factor in producing reliable data (Taylor 1983). The relative ease of transferring technology from a method's developer to others is a gauge of a method's ruggedness. Ruggedness is a measure of the reproducibility of test results under normal, expected, operational conditions for a significant span of time, from laboratory to laboratory, and from analyst to analyst (U.S. Pharmacopeial Convention 1988). Investigators interested in using an ozone sampler in a field study need to demonstrate their own ability to use the sampler; furthermore, they must demonstrate that the method will provide suitable accuracy and precision appropriate for the design of their proposed study.

A critical parameter in evaluating the performance of each sampler is its accuracy (defined as the extent to which the readings of an instrument approach the true values of the measured quantity) in detecting ozone levels. Each team of investigators calculated the ozone concentrations detected by its experimental sampler using equations that included ozone levels obtained from a reference ozone monitor. (See the Evaluation of a Nitrite-Based Sampler section for a detailed description of one method.) The investigators then assessed their samplers' accuracy by comparing the concentrations detected by the experimental samplers to those measured by the reference monitors. Because data obtained with the reference monitors were used to determine the sampling rate, and, hence, the ozone levels detected by the experimental samplers, good agreement between the reference monitors and experimental samplers is not surprising. Such methods of calibrating the experimental samplers are not scientifically rigorous, but do permit a self-adjustment in the bias, if any. Calculating the ozone concentrations de-

tected by groups of experimental samplers by these methods provides an estimation of precision. Determining the ozone concentrations and comparing them to the values obtained with a standard reference ozone monitor provides an estimation of each experimental sampler's accuracy.

TECHNICAL EVALUATION OF THREE OZONE SAMPLERS

EVALUATION OF A SAMPLER BASED ON OZONE'S REACTION WITH A BINARY REAGENT (Hackney and Associates)

Principle of the Sampler

The approach taken by Dr. Hackney and coworkers[1] at Los Amigos Research and Education Institute was to coat filter papers with a binary reagent (3-methyl-2-benzothiazolinone acetone azine with 2-phenylphenol) that forms a pink reaction product after exposure to ozone. The reaction product was eluted from the filter paper with an organic solvent, and the amount of product formed was quantified by spectrophotometry. The binary reagent was originally formulated by Lambert and colleagues (1989) for visual comparison with prepared color standards after exposure to ozone. Its promise in this application led Dr. Hackney and colleagues to incorporate this reagent in the design of their ozone samplers.

Objectives

The investigators' specific objectives were to:

1. Determine the optimum design for active and passive ozone samplers based on ozone's reaction with a binary reagent;
2. Compare each sampler's performance with that of conventional ozone measuring equipment;
3. Evaluate the samplers' performance when worn by human volunteers exercising in an exposure chamber and outdoors; and
4. Evaluate alternative methods for detecting ozone developed by other investigators.

Two additional objectives were added to address problems with the reagent that arose during the course of the study:

1. To reformulate the binary reagent to address problems associated with light sensitivity and combinations of temperature and humidity; and
2. To determine the structure of the product obtained following the reaction of the binary reagent with ozone (information that might aid in developing alternative reagents).

Methodology

The experimental design and methods used are described succinctly in the Investigators' Report. The sequence of laboratory and outdoor testing was logical, and the results follow clearly from the methods and study design. The tests investigating effects of temperature, humidity, and light intensity demonstrated the investigators' awareness of potential problems. The investigators' approach for determining the reasons for the passive sampler's performance problem outdoors was logical and provided good evidence for its cause.

Dr. Hackney and colleagues did not describe their method of calculating the ozone concentration estimated by their samplers. However, because the investigators measured ozone concentrations with a commercial ultraviolet photometer during all indoor and outdoor testing, we can infer that their evaluation of the samplers' accuracy depended on the use of the standard reference monitor. Thus, this method is subject to the general comment on determining sampler accuracy discussed in the General Principles of Sampler Validation section.

The statistical methods ranged from visual inspection of the data plotted in figures to multiple regression analysis. Except for the cases in which the investigators relied solely on visual inspection of the data, the statistical methods were appropriate and were clearly explained and presented. Visual inspection was employed to evaluate the results of laboratory testing of active samplers. The investigators concluded that the data on absorbance plotted against the amount of ozone that passed through the sampler were "fairly linear." The data, in fact, display nonlinearity and heterogeneity, with the variability of the absorbance increasing as a function of the ozone levels. A more detailed analysis of these data by weighted linear regression would have been more appropriate.

Linear regression analysis was used to examine the active sampler's response to different combinations of temperature and humidity when samplers were worn outside by volunteers. These methods are well-suited for analyzing these data. Linear regression methods were also used appropriately to analyze the data obtained from laboratory tests of the passive sampler.

The investigators also performed indoor tests of the sampler designed by Dr. Koutrakis and colleagues, with the subsequent chemical analyses performed by Dr. Koutrakis.

[1] Prior to the initiation of the HEI study, financial support for developing Dr. Hackney's samplers had been provided by the American Petroleum Institute and the Motor Vehicle Manufacturers' Association.

These data also were appropriately analyzed by linear regression.

Results and Interpretations

Dr. Hackney's initial experiments with a prototype sampler indicated that the binary reagent decomposed in the presence of ambient light, and formed a brown product that interfered with the colorimetric analysis of the pink, ozone-derived product. Dr. B.R. Daube, of the California Institute of Technology, overcame this problem by designing a light-tight holder with a baffle that provided a tortuous entrance path for incoming air. The investigators also decreased the intensity of ambient light reaching the reagent-impregnated filter paper by using black Nylatron to fabricate the sample holder, in place of the original FEP-Teflon. When the newly-designed sample holder was exposed to ozone in chambers at both high and low light intensities, no difference in response was noted. Thus, the investigators solved the problem caused by the binary reagent's light sensitivity.

The investigators then tested the active and passive samplers in exposure chambers at defined ozone concentrations, under varying conditions of temperature and humidity, and under ambient outdoor conditions.

Active Sampler. Because the volume of air pumped through the sampler and the ozone concentrations were known, the total mass of ozone (reported in micrograms) that contacted the reagent-coated filter was compared with the absorbance produced (see Figure 6 in the Investigators' Report). When the investigators exposed the sampler to 250 ppb ozone, they obtained a generally linear response with time at a combination of 25°C and 75% relative humidity. The response characteristics at combinations of 25°C and 30% relative humidity, and at 40°C and 25% relative humidity were less satisfactory. In the latter case, the response was flat after exposure to a total of 140 μg ozone; and at 25°C and 30% relative humidity, the response slope in the 0- to 200-μg ozone range was significantly lower than the slope obtained in the other exposures.

Humidity had a similar effect at a lower (150 ppb) ozone concentration. The response appeared satisfactory at combinations of 25°C and 75% relative humidity and 40°C and 75% relative humidity, but the responses at lower relative humidities (25% and 32%) were again less satisfactory. The results obtained after exposing the samplers to 50 ppb ozone are difficult to interpret because the data points cluster together. However, at 40°C and 25% relative humidity, the response was flat after exposure to 50 μg of ozone. Analyzing the data presented in Figure 6 by linear regression revealed that relative humidity showed a highly significant positive effect on the sampler's response to ozone and that temperature had no consistent effect. These results suggest that the colored product was either formed more rapidly, or lost more slowly, at high relative humidity.

Outdoors, the active sampler showed a reasonably good agreement with the ozone concentrations detected by the reference monitor over a one- to two-hour exposure period; the sampler's response after longer outdoor exposures was not reported.

Passive Sampler. In chamber tests of the active sampler, the investigators knew the ozone concentration and the amount of air they pumped through the sampler; this allowed them to calculate the mass of ozone contacting the filter. In contrast, passive samplers, which depend on gaseous diffusion of air and pollutants to the filter, do not allow the mass of ozone contacting the filter to be determined readily. For this reason, the investigators expressed their data as the absorbance produced by exposure of the reagent-coated filter to a specific level of ozone for a known time (for example, ppm•minutes).

When the investigators tested the passive sampler in an indoor exposure chamber, they observed a reasonably linear response to ozone between 200 and 2,000 ppm•minutes. The passive sampler's response was not dependent on temperature and humidity conditions, except at one combination of high temperature and high (75%) humidity. Under this condition, there was greater color formation than had been seen at lower humidity levels.

Testing the passive sampler outdoors produced unexpected results. The sampler consistently overestimated ambient ozone concentrations by more than one order of magnitude. Because the passive sampler's performance outdoors was unsatisfactory, it was not tested with volunteers.

Instead, the investigators performed experiments intended to explain the causes of the passive sampler's overestimation of ozone. They eliminated the possibility that the overestimation was related to the size difference between the larger passive sampler and the smaller active sampler. Because ozone levels were overestimated only when ambient air diffused slowly (passively) to the filter, and not when air was drawn through the filters by a pump, as with the active sampler, the investigators concluded that the large false positive results were caused by exposure of the binary reagent to an unknown reactive component of outdoor air for a long time period.

The investigators thought that determining the structure of the colored product formed by the reaction between the binary reagent and ozone might provide information about the reaction mechanism that would allow them to redesign the reagent to eliminate interferences. Dr. Walter Trahanovsky of Iowa State University identified four possible structures of the reaction product obtained following ozone's reaction with the binary reagent (see Appendix B in

the Investigators' Report); however, no alternative reagents were developed. Furthermore, Dr. Jack Lambert of Kansas State University was unsuccessful in attempts to eliminate the binary reagent's sensitivity to light and it's poor performance at low humidity by reformulating the reagent using different combinations of azines and hydroxyaromatic compounds (see Appendix A in the Investigators' Report).

Conclusions

The binary reagent-based active and passive samplers demonstrated acceptable responses to ozone in indoor exposure chambers under certain conditions of temperature and humidity.

Three general conclusions can be drawn from the studies on the active sampler. First, the sampler's response was less satisfactory when the total amount of ozone contacting the filter exceeded 100 μg than at lower ozone levels. Second, the sampler's response was more consistent and more linear at high relative humidity levels than at low levels. Third, the sampler's usefulness outdoors appeared to be limited to one- to two-hour exposures.

Although the passive sampler's response was generally acceptable indoors in purified air containing ozone, it greatly overestimated ozone concentrations under ambient outdoor conditions. Overall, further development of these samplers was precluded by problems associated with the binary reagent's response to certain temperature and humidity conditions indoors, and to unknown components of outdoor air. However, the light-tight sample holder designed by the investigators during the course of these investigations may have application to other samplers that use light-sensitive reagents.

EVALUATION OF A SAMPLER BASED ON OZONE'S REACTION WITH NITRITE (Koutrakis and Associates)

Principle of the Sampler

The passive sampler designed by Dr. Koutrakis and coworkers[2] at the Harvard School of Public Health is based on ozone's oxidation of nitrite ion, which is coated onto glass fiber filters as sodium nitrite, to nitrate ion. The filters are extracted with water and the nitrate released is quantified by ion chromatography.

When ozone reacts with nitrite ion, two concurrent reactions occur: a two-electron oxidation of nitrite ion to nitrate ion, and a two-electron reduction of ozone to oxygen. The coupled redox reaction can be expressed as:

$$NO_2^- + O_3 \rightarrow NO_3^- + O_2$$

The redox potential for the coupled reactions (+1.23 volts) favors the production of nitrate ion.

Objectives

Dr. Koutrakis and colleagues had previously designed both active and passive ozone samplers based on ozone's oxidation of nitrite to nitrate. The specific objectives of the six-month study supported by HEI were to evaluate further the passive sampler's performance. The investigators proposed to:

1. Investigate the effects of temperature and relative humidity on the sampler's collection rate;
2. Examine the effects of air speed and angle of orientation on the collection rate;
3. Study the effects of other oxidants on ozone detection;
4. Calculate the precision and accuracy of the sampler; and
5. Determine the collection capacity of the sampler.

Methodology

The testing protocol was carefully designed and executed, but was limited in scope. For example, the investigators developed an efficient ion chromatographic procedure for quantifying nitrate ion; however, the range of ozone levels they used in their indoor chamber testing was small (20 to 60 ppb).

As stated above, in the General Principles of Sampler Validation section, a major uncertainty associated with each of the three studies in this Research Report is the method used to determine the accuracy of the experimental samplers. Because the nitrite-based sampler is closest to being used in epidemiological studies, this issue will be discussed in relation to this sampler.

The investigators used data from a continuous ozone reference monitor to calculate the ozone collection rates for their sampler (Equation 3 in the Investigators' Report):

$$S_E = \frac{M \times V \times \dfrac{MW_{O_3}}{MW_{NO_3^-}}}{C_{TRUE} \times T}$$

In this equation, S_E is the experimental collection rate, C_{TRUE} is the true mean ozone concentration, MW is the molecular weight, M is the net nitrate concentration, V is the extraction volume, and T is the sampling time.

The investigators obtained the true mean ozone concentration, C_{TRUE}, by averaging the data from the standard ozone reference monitor over the exposure period (see the Investigators' Report). Collection rates were then determined

[2] This sampler was developed with support from the United States Environmental Protection Agency under Cooperative Agreement CR 816740-01 to the Harvard School of Public Health. A six-month evaluation of the sampler was supported by HEI.

for all exposed passive samplers by Equation 3. A mean collection rate was then calculated for each group of colocated passive samplers in a single test. By averaging the colocated mean collection rates from several tests of the passive samplers, a reference collection rate, S_R was obtained. The reference collection rate was then used to calculate the average ozone concentration detected by the samplers (Equation 2 in the Investigators' Report):

$$C_{PASS} = \frac{M \times V \times \frac{MW_{O_3}}{MW_{NO_3^-}}}{S \times K \times MW_{O_3} \times T}$$

In this equation, C_{PASS} is the average ozone concentration detected by the passive sampler; S is the collection rate (from Equation 3); and K is 0.0409 μmol/ppb•m^3 (K and MW_{O_3} were added for unit conversion purposes).

The investigators propose that their ozone samplers are accurate because the average ozone levels, obtained in Equation 2, agree closely with the ozone concentrations detected by the standard reference monitor. However, because collection rates calculated using measurements obtained with a standard reference monitor were used in the equation to determine the ozone levels detected by the passive samplers, such agreement is not surprising. Thus, this method of calculating the sampler's accuracy is subject to the reservations discussed above in the General Principles of Monitor Validation section.

There are also statistical concerns associated with Equations 2 and 3. The experimental collection rate (Equation 3) is an estimate, and can be expected to contain sampling errors. Even if the mean collection rate for colocated samplers were an unbiased estimate for the true collection rate, its reciprocal, as used in Equation 2, would not be an unbiased estimate. The implications of these two points are that the estimated average ozone concentration, C_{PASS}, may contain variability that is not taken into account in the data analysis; thus, this estimate may be biased. If estimates of collection rates are to be used, investigators should evaluate the variability and biases that are introduced. Future investigators might also consider alternative ways of estimating ozone concentrations that do not use data from a reference monitor to calculate a sampler's collection rate. For example, the literature suggests that Fick's First Law of Diffusion (the equation that defines the theoretical collection rate for a passive sampler) could provide a standard approach to calculate the collection rate (Mulik et al. 1989).

The average ozone concentrations presented in this study are the mean concentrations obtained from colocated samplers in a particular experiment. To compare the ozone concentrations detected by the passive samplers with the standard reference monitor, relative error (defined in Appendix A of the Investigators' Report by Koutrakis and associates) was employed. Relative error provides one means of comparison; however, it is lacking in at least three aspects: First, the relative error provides only one summary number for comparison, and does not provide information on how the agreement (or error) varies as a function of the value of the true concentration. Second, the relative error does not estimate the error of a single sampler. Rather, it estimates the relative error based on the averages of groups of colocated samplers in a particular experiment. This would be appropriate if, in practice, the samplers were always to be used in groups, and estimates provided by the passive samplers were always given as averages of these groups. This does not inform a prospective user of the performance level that can be expected from a single sampler. Taking the average values from a group of samplers produces less variability than comparing individual measurements among the group. Therefore, by using the average of colocated samplers, variability is underestimated. Third, the relative error does not provide a clear estimate of what to expect of the passive sampler in practice. To achieve this, confidence intervals or prediction intervals would also have to be supplied.

Additional methods of comparison can provide more information on the sampler's performance than the investigators obtained by using the average values of colocated samplers. One method would be to estimate relative error as the investigators did, but use a single sampler as the unit of analysis, rather than the average of colocated samplers. Next, bias could be estimated as the difference between the mean of the samplers and the mean of the true concentrations. The bias then could be put on a relative basis by dividing it by the mean of the true concentrations. Further, regression analyses could quantify the relation between the true concentrations and the sampler values in more detail: Regression through the origin would quantify the bias; the regression slope could be tested for deviation from unity; nonlinearity of the regression would indicate the range of linearity and validity of the passive samplers' measurements; and confidence intervals and prediction intervals could indicate what performance level might be expected in the future.

Weighted regression might need to be applied if the variance of the passive samplers varied with the level of the true ozone concentration. In all analyses, the unit of analysis should be the individual samplers, rather than mean values, and the analysis should take into account the correlations across colocated samplers.

Results and Interpretation

By using Equations 2 and 3, discussed above, the investigators concluded that there was good agreement between

the mean ozone concentrations detected by groups of passive samplers and those recorded by a colocated standard reference ozone monitor when exposure was carried out in an indoor exposure chamber at ozone levels between 17 ppb and 62 ppb. Tests of three groups of samplers exposed to approximately 270 ppb ozone for 11 to 48 hours in Dr. Hackney's laboratory showed values within 7% of the reference ozone monitor.

The collection rate determined in the indoor exposure chamber was not affected by temperatures between 0°C and 40°C, or by relative humidities between 10% and 80%.

The investigators designated the limit of detection for ozone as three times the standard deviation of the blanks in a batch of filters. From this value, they calculated a limit of detection for ozone of approximately 201 ppb•hr. The sampler's capacity was defined as the conversion of 5% of the total nitrite ion on the filters to nitrate ion. The investigators' conservative estimate of the sampler's capacity was approximately 19,865 ppb•hr; however, this was not confirmed experimentally.

To provide an overall picture of the sampler's performance, the investigators included in their Report the results of the outdoor field tests of the passive sampler that had been conducted earlier (Koutrakis et al. 1993).

These outdoor field tests showed the passive sampler's linear response between approximately 15 ppb to 50 ppb ozone; however, the collection rates differed by 60% in the laboratory and field studies, with the higher values obtained outdoors. To determine the reason for this discrepancy, the investigators carried out additional laboratory experiments. These experiments, carried out in an indoor wind tunnel, indicated that the collection rate depended both on wind velocity and on the orientation of the sampler's face to the wind. The results of these face velocity and orientation experiments led Dr. Koutrakis and colleagues to suggest that the differences in indoor and outdoor collection rates were due largely to differences in mean wind velocities.

By clipping individual samplers into inverted polypropylene jars, which acted as protective cups, the investigators achieved a stable collection rate in indoor wind tunnel tests spanning a range of wind velocities from approximately 28 to 173 cm/second.

When the investigators initially tested their passive samplers outdoors in protected cups, the samplers did not accurately detect ozone, perhaps due to overheating by the sun. By substituting opaque white polyvinyl chloride caps as wind protection, Dr. Koutrakis and colleagues reported that they achieved satisfactory ozone readings (data not shown).

The dynamic range over which the investigators tested their sampler in their controlled chamber studies was approximately a factor of three. For field use, the range should be at least a factor of 100 (two orders of magnitude). This broader range would permit a variety of sampling strategies to be employed (for example, sampling for a few hours to a few days and spanning a range of 20 ppb to 200 ppb ozone) in addition to gathering accurate and precise data. A small dynamic range, such as that explored here, compromises the accuracy of measuring high and low levels of exposure, and thus increases the uncertainty in estimating the tails of distribution of exposures in a population. By combining the laboratory chamber experiments and the outdoor field study, the investigators proposed that the dynamic range of the sampler was studied between 400 ppb•hr and 12,000 ppb•hr. However, this conclusion was arrived at by comparing two different sets of data. Because there are uncertainties associated with comparing data obtained under different experimental conditions, it would be more appropriate to determine the dynamic range of their sampler in a single experiment performed under uniform conditions.

Because NO_2 did not affect the performance of their active ozone sampler, which is based on the same principle as the passive sampler, the investigators did not test the effect of NO_2 on the passive sampler's performance. Attempts to study interference with ozone detection by PAN (performed by an outside laboratory) were inconclusive, most probably because the collection rate was too low to supply an adequate amount of ozone to the nitrite-coated filter. Because of this "starvation effect," the investigators proposed that it was not possible to assess the effect of PAN when the sampler's response to ozone was compromised by the low collection rate.

Recent studies with this sampler by other researchers (F. Lurman and S. Colome, personal communication) have shown that PAN, NO_2, sulfur dioxide, and nitrous acid do not significantly interfere with the passive monitor's performance. Although there was significant interference by high concentrations of hydrogen peroxide, its interference at ambient conditions is expected to be negligible.

A critical step in the use of Dr. Koutrakis' sampler is the analysis of nitrate ion. Ion chromatography produced a good separation of a relatively small amount of nitrate ion from unreacted nitrite ion (see Appendix B in the Investigators' Report). Because an important feature of any analytical method that may be used in large epidemiological studies is the rapidity of analysis, the 12-minute time period required for one separation by ion chromatography should allow a large number of experimental samples to be processed in a reasonable amount of time. An additional positive factor is the relative stability of the extracted nitrate ion in storage. There was a maximum change of ± 0.5 ppm nitrate after ten weeks storage at 5°C, corresponding to a maximum change of approximately ± 4 ppb ozone. This precludes the necessity of performing analyses soon after exposure.

Conclusions

The passive sampler developed by Dr. Koutrakis and colleagues represents a promising approach to a practical personal ozone sampler. The redox potential for ozone's oxidation of nitrite ion favors nitrate formation, and the rapidity of the ion chromatographic quantification of nitrate confers the ability to process multiple samples in a short time. The investigators found that the sampler's collection rate was affected by wind velocity; however, they made progress in attenuating this effect, and reported that their current method of protecting the samplers from the wind provides satisfactory results. Interference by common atmospheric copollutants does not appear to be a problem.

EVALUATION OF A SAMPLER BASED ON OZONE'S REACTION WITH IODINE (Yanagisawa)

Principle of the Sampler

Dr. Yanagisawa, also of the Harvard School of Public Health, developed a method for measuring ozone (and other oxidant gases) based on ozone's oxidation of iodide ion (I^-), in the form of potassium iodide (KI), to iodine (I_2).

During these reactions, iodide ion loses two electrons and is oxidized to iodine, and ozone gains two electrons and dissociates in the presence of water to form oxygen and two hydroxyl ions (OH^-). The coupled redox reaction can be expressed as:

$$O_3 + 2I^- + H_2O \rightarrow I_2 + O_2 + 2OH^-$$

The redox potential for these coupled reactions (+1.77 volts) favors the formation of iodine. The magnitude of the redox potential for ozone's reaction with iodide ion indicates that this reaction is slightly more facile than ozone's reaction with nitrite ion.

The unique feature of Dr. Yanagisawa's sampler is that: as the reaction proceeds on a carbon disk coated with a nylon derivative (nylon 6) and potassium iodide, the volatile iodine produced stabilizes by forming a charge-transfer complex with the nylon. Forming the charge-transfer complex increases the electrochemical potential of the nylon polymer, and can be likened to charging a battery. Because the charge-transfer complex acts as a positive electrode, adding a suitable counter electrode such as a zinc plate forms a galvanic cell. The final electrochemical potential of the nylon polymer (indicating the amount of iodine bound) is determined by measuring its total discharge current over time. During these reactions zinc releases two electrons and is oxidized to a positively charged ion, and the iodine in the charge-transfer complex gains two electrons and is once again reduced to the negatively-charged iodide ion. The equations describing the current discharged by these reactions can be expressed as:

$$Zn \rightarrow Zn^{++} + 2 \text{ electrons } (+0.76 \text{ volts})$$

$$I_2 + 2 \text{ electrons} \rightarrow 2I^- \ (+0.53 \text{ volts})$$

Because of this unique design, the oxidant concentration is easily determined.

Objectives

The investigator's objectives were to:

1. Determine the optimal composition for the polymer electrode;
2. Determine the applicability of the sampler to general population studies, and examine the effect of potential interferences, including meteorological factors and other pollutants; and
3. Automate the reading of the charge-transfer complex's discharge time.

Methodology

Dr. Yanagisawa used an iterative approach to testing for problems, modifying the sampler design, and retesting. The laboratory experiments were well designed to test the sampler for its performance under different atmospheric conditions of temperature, humidity, wind speed, and angle of incidence. The preparation of the ozone battery (see Principle of the Sampler section above), the wind tunnel experiments evaluating the effect of face velocity on the sampling rate, and the effects of temperature, time, and container volume on the stability of the change-transfer complex during storage before galvanometric analysis were all well documented. The investigator also tested for the effect of other atmospheric oxidants on ozone detection.

Buffering capacity is critical for accurate ozone detection by this method. Hydroxide ions, formed during the oxidation of iodide to iodine (see redox equation above), produce an alkaline medium. Under these conditions, the formation of iodine becomes less than unity because of the partial conversion of iodine to hypoiodite and iodate (for a further explanation see the Investigator's Report). Adding potassium phosphate buffer to the coating solution prevented hydroxide ions from accumulating.

Equation 2 in the Investigator's Report indicates that the actual ozone concentration (as determined by a reference monitor) was used in the calculation of the ozone concentration detected by the passive sampler. Thus, this method is subject to the same concerns regarding the use of data from reference monitors to calculate ozone concentrations detected by the experimental samplers expressed above.

Linear regression (at times called "normal regression" by the investigator) was the main statistical method used for

data analysis. Although this method was often appropriately used, it was at times not employed as rigorously and completely as the data require. For example, in Figure 8, a linear regression line was obtained by omitting the discharge time at 1,800 ppb•hr, which did not conform to linearity. It is incorrect to remove a data point because it does not fit an assumption. Therefore, the actual linearity range is not established by these data. The investigator also excluded a data point in Figure 11, analyzing the effect of relative humidity on the sampling rate.

Linear regression was used in an incomplete manner to analyze the effects of NO_2 interference on the sampler's performance. Separate regressions were computed in the presence and absence of NO_2. Tests of differences of the regressions or a multiple regression could have been used to evaluate NO_2's effect, rather than depending on visual comparison of the separate regressions. Confidence intervals for the regressions would have provided additional information.

Experiments determining the effects of temperature, humidity, wind effects, and NO_2 were performed using four colocated samplers. Taking the average values from a group of samplers can result in less variability than comparing individual measurements among the group of samplers. Thus, in this study, as well as in Dr. Koutrakis', the intersampler variation is not known.

Results and Interpretation

The sampling rate for ozone depended on the presence of a humectant (potassium acetate), which provided the stable water content that was needed for the chemical reaction to proceed. The sampler's response was constant when the amount of water on the electrode varied between 1.7 mg to approximately 8 mg. The sampling rate was also constant when the sampler was exposed to wind velocities between 10 and 100 cm/sec and at temperatures between 5.6°C and 40°C. The sampling rate showed only a slight increase between relative humidities of 25% and 72%, but it dropped sharply when the relative humidity fell below 20%.

The sampler's detection range seemed to lie between 400 to 1,450 ppb•hr ozone. Between these limits the investigator observed a linear response in terms of the discharge times of the charge-transfer complex; saturation of the charge-transfer complex at the gas-electrode interface was proposed as causing the sampler's decreased sensitivity at 1,800 ppb•hr.

Sulfur dioxide, a common air pollutant, decreased the amount of the charge-transfer complex formed in the presence of ozone. By adding a filter containing potassium permanganate to absorb the sulfur dioxide, the investigator eliminated this interference. Nitric oxide had no effect on ozone detection; however, exposing the sampler to equivalent amounts of NO_2 and ozone caused an additive effect (approximately 28%) on the formation of the charge-transfer complex.

Temperature was a major factor affecting the charge-transfer complex's stability on storage. After exposure to ozone, 90% of the initial charge-transfer complex was retained during storage in a refrigerator for 30 days. Storing the samplers at room temperature reduced the recovery of the charge-transfer complex to below 80%.

Conclusions

The ozone sampler designed by Dr. Yanagisawa is a clever device with a great potential for personal exposure measurement. One advantage of this sampler is the simplicity of quantifying ozone levels by measuring the discharge time of a charge-transfer complex. Because the charge-transfer complex is also stable for at least one month in the cold, analyses do not have to be performed soon after exposure.

Additional research is needed to improve the dynamic range of the sampler, especially its sensitivity at low ozone concentrations. Most of the performance data on this sampler were collected at relatively high ozone concentrations (for example, 200 ppb to 350 ppb); therefore, it is necessary to determine whether the sampler provides similar responses under conditions of low concentrations and long sampling durations. The field test reported in Appendix H of the Investigator's Report was performed at an early stage of sampler development; therefore, tests of the current sampler under field conditions are needed.

Because the sampler showed a positive interference by NO_2 that could not be attenuated, it must be considered a "total oxidant" sampler. In the event that sensitivity can be enhanced at low ozone levels, interference by NO_2 must be readdressed. Such interference may not be a problem at high ambient ratios of ozone to NO_2, but may represent substantial interference at lower ozone levels.

SUMMARY AND RECOMMENDATIONS FOR FUTURE RESEARCH

Drs. Hackney, Yanagisawa, Koutrakis and their collaborators each developed small, personal ozone collection devices based on different ozone reactions. There are positive aspects and notable limitations resulting from each group's efforts. One limitation in experimental design that was common to all three studies was that data from a reference ozone monitor were used in equations to calculate the sampling rate, and, hence, the ozone concentrations detected by the

experimental samplers. This concern was discussed in detail in the section on General Principles of Monitor Validation and in the evaluation of Dr. Koutrakis' nitrite-based sampler. In addition, each study could have used sophisticated statistical techniques that would have provided information on the optimal placement of the samplers, their accuracy and precision, the nonlinearity of the samplers' responses and limits of detection, and the samplers' responses to simultaneous changes in both temperature and humidity. None of the investigators took advantage of these techniques.

Both Drs. Koutrakis and Yanagisawa employed methodology related to ozone's redox potential; however, neither investigator provided compelling reasons why either method would be the best one available for ozone detection. A review of the theoretical reactions between ozone and other redox reagents may reveal comparable or superior reagents for ozone detection. Redox potentials are also important factors in designing a detection system that has minimal interferences from other atmospheric constituents.

The samplers designed by Dr. Hackney and colleagues are not amenable to further development because of the binary reagent's inaccuracy in detecting ozone at low levels of humidity in the active sampler and under ambient outdoor conditions in the passive sampler. Although the binary reagent appeared promising in early laboratory tests, the investigators' careful experimental work provided valuable information showing that it was problematic in a practical application. The light-tight sample holder they designed in this study may prove useful for other pollutant detection methods using light-sensitive reagents.

In terms of ruggedness, the iodide-based sampler developed by Dr. Yanagisawa has the advantage of simplicity; ozone concentrations are determined by measuring the discharge time of the charge-transfer complex formed between iodine and the nylon-coated disk. This can be done easily by technicians. However, before the sampler is ready for validation studies, its performance requires further improvement, particularly in its ability to detect low ozone concentrations over extended time periods. In addition, because of the positive interference by NO_2, the sampler must be considered a total oxidant, rather than an ozone-specific, sampler.

Dr. Koutrakis' nitrite-based sampler has already been used for microenvironmental and personal sampling of ozone levels indoors and outdoors (Liu et al. 1993). A positive feature of this method is the efficient separation of nitrate from unreacted nitrite ion. Although the ion chromatographic analysis requires somewhat greater technical expertise than does Dr. Yanagisawa's iodide-based sampler, the short time required for the separation of nitrate from nitrite makes this an attractive method for large epidemiologic studies. Recent unpublished data from other investigators (not presented in this report) indicates that interference by possible atmospheric copollutants appears to be minimal. Validation of Dr. Koutrakis' nitrite-based sampler by an independent laboratory would allow investigators to determine if the sampler's performance was adequate to meet the data quality objectives of a proposed study.

As part of a validation study, the sampler's accuracy should be established without using a standard reference monitor for calculating collection rates. For example, Dr. Koutrakis and colleagues have developed an active sampler using the same principle of ozone detection as their passive sampler. By colocating the active sampler with the passive sampler, the collection rate of the active and passive samplers could be compared in terms of the range of sampling rates actually experienced, the deviation of the passive sampler's collection rate from Fick's First Law of Diffusion, and the ozone levels measured by the two samplers. Such studies would provide information on each sampler's accuracy and precision. If the data obtained with the passive sampler are not significantly different from those obtained with the active sampler, and if the sampler's performance meets the quality assurance objectives of a proposed epidemiological study, it may be considered as valid for that study.

Reliable estimation of ozone concentrations experienced by individuals in their many daily microenvironments is critical to assess the health risks of ozone exposure. The contributions of each group of investigators, together with those of others who have developed ozone samplers as described in Appendix A, have moved researchers closer to achieving this goal.

ACKNOWLEDGMENTS

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APPENDIX A. Personal Samplers for Ozone

GROSJEAN AND HISHAM

DGA Inc, Ventura, CA. 1992

Methods. Passive. Direct reflectance spectroscopy. Loss of color by indigo carmine coated onto paper filters.

Range of Linearity. Indoor exposure chamber: sampler with plastic grid as diffusion barrier, 50 to 350 ppb•day ozone; sampler with Teflon filter as diffusion barrier, 200 to 400 ppb•day ozone. Field study of sampler with Teflon filter as diffusion barrier: 150 to 900 ppb•day ozone.

Limits of Detection. Plastic grid: 30 ppb•day (4.3 ppb•week) ozone. Teflon filter: 120 ppb•day (17 ppb•week) ozone.

Humidity Effect. Indoors: tested at 55% relative humidity. Field study: authors concluded that there was no effect (data not reported).

Temperature Effect. Field study: authors concluded that there was no effect (data not reported).

Interferences. Based on a common pollutant dose (including ozone) of 150 ppb•day: NO_2, +15%; PAN, +16%; HCHO, +4%.

Stability in Storage. Color stable for at least 12 months at room temperature.

HACKNEY AND ASSOCIATES

Environmental Health Service, Rancho Los Amigos Medical Center, Downey, CA. Investigators' Report in this volume. See also Avol et al. 1990.

Methods. Active and passive samplers. Spectrophotometric (visible) determination of product extracted from filter paper coated with a binary reagent.

Range of Linearity. Active sampler, indoor chamber tests: response flattened after 100 μg ozone collected by filter; response decreased at low (25%) relative humidity; no effect

of temperature. Active sampler, outdoor field tests: 50 to 150 ppb ozone; useful only for a one-hour exposure. Passive sampler, indoor chamber tests: relatively linear 200 to 2,000 ppm-min ozone; No effect of temperature and humidity combinations with the exception of an increased response at 39°C and 75% relative humidity. Passive sampler, outdoor field tests: overestimated ozone levels; sampler development was discontinued due to problems with the binary reagent used to detect ozone.

KANNO AND YANAGISAWA

Harvard School of Public Health, Boston, MA. Investigator's Report in this volume. See also Kanno and Yanagisawa 1992.

Methods. Passive. Oxidation of potassium iodine on nylon 6-coated carbon filter to I_2, followed by coulometric determination of charge-transfer complex formed between I_2 and nylon-6.

Range of Linearity. 400 to 1450 ppb•hr oxidants.

Limits of Detection. 400 ppb•hr oxidants.

Collection Rate. Unaffected by face velocity, temperature (5°C to 40°C), or 30% to 70% relative humidity; collection rate dropped at approximately 12% relative humidity.

Interferences. Negative effect of sulfur dioxide eliminated by potassium permanganate-coated filter; no effect of NO; NO_2 caused an increased response of 28% when added at the same level as ozone.

Stability in Storage. 90% of the charge-transfer complex was retained after storing the filters for 30 days at 4°C.

KOUTRAKIS AND ASSOCIATES

Harvard School of Public Health, Boston, MA. Investigators' Report in this volume. See also Koutrakis and Yanagisawa 1993.

Method. Passive. Oxidation by ozone of nitrite on glass fiber filter to nitrate. Ion chromatographic separation of nitrite and nitrate.

Range of Linearity. Indoor chamber tests: 20 ppb to 60 ppb ozone. Outdoor field tests: 15 ppb to 50 ppb ozone. Range: 400 to 12,000 ppb•hr; results from two separate data sets (indoors and outdoors).

Limits of Detection. 201 ppb•hr ozone (calculated).

Collection Rate. Increased with increased face velocity; affected by orientation of sampler to the wind; no effect between 10% and 80% relative humidity; no effect between 0°C and 40°C.

Interferences. Not reported in this study. Unpublished data from others (S. Colome, personal communication) indicates little interference by PAN, NO_2, sulfur dioxide, or nitrous acid; interference by hydrogen peroxide not expected to be significant at ambient levels.

Stability in Storage. Change of ± 0.5 ppm NO_3^- after ten weeks at 5°C.

MONN AND HANGARTNER

Federal Institute of Technology, Zurich, Switzerland. 1990.

Methods. Passive. Visible Spectrophotometry. Glass fiber filter coated with 1,2-di-(4-pyridyl)-ethylene.

Limits of Detection. 1.5 ppb ozone over a one-week period.

Humidity Effect. Small, unsystematic increase in color formation with increased humidity.

Temperature Effect. Not reported.

Interferences. Not reported.

Stability in Storage. 26.7% color loss over 28 days at 4°C.

PENROSE AND ASSOCIATES

Transducer Research Inc., Naperville, IL. See Penrose et al. 1990a,b.

Methods. Active. Amperometric electrochemical sensor with a selective chemical filter for ozone.

Range of Linearity. 5 to 500 ppb.

Limit of Detection. 10 ppb.

Humidity Effect. Small positive effect (+30% from 0% to 90% relative humidity).

Temperature Effect. Small positive effect.

Interferences. Sensor removes greater than 95% of O_3 and less than 5% NO_2.

Stability in storage. N.A.

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14	The Effects of Ozone and Nitrogen Dioxide on Lung Function in Healthy and Asthmatic Adolescents	J.Q. Koenig	1988
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