A Continuous, Real-Time, Miniature Ozone Monitor

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Abstract

In this study, a portable real-time ozone monitor has been developed. The ozone sensor consists of a piezoelectric quartz crystal coated with polybutadiene. The polybutadiene coating reacts irreversibly with ozone resulting in a mass increase on the surface of the crystal which, in turn, alters the natural oscillation frequency of the crystal. The rate of change in frequency is proportional to the concentration of ozone and is recorded by a datalogger with a time resolution of 10 minutes.

Major effort was devoted to designing and optimizing the configuration of the ozone sensor. The design variables included: (i) direction of sample air flow over the crystal, (ii) sample air flow rate, (iii) type of polybutadiene coating, and (iv) amount of coating. Experiments were conducted to investigate the sensor's response, useful lifetime, and potential interferences related to these variables. Monitor components such as a pump, power supply, and datalogger were specified and arranged to fit within a compact enclosure. Five ozone monitors have been assembled and evaluated in the laboratory and in a field study of two offices and two residences in Southern California. Measurements of indoor ozone concentrations were also made in a photocopy room in Berkeley, CA.

The ozone monitor has been shown to measure ozone levels with a response time comparable to ultraviolet (UV) photometric analyzers. Field measurements made with two quartz crystal-based ozone monitors and a UV analyzer exhibited precision and accuracy within 10 and 20%, respectively. When the monitor's detection limit for ozone was set to 30 ppb it exhibited a useful lifetime of ~20 hours at an average ozone concentration of 50 ppb (1000 ppb-hr). This new monitor is smaller, lighter, and more affordable than existing UV ozone analyzers.

Executive Summary

Introduction

Ozone is a widespread air pollution problem in California: five of the largest urban areas (Fresno, Los Angeles, Sacramento, San Diego, and San Francisco) currently do not meet State or Federal ozone air quality standards.

While ozone concentrations are monitored routinely in outdoor air, most people spend the majority of time indoors where ozone concentrations are not well known. To assess and reduce exposure, better knowledge is needed of ozone concentrations in indoor microenvironments.

Existing measurement methods for ozone include both real-time (continuous) and time-integrated samplers. The main real-time method involves ultraviolet (UV) photometric detection; this method is accurate and reliable, but the monitors are heavy, large, and expensive. They are cumbersome for microenvironmental sampling, and totally unsuitable for personal sampling. Current badge samplers provide only a single integrated measure of ozone concentration, are sensitive to face velocity in some cases, and may involve significant time and analytical expense before measurements are available. Since ozone concentrations exhibit a strong diurnal cycle, a small portable real-time sensor is desired to measure time-varying ozone concentrations in various indoor microenvironments.

Portable Ozone Monitor

The portable ozone monitor (POM) developed in this study uses a polybutadiene-coated piezoelectric quartz crystal. Ozone reacts irreversibly with polybutadiene and causes a mass increase on the crystal surface which is sensed as a shift in the crystal's oscillation frequency. An uncoated reference crystal compensates for the effect of changes in temperature on crystal response.

Performance objectives for the ozone sensor developed in this study are:

(1) dynamic range from 30 to 300 ppb,

(2) precision of 10% or better and accuracy of 20% or better when ozone is above 80 ppb,

(3) temporal resolution of 30 minutes or better,

(4) absence of significant interferences, defined as less than 10% of measured ozone at typical levels,

(5) light-weight and portable design of sampler suitable for microenvironmental sampling and personal monitoring, and

(6) unit production cost of $2,500 or less. Economies of scale should result in lower unit costs when multiple ozone monitors are built at the same time.

The approach to developing this sensor involved laboratory and field testing, sensor refinement and packaging, and microenvironmental sampling in two residences, two offices, and a photocopy room.

Sensor Design, Development, and Testing

Quartz crystals with 9.5 mm diameter gold electrodes and resonant frequencies of 10 MHz were coated on both sides with polybutadiene. Coatings were applied using a fine-bristled artist brush; crystals can be cleaned and reused after sampling. The coated crystal was configured in an impactor flow geometry with jets of sample air impinging on the crystal electrodes from both sides at an overall flow rate of 0.13 LPM. Air flow is provided by a small pump. Flow control is provided by a critical orifice; flow may be altered by substituting a different orifice and trading off sensitivity against useful sampler lifetime. A Nafion dryer is used upstream of the crystals to reduce artifacts related to differing uptake of water vapor by coated and uncoated crystals. The monitor components are configured in an enclosure measuring 25 cm x 35 cm x 13 cm with a total weight of 5 kg. The total cost of one monitor is less than $1700 and the cost of additional equipment needed to operate one or more monitors, not including 5 VDC power supply, frequency counter, and personal computer, is $750. The

monitor is relatively easy to operate for anyone familiar with gas analysis equipment. The coating procedure requires some practice, but can easily be mastered.

Sensor Performance

In laboratory testing, the ozone sensor measured ozone concentrations from 30 to 300 ppb accurately with a time resolution of 10 minutes or better. Initial response of the sensor to ozone was not linear, so a sampler preconditioning step (exposure to ~300 ppb of ozone for 40 minutes) was used to ensure the sampler operated in a linear regime. Useful lifetime of the sensor in laboratory tests was about 1000 ppb-hr.

Sensor response to nitrogen dioxide (NO_2) was 3% as strong as that of ozone at the same concentration (a higher interference by NO_2 was found with one type of polybutadiene coating that did not have a stabilizer included in its formulation). No interferences were detected in lab testing with nitric oxide (NO), nitric acid (HNO_3), and toluene. Sudden changes in water vapor concentration caused spikes in sensor response when a Nafion dryer was not used.

Field Evaluation

The ozone monitor was evaluated under real-world sampling conditions in two offices, two residences, and a photocopy room. Measurements were made inside each location with two piezoelectric ozone samplers and a UV photometric analyzer. At each residence, outdoor measurements were made with a piezoelectric and a UV photometric ozone monitor. Indoor readings made by the ozone monitor exhibited a precision of 4 to 9% (6% on average). All measurements made by the ozone monitor were within 2 to 17% (9% on average) of the UV photometric readings and exhibited a bias ranging from -17 to 3% (-5% on average) when ozone levels were greater than 30 ppb. The ozone monitor responded to rapid changes in indoor ozone levels caused by changing ventilation conditions and the use of a photocopier.

Summary and Conclusions

This study is the first demonstration of a portable, affordable, real-time ozone monitor. All performance objectives stated above were met or exceeded. The monitor provides new capabilities to measure diurnal variations in human exposure to ozone, and represents a major advance in the state of the art in techniques for ozone exposure assessment.

Recommendations

1. Further Interference Testing

The results of the interference testing conducted in this study are promising, but they do not address the questions of all indoor and outdoor interferences likely to be encountered in the field. Further laboratory and field interference testing should examine indoor pollutants such as cleaners, solvents and emissions from indoor combustion sources (e.g. gas stoves).

2. Further Sensor and Monitor Refinements

As described in section 2.2.1, the sensing crystal must be coated and conditioned with ozone before the POM can be used. Field studies conducted with the POM would be simplified if a batch of crystals could be coated, conditioned, and stored prior to the study. Further investigation of storage methods should be conducted. One possible method may be to continuously pass filtered air over the coated crystals during the storage period. This could be accomplished with an appropriate container, an activated carbon filter, and a small battery-operated pump.

The POM performed well during the microenvironmental sampling conducted in this study. However, as discussed in section 3.3.1, an initial POM measurement lag was observed during some sampling sessions. This initial lag should be examined further in laboratory and field testing. A possible remedy may include refining the conditioning procedure; this may include changing the ozone concentration and/or the duration of conditioning. A suitable storage scheme as described above may

also eliminate the lag by allowing the installation and immediate use of coated crystals at the sampling location.

The ability to sample for more than one day with the same coated sensing crystal would greatly improve the POM's ease of use. This could be accomplished by incorporating a partial duty cycle sampling scheme in which the sensor would only be exposed to sample air containing ozone for a fraction of the total sampling time and, thus, only a fraction of the coating would be exhausted compared to full duty cycle sampling. Sample air could be directed through the sensor for a period of time and then re-routed, via an automated valve, through a charcoal filter to remove ozone before reaching the sensor. For example, sample air could be monitored for 10 minutes every 30 minutes to provide an ozone concentration reading every 30 minutes. This would diminish the time resolution of the data compared to the current sampling scheme, but would improve sampler lifetime by a factor of three.

The POM performance described in this report can only be expected when Aldrich part no. 38-369-4 polybutadiene is used. If any other polybutadiene formulations are used calibration and interference testing must be repeated.

3. Further Field Testing

The field testing of the POM conducted in this study should be repeated for other microenvironments during other seasons. Sampling should be conducted both indoors and outdoors during the Spring and Summer in order to evaluate the performance of the POM at higher ambient ozone levels. Microenvironments to examine include residences and offices with different ventilation characteristics than those used in this study, schools, hospitals, and inside vehicles. To use the POM inside a vehicle would require that the POM be converted solely to battery power; this would require some simple re-wiring and a larger capacity rechargeable battery.

4. Microenvironmental monitoring

One suggested approach to estimating personal ozone exposure involves real-time monitoring of ozone concentrations in all microenvironments in which an individual spends time. The sensor developed in this project is well-suited to this task, and its capabilities should be demonstrated during an upcoming "instrumented house" study in California. Further development of the sensor will be needed to allow for larger-scale deployments in field studies designed to assess ozone exposure. Eliminating the need for sensor preconditioning at the beginning of each sampling day would reduce the set-up time and costs of using the sensor.

5. Personal monitoring

We believe an exciting future application of piezoelectric crystal-based sensing will be in real-time personal ozone monitoring. This application should be pursued and compared with results of ozone exposure assessment that are based on microenvironmental monitoring and time-activity diaries. Further reductions in the weight, size, and energy demand of the sensor will be required for use as a personal monitor.

1 Introduction

Ozone is a common air pollutant that is known to have adverse effects on human health. There is extensive evidence of acute effects at concentrations well within the typical range of ambient levels (Lippmann, 1993; Burnett, 1997). Limited data also suggest chronic effects (Tyler 1992; Kunzli et al., 1997). Ozone is a widespread air pollution problem in California — five of the largest urban centers (Fresno, Los Angeles, Sacramento, San Diego, and San Francisco) currently do not meet State or Federal ozone air quality standards.

1.1 Need for Indoor and Personal Ozone Monitoring

Both the epidemiological evaluation of the adverse human heath effects associated with ozone exposure and the development of effective ozone control strategies require monitoring in all environments in which people are exposed to ozone. Ozone concentrations are routinely measured outdoors. However, in-transit and indoor exposures may dominate the total ozone exposure, and perhaps, total ozone dose. Time activity studies funded by the California Air Resources Board demonstrated that people over the age of 11 spend an average of 87% of all time indoors or in-transit (Jenkins et al., 1992). Children under the age of 12 spend an average of 90% of all time indoors or in-transit (Phillips et al., 1991). Therefore, detailed knowledge of indoor and in-transit exposure levels is needed to assess acute ozone exposures accurately. Neither of these environments is well-represented by outdoor measurements of ozone concentrations, and indoor-outdoor concentration ratios are highly variable. Indoor occupational exposures from copy machines, computer laser printers, and arc-welding equipment also may be significant.

With current ozone monitoring data it is difficult to estimate individual exposure levels. Indoor ozone concentrations are not measured routinely. Special studies, such as those of Avol et al. (1998),

Weschler et al. (1989, 1991), Nazaroff and Cass (1986), and Shair and Heitner (1974), indicate that indoor levels range from 10 to 80% of outdoor levels, depending on the type and rate of ventilation. Especially high indoor ozone concentrations can occur during the late afternoon and early evening if windows and outside doors are opened to provide cooling. More extensive microenvironmental measurements are necessary to quantify ozone levels in indoor environments where people spend the majority of their time. Knowledge of indoor ozone concentrations is also needed to determine the indoor rates of chemical reactions (e.g., ozone/olefin reactions) that form other secondary pollutants. For example, indoor concentrations of acetaldehyde, C_5-C_{10} aldehydes, and particles have been correlated with indoor ozone concentrations (Zhang et al., 1994; Weschler and Shields, 1999).

Because ozone is formed photochemically in the atmosphere, there is a strong diurnal cycle in ambient ozone concentrations. Research has shown that an individual's response to ozone is more strongly associated with the shape of the ozone concentration profile than the total exposure dose (Hazucha et al., 1992). Therefore, high temporal resolution is needed for both microenvironmental and personal ozone monitoring. To compute personal ozone dose accurately, detailed knowledge of indoor and outdoor ozone concentrations must be related to activity/exercise level and respiration rate. Use of 8-hr average ozone concentrations and respiration rates can seriously underestimate the total ozone dose, especially if peak activity periods occur when outdoor ozone is highest. For example, people are often active outdoors at times when ambient ozone concentrations are elevated. As discussed below, existing personal ozone monitors yield a single integrated measurement averaged over 8 hours or longer.

To quantify the exposure of a subject population to ozone, small and unobtrusive, real-time, and inexpensive indoor and personal monitors are needed. Such monitors are needed to quantify ozone in indoor environments, and to develop further and validate exposure assessment models (Peters, 1994). Improved time resolution in tracking ozone concentrations is needed for exposure model development and evaluation (Lurmann, 1998). This information is needed to develop cost-effective strategies to reduce ozone exposure. For example, with an improved ability to measure indoor and outdoor ozone concentrations, the effectiveness of different ventilation and air conditioning strategies for reducing indoor ozone could be tested.

1.2 Review of Existing Methods

The EPA-approved method for measuring ozone in ambient air is UV photometric detection. These monitors, while well-tested and reliable, are expensive, large, and noisy. As such, they are not ideal for microenvironmental sampling, and are totally unsuitable for personal monitoring. As an alternative, diffusive and pumped ozone badges have been developed for microenvironmental and personal monitoring. As described below, these badge and tube samplers provide a single integrated measurement of ozone concentration.

A diffusive ozone badge has been developed by Koutrakis et al. (1991, 1993). It uses a sodium nitrite-impregnated filter which is oxidized to nitrate in the presence of ozone. The sampler measures 4 x 3.4 cm and is easily clipped onto the subject's shirt. The detection limit of the badge, defined as three standard deviations of the blanks, is 200 ppb-hr, which corresponds to 25 ppb over eight hours of sampling. The total capacity of the badge, defined as 5% of the conversion of the total nitrite ion, is 20,000 ppb-hr. One disadvantage is that the effective sampling rate can vary by a factor of two depending on ambient air face velocity, as shown by laboratory wind tunnel tests (Koutrakis et al., 1993). Interferences for this sampler have been studied in chamber tests which show insignificant influences from PAN, HONO and SO_2 (Lurmann et al., 1994).

A timed exposure diffusion (TED) ozone sampler was developed for and used in a children's health study conducted in Southern California (Peters, 1997). The TED sampler provides controlled airflow across two sodium nitrite-impregnated filters. The sampler uses a 7-day timer that can be set to sample for specific hours of the day on specific days of the week. The TED sampler responded to nitric acid and hydrogen peroxide in laboratory tests (Lurmann et al., 1994). In field evaluations the sampler measured ozone with a +6% bias and ±12% precision on average compared to a continuous monitor (Lurmann et al., 1994).

Because of the limitations of the diffusive badge design, in particular the influence of wind speed on the measured ozone, Koutrakis and coworkers have developed an active sampler consisting of a pumped hollow-tube diffusion denuder. The hollow etched Pyrex tube is 10 cm long, has an inside

diameter of 1.4 cm, is pumped at 65 mL/min, and is coated with the same sodium nitrite reagent used in the diffusive badge design described above. Chamber tests show no response to relative humidity, and an improved detection limit of 45 ppb-hr (Geyh et al., 1994).

Another passive ozone badge has been developed for long-term sampling of atmospheric ozone in remote locations (Grosjean and Hisham, 1992). It uses indigo carmine colorant, which fades upon reaction with ozone. The color change is measured by reflectance spectroscopy. Depending on sampler configuration, detection limits are 30 to 120 ppb-day. In laboratory chamber studies, Grosjean and Hisham found positive biases of 15%, 16%, and 4% when NO_2, PAN, and formaldehyde concentrations, respectively, were equal to ozone levels being tested. Field comparison of the method using a continuous ozone monitor gave a regression slope of color change versus ozone dose which differed by only 2.4% from that obtained in laboratory studies with pure ozone, indicating that interferences were small. The effects of variation in wind velocity on sampler performance have not been evaluated.

A third ozone badge is that of Kanno et al. (1992). This sampler uses a carbon paper disk coated with nylon-6 polymer and potassium iodide (KI). Iodine is liberated by the oxidation of KI with ozone; the I_2 is then stabilized by forming a charge transfer complex with the nylon-6 and is later analyzed by constant current coulometry. Kanno et al. achieved a time resolution of 1 hour at an ozone concentration of 300 ppb; detection limit was not reported. Kanno et al. report substantial positive response resulting from water vapor and decreased response for temperatures above 40 °C. Face velocity effects on sampler performance are not known.

Avol et al. (1989) evaluated a pumped ozone badge that employs a personal sampling pump. It uses a solid monitoring reagent which develops a visible color change that is quantifiable with acetone extraction and spectrophotometric analysis. For stationary ambient sampling, Avol et al. found excellent agreement between their badges and a continuous ozone analyzer. Linear regression gave a slope of 0.98, intercept of -0.8 $\mu g/m^3$ (0.4 ppb), and a correlation coefficient of 0.90. Badges worn by subjects gave lower ozone readings, slope = 0.80, but the correlation coefficient of 0.92 indicated good

agreement between measurements made by ozone badges worn by subjects and continuous ozone analyzer measurements.

There are other commercially available ozone sensors. The authors were unable to fully evaluate these sensors because published performance data were not available. These include the Ecosensor and the Ecobadge that measure ozone with a heated metal oxide semiconductor and a colorimetric badge, respectively.

1.3 Limitations of Existing Methods

A limitation of all of the above badge methods is that they only yield a single integrated ozone measurement over averaging times that are long relative to time scales over which ozone concentrations change. While such measurements may be useful in calculating long-term average ozone exposures, they do not supply sufficient information regarding ozone peaks for estimating acute ozone exposures. Most badge samplers are sensitive to face velocity (i.e., measured concentrations can change with wind speed and how fast the subject is moving). Furthermore, the time and expense involved in extracting and analyzing the badge samples can be high.

1.4 Piezoelectric Ozone Sensor

The ozone monitor developed in this study consists of a polybutadiene-coated piezoelectric crystal. A jet of sample air is directed at each side of the crystal, and the polybutadiene coating on the crystal reacts irreversibly with ozone. This reaction causes a mass increase on the crystal which is sensed as a shift in the beat frequency between the coated crystal and an uncoated reference crystal. The rate of change of the beat frequency is proportional to the concentration of ozone in the sample air.

Piezoelectric crystals have been used for several decades to measure airborne particulate matter mass concentrations (Chuan, 1970; Olin and Sem, 1971). The use of piezoelectric crystals for mass and chemical measurements has been reviewed by Guibault and Jordan (1988). Gaseous pollutant concentrations have been measured using chemically-coated piezoelectric crystals, for a variety of compounds including ammonia, formaldehyde, hydrogen cyanide, hydrogen sulfide, and phosgene,

among others. There is one previous study (Fog and Reitz, 1985) reporting the use of polybutadiene-coated piezoelectric crystals for ozone measurement over short periods of time (~15 minutes).

Performance objectives for the ozone sensor developed in this study are:

(1) dynamic range from 30 to 300 ppb,

(2) precision of 10% or better and accuracy of 20% or better when ozone is above 80 ppb,

(3) temporal resolution of 30 minutes or better,

(4) absence of significant interferences, defined as less than 10% of measured ozone at typical levels,

(5) light-weight and portable design of sampler suitable for microenvironmental sampling and personal monitoring, and

(6) unit production cost of $2,500 or less. Economies of scale should result in lower unit costs when multiple ozone monitors are built at the same time.

1.5 Approach

Sensor Development and Laboratory Evaluation

Development of a polybutadiene-coated quartz crystal sensor for ozone measurement will be described. Issues addressed in the laboratory testing include (i) development of an appropriate coating technique with the objectives of maximizing dynamic range and lifetime, (ii) optimized flow geometry for the sensor, and (iii) interferences from water vapor, NO, NO_2, and nitric acid.

Preliminary Field Testing

The polybutadiene-coated quartz crystal-based sensor was operated outdoors alongside a UV photometric ozone monitor and intercompared. Replicate piezoelectric ozone monitors ran side-by-side with the photometric monitor: three days of field sampling were performed. The primary purpose of the preliminary field testing was to evaluate interferences which are beyond those that were tested in the laboratory.

Sensor Refinement, Packaging, and Retesting

Laboratory and field testing pointed to some improvements to the design of the sensor. These improvements were implemented and the sensor was retested in the laboratory. Additionally, the sensor was packaged in a way which is suitable for microenvironmental measurements for use in homes, schools, and offices. The resulting piezoelectric ozone monitor (POM) was enclosed in a small, tamper-resistant box with a datalogger so that unattended operation is possible.

Microenvironmental Field Testing

The new ozone monitor was used to measure ozone concentrations in five locations—two residences, two offices, and a photocopy room. Indoor ozone concentrations were measured in each location independently using a UV photometric monitor. Data were analyzed to quantify the performance and interferences of the ozone monitor. Statistical and graphical analyses of the data are presented to assess the accuracy and precision of the ozone monitor in comparison to the UV photometric monitor.

2 Sensor Design, Development, and Testing

2.1 Materials and Methods

2.1.1 Piezoelectric Crystals

Piezoelectric crystals are materials that have specific electromechanical properties. When an electric field is applied across a piezoelectric crystal it mechanically vibrates at a stable resonant frequency. An electronic oscillator circuit connected to the crystal will, in turn, oscillate at the crystal's resonant frequency (Olin and Sem, 1971). The stability of the resonant frequency makes piezoelectric crystals useful for a wide array of sensing applications. Mass-based sensing applications are possible because mass changes on the surface of the piezoelectric crystal alter the rate of vibration of the crystal and thus alter the resonant frequency.

The piezoelectric material selected for the ozone sensor in the present study was alpha quartz, the most widely used material for piezoelectric crystal sensors (Olin and Sem, 1971). The frequency characteristics of quartz crystals depend upon the cut of the quartz plates. Quartz plates cut with what is known as an AT cut achieve the best mass response (Hiavay and Guilbault, 1977). In the present study AT cut quartz crystals with diameters of 14 mm were used.

The electric field necessary to drive the quartz crystal is typically applied by means of electrodes attached to each side of the crystal (Figure 2.1). Each electrode is circular with a tab that connects to a wire contact/support on one side of the crystal. The amount and distribution of the electrode material determines the resonant frequency of the crystal. Each crystal used in this study had a resonant frequency of 10 MHz. Initial experiments were conducted with electrodes that consisted of multiple layers of metals such as chromium, nickel, and silver. However, it was discovered that single-layer gold electrodes could be produced within closer tolerances of the
10 MHz resonant frequency. Therefore, the majority of sensor development was conducted with

single-layer gold electrodes with a diameter of 9.5 mm. Diameters of 5 mm and 11.5 mm were also examined. All crystals were supplied by International Crystal Manufacturing Co. (Oklahoma City, OK).

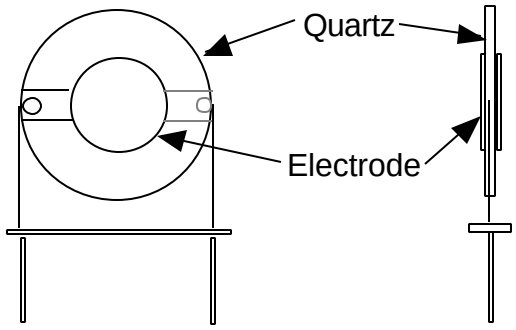


Figure 2.1. Piezoelectric quartz crystal (typical quartz crystal and electrode diameters are 14 and 9.5 mm, respectively).

While the resonant frequency of a quartz crystal is exceptionally stable with respect to time, it varies slightly with temperature. A type AT crystal typically has a temperature coefficient of about 0.05 ppm per degree Celsius over the range of outdoor temperatures (Olin and Sem, 1971). In other words, a temperature change of 2 °C will cause a 1 Hz frequency shift with a 10 MHz crystal. The temperature coefficient of quartz crystals is not constant; it can vary from crystal to crystal. Frequency shifts may also be caused by the adsorption of gases, such as water vapor, onto the electrode surface (Olin and Sem, 1971).

Because of these extraneous causes of frequency shift, the ozone sensor developed in this study uses two quartz crystals—a chemically-coated sensing crystal and an uncoated reference crystal. Both crystals are exposed to the sample air flow and should respond similarly to changes in air temperature and humidity, while only the coated sensing crystal will respond to ozone. Both the sensing and reference crystals must be temperature matched to prevent sensor drift as temperature varies. Crystals that have AT cut angle values (provided by the manufacturer) within 0.1 degrees can be considered temperature matched.

The beat frequency is defined as the difference between the coated crystal frequency and the uncoated crystal reference frequency. The electronic components that drive the crystal frequencies and mix the beat frequency are configured on a circuit board supplied by California Measurements, Inc. (Sierra Madre, CA). The beat frequency is generated by subtracting the sensing crystal oscillator circuit frequency from the frequency produced by the reference crystal oscillator circuit. The beat frequency, therefore, is intended to minimize sensor drift due to changes in temperature and humidity.

2.1.2 Polybutadiene

It has long been known that ozone reacts with the carbon-carbon double bonds found in natural rubber. In fact, in the 1950s ozone concentrations in ambient air were monitored by measuring the time for cracking to appear in a stretched section of rubber (Finlayson-Pitts and Pitts, 1986).

Polybutadiene is an unsaturated polymer with one double bond for every four atoms of carbon, and has been shown to be a suitable crystal coating for sensing ozone (Fog and Reitz, 1985). Ozone reacts with the double bond to form an unstable ozonide. The ozonide breaks down into a variety of species including aldehydes and alkyl radicals (Razumovski, 1984). It is not clear what products of the ozone/polybutadiene reaction remain attached to the crystal surface, but it has been shown that the mass of the coating increases upon reaction with ozone (Fog and Reitz, 1985).

Polymers consist of a long chain of monomers. In the case of polybutadiene, the polymer can have two forms—1-4 addition and 1-2 addition (Figure 2.2). A butadiene monomer has two double bonds and four carbon atoms (Figure 2.2). A butadiene polymer has only one double bond for every four carbon atoms because one of the double bonds is broken and used to connect the monomers to form the polymer chain. The monomers are named to indicate which carbon atoms are bonded when monomers are connected (added) to form a polymer. For example, 1-4 addition indicates that the first carbon atom in one butadiene monomer bonds to the fourth carbon atom in the adjacent butadiene monomer.

Two compositions of polybutadiene were evaluated in the present study; both were supplied in the form of a viscous liquid (Aldrich Chemical Co., Milwaukee, WI). One had an average molecular

weight of 5000 and consisted of 80% 1-4 addition and 20% 1-2 addition polymers (coating A; part no. 38-369-4). The other type of polybutadiene had an average molecular weight of 3000 and consisted of 99% 1-4 addition and 1% 1-2 addition polymers (coating B; part no. 43-478-7). The average molecular weight indicates the average length of the polymer chains. The polybutadiene described above, therefore, consisted of chains of ~90 and ~60 monomers, respectively. The 1-4 addition polymers form straight chains while the 1-2 addition polymers form branched chains (Figure 2.2).

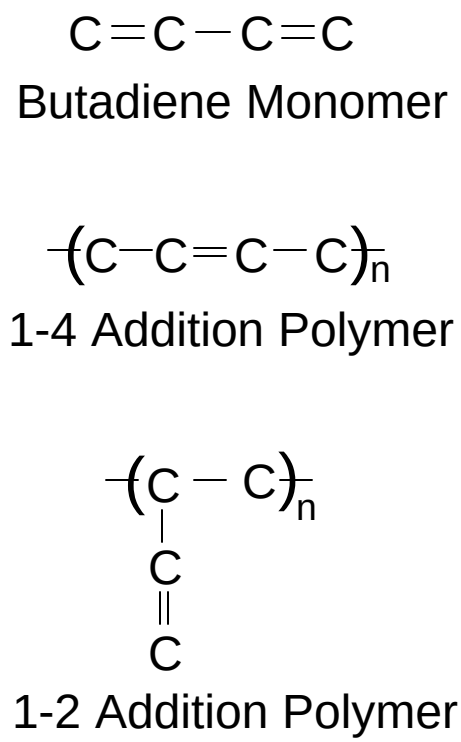


Figure 2.2. Butadiene monomer and its polymers. (n=number of monomers in chain)

2.1.3 Coating and Cleaning Procedures

A critical issue affecting the performance of piezoelectric crystals as ozone sensors is the method used to apply polybutadiene to the surface of the crystal's electrode. The amplitude of the vibration of the crystal attenuates rapidly outside the perimeter of the electrode-covered portion of the crystal (Hillier and Ward, 1992). Thus, only the electrode was coated with polybutadiene. The amount

of polybutadiene applied to the surface of the sensing crystal was measured as a shift in the sensor's beat frequency in units of kHz. To measure the mass of coating applied, a frequency counter such as those found on many standard electronic multimeters was required. In this study a Fluke 79 Series II multimeter was used. During coating, the sensing and reference crystals were installed in a fixture that contains the signal mixing electronics discussed above.

There is an electrode on each side of the quartz crystals. Thus, if both sides of the crystal are exposed to sample air, coating both electrodes of the sensing crystal with polybutadiene effectively doubles the response to ozone, compared to coating only one electrode. In the present study, the total amount of coating applied on both electrodes is reported as a single increase in beat frequency. The mass of coating was divided equally between the two sides of the crystal by applying half of the total desired mass of coating to one electrode and then applying an equal mass of coating to the other electrode.

Variations in coating thickness or area of coverage could lead to variability in sensor response to ozone, so it was important to create a repeatable coating procedure. Initially, an air brush was used to apply a 0.1% mixture of polybutadiene in toluene. Coatings applied with the air brush were often irregular and required several passes before a sufficient amount of coating was applied. The air brush could not be used to coat the sensing crystal while it was installed in the electronics fixture because the reference crystal blocked one side of the sensing crystal. The air brush was therefore used to apply polybutadiene to the sensing crystal while it was outside of the electronics fixture. The crystal was then installed in the fixture to measure the amount of coating that had been applied, and removed again to apply additional coating. This laborious and time-consuming process was repeated until the desired amount of coating was applied.

As an alternative to the air brush technique, pure polybutadiene was applied directly to the crystal surface with a cotton-tipped swab. A major benefit of this method was that the coating could be applied quickly while the sensing crystal was installed in the electronics fixture. Coatings produced with this technique had fairly uniform thickness, however, they were sometimes contaminated by cotton fibers left by the swab.

The coating technique was further improved by using a fine-bristled artist brush in place of the cotton-tipped swab to apply polybutadiene to the sensing crystal while it was installed in the electronics fixture. An amount of coating greater than desired was applied to one electrode and spread evenly. Excess coating was then removed by wiping the brush with a lint-free tissue between brush strokes that were made in an even pattern. When the desired amount of coating was achieved the process was repeated for the other electrode. This method of polybutadiene application proved to be highly reliable and repeatable.

Coated crystals were cleaned after each use so that the crystal could be reused (the reuse of crystals reduces the operating cost of the ozone sensor). Used polybutadiene was removed with a cotton swab and a solvent such as toluene.

2.1.4 Sensor Housing Test Fixtures

The majority of sensor development was conducted with two sensor housing test fixtures: (i) a Teflon housing with a parallel flow configuration in which sample air flows across both sides of the sensing and reference crystals (Figure 2.3) and (ii) a Teflon housing with an impactor flow configuration in which sample air impacts each side of the sensing crystal and passes over the reference crystal before exiting the fixture (Figure 2.4).

Parallel Flow Test Fixture

Two prototype fixtures were designed, machined, and assembled at UC Berkeley. The base of the prototype consists of an aluminum plate with four legs (Figure 2.3). The printed circuit board containing the oscillation and mixing electronics that produce the beat frequency output was mounted to the underside of the base plate and requires a 5 VDC power supply. A Teflon platform mounted on top of the base plate holds two quartz crystal sockets (Figure 2.3). Leads from the sockets pass through an opening in the base plate and connect to the circuit board. To achieve parallel flow, the Teflon housing guides the sample air across the crystals and has an inside diameter of 2.5 cm. The ends of the housing are equipped with Swagelok fittings made of stainless steel. The 10 cm length of the flow cell inside the housing insures a uniform flow across the crystals at flow rates up to 2 LPM. An o-ring seals the connection between the Teflon housing and the platform, making the assembly leak-tight (Figure 2.3).

Impactor Flow Test Fixture

The impactor test fixture was created by modifying the parallel flow fixture described above. In order for sample air to impact both sides of the sensing crystal it must be raised above the reference crystal with a socket (Figure 2.4). Since jets of air must enter each of the two openings along the axis of the flow cell, air must be drawn through an opening near the base of the flow cell. An adapter was fitted to the fixture to accommodate both the increased height of the crystal and the air flow requirements. Several different sizes of Swagelock fittings were machined so that Teflon tubing of various diameters could pass through them, but still maintain an airtight seal around the tubing. This accommodated testing of jet diameters of 3/16 and 5/16 inch. The jets could also be positioned at various distances from the surface of the sensing crystal. Distances of 1/2 and 1 inch were examined.

2.1.5 Pumps and Flow Control

The flow rate of sample air over the crystals was controlled with a diaphragm pump fitted with a needle valve and a standard glass-ball rotameter. The rotameters were calibrated with a bubble flow meter provided by Gilian Inc. (Johannesburg, South Africa). Before air entered the sensor housing it first passed through a 47 mm diameter Teflon filter holder (Savillex, Minnetonka, MN).

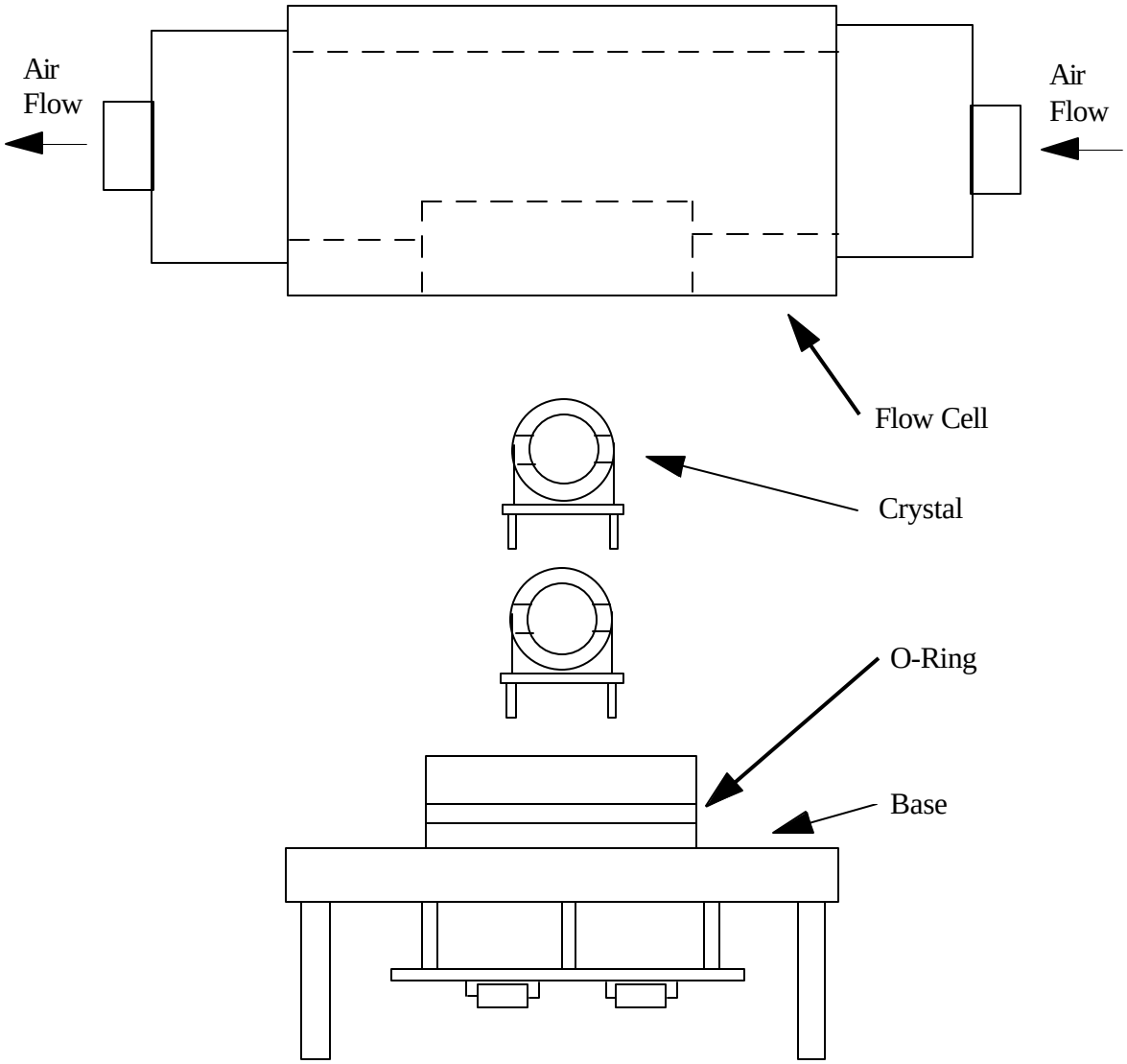


Figure 2.3. Parallel flow test fixture.

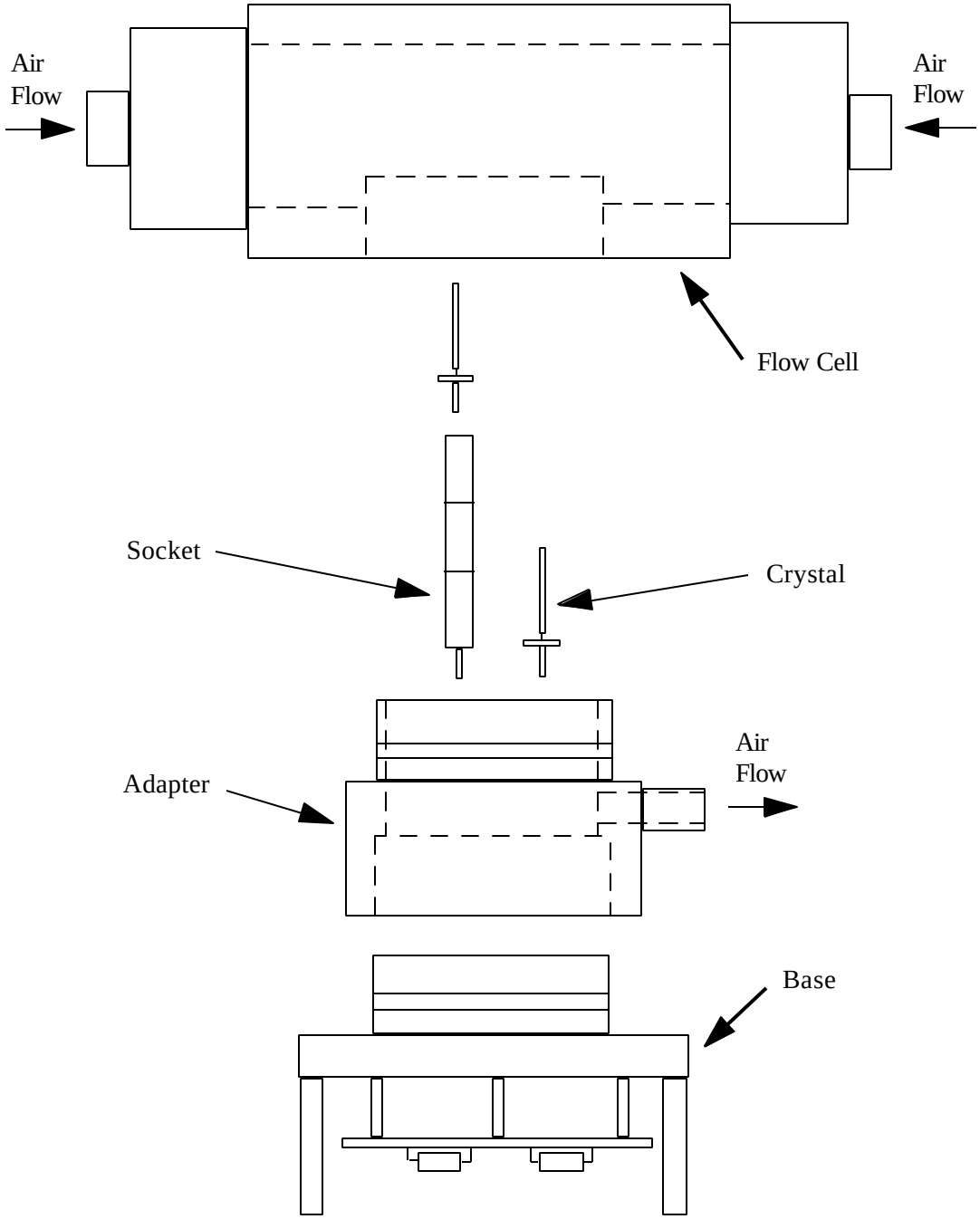


Figure 2.4. Impactor flow test fixture.

2.1.6 Datalogging and Conversion to Ozone Concentration

The beat frequency output of the quartz crystal ozone sensor was recorded by a laptop computer equipped with a Labview data acquisition system (National Instruments, Austin, TX). The Labview system was programmed to measure the frequency of the sensor output by increasing a counter each time the output square wave passed from low to high. To determine the frequency, the number of counts was divided by the period of time over which the counting occurred. The resolution of the frequency measurement was inversely proportional to the counting time period. For example, time periods of 1 sec and 4 sec provided resolutions of 1 Hz and 0.25 Hz, respectively. However, the time period was limited by the capacity of the counter. The Labview system used a 16 bit counter and, thus, could make a maximum number of 65,536 counts. For resolutions of 0.25 and 1 Hz the maximum frequency that could be measured was 16,384 and 65,536 Hz, respectively. The maximum beat frequency observed during the sensor development was ~20 kHz, but it was typically below 16 kHz. Therefore, the majority of the development was conducted with the Labview system configured to record data with a resolution of 0.25 Hz.

The output frequencies of two sensors were logged simultaneously to a spreadsheet file at 20 second intervals. The ozone level measured by each sensor was proportional to the rate of change of its beat frequency (Hz min^{-1}), and this rate was determined by analysis of the acquired data.

Two steps were required to convert the beat frequency data to ozone concentration. First, a running average of the rate of change of the beat frequency was calculated; the averaging time determines the time resolution of the sensor measurements. Second, the rate of change of the frequency was multiplied by a calibration factor that converts Hz min^{-1} to ppb of ozone. The calibration factor depended on the sensor flow geometry, air flow rate, electrode diameter, and type of polybutadiene coating. Calibration factors were determined using known levels of ozone measured simultaneously by a UV photometric ozone monitor.

2.1.7 Portable Ozone Monitor (POM) Design

The components described above can be configured to make ozone measurements. The resulting assembly, while useful for development purposes, was not optimized for use in field sampling. To meet our design objectives, small and lightweight, yet robust versions of the components described above had to be specified. These components were then configured to fit within a portable enclosure (Figure 2.6 and 2.7). The monitor measures 25 cm x 35 cm x 13 cm and weighs 5 kg.

Enclosure

A rectangular metal enclosure measuring 25 cm x 35 cm x 13 cm and weighing 2.5 kg was selected to house the POM. The lid of the box wraps halfway down two sides of the box to provide easy access to the monitor components. The components could fit within a smaller enclosure (23 cm x 23 cm x 13 cm), but the larger size was chosen to allow for layout modifications that might have been needed as testing of the monitor progressed. The metal enclosure was selected for its structural durability, however, it accounts for half of the monitor's total weight. Use of a plastic enclosure could greatly reduce the total weight of the monitor.

Sensor Housing

As described in section 2.2.1, an impactor flow configuration was chosen for the final monitor design. The base of the sensor is similar to the prototype fixtures described above and consists of an aluminum plate with four legs (Figure 2.8). The printed circuit board containing the oscillation and mixing electronics that produce the beat frequency output is mounted to the underside of the base plate. The base is isolated from the metal enclosure with rubber washers. A Garolite platform mounted on top of the base plate holds four gold sockets, two for each crystal (Figure 2.5 and 2.8). Garolite is a material that circuit boards are often made from and was chosen for its resistance to high temperatures associated with soldering. The round sockets are press fit through holes in the platform and wire leads are soldered to the sockets. The leads from the sockets pass through an opening in the base plate and connect to the circuit board. The platform is rectangular with round corners. The rectangular shape is

smaller than a corresponding circular shape and the rounded corners enable sealing with an o-ring. Viton was selected as the o-ring material due to its resistance to a wide range of chemicals.

The sensing and reference crystals are covered with a rectangular aluminum housing (Figure 2.8). The housing press fits over the o-ring on the platform and is secured by four screws. The sensor housing, including the base, measures 7 cm x 8 cm x 9 cm and weighs about 500 g. The impactor configuration allows the use of aluminum instead of Teflon because sample air passes directly from the stainless steel fittings mounted in the sides of the housing to the surface of the sensing crystal. Aluminum is also inexpensive, lightweight, and easy to machine. Stainless steel was chosen for the inlet fittings because of its low reactivity with ozone and its low cost and higher durability compared to Teflon. After sample air impacts the sensing crystal it passes over the reference crystal in parallel flow before exiting through a Swagelock fitting mounted in the end of the housing (Figure 2.8).

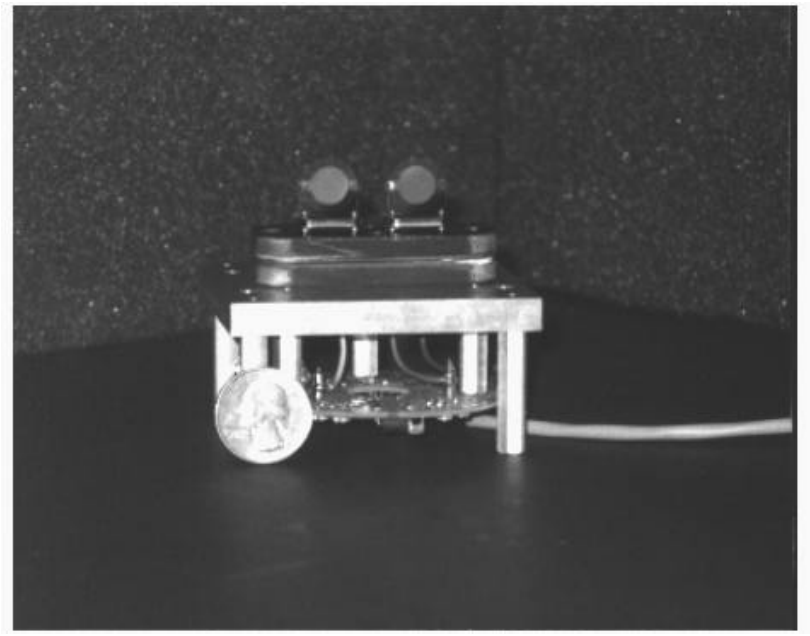


Figure 2.5. Sensor base with crystals exposed. Quarter shown for scale.

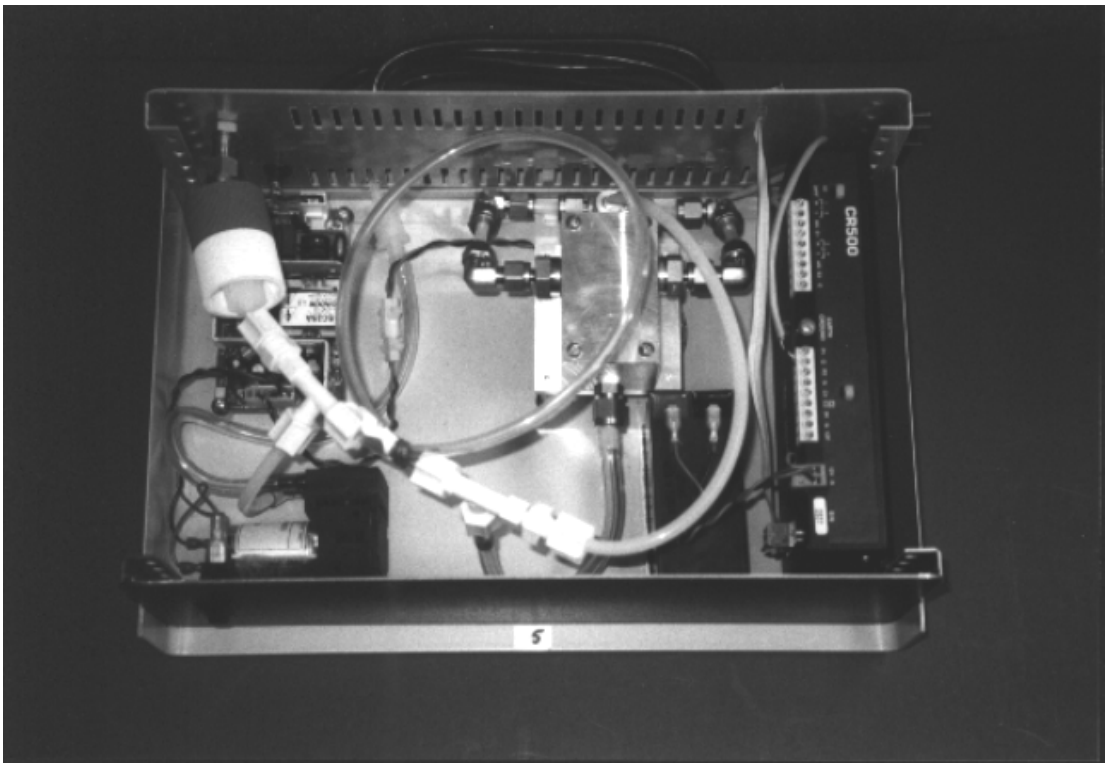


Figure 2.6. Overhead view of portable ozone monitor (POM) with lid off.

Sample Air Flow Control and Filtering

Before sample air reaches the sensor housing it passes through a 25 mm diameter Teflon filter holder (Savillex, Minnetonka, MN) and a Nafion gas dryer (Perma Pure, Toms River, NJ). The filter and dryer limit sensor interferences that could be caused by particle impaction and water vapor adsorption. The Nafion membrane is a polymer containing Teflon and a compound that reacts with water molecules, but does not react with gases such as ozone. Captured water molecules are passed from inside to outside the Nafion material allowing the Nafion to continuously remove water vapor from sample air. Laboratory experiments have shown that the relative humidity (RH) of air downstream of the dryer is 9-13% when the RH of the upstream air is 30-86% (Table 2.1). Also, minimal difference in ozone levels upstream and downstream of the dryer were observed for ozone levels of 30, 50 and 100 ppb (Table 2.1).

Table 2.1. Performance of Nafion dryer when presented with ozone and water vapor.

		Upstream		**Downstream**		
Q (LPM)	**DP (in. Hg)**	**RH (%)**	**[O_3] (ppb)**	**RH (%)**	**[O_3] (ppb)**	**D[O_3] (ppb)**
0.13	18	30	31.4	11	31.2	-0.2
0.13	18	38	52.5	11	52.1	-0.4
0.13	18	80	110.2	12	109.6	-0.6
0.2	17	32	29.7	10	29.5	-0.2
0.2	17	51	46.7	9	46.2	-0.5
0.2	17	86	100.2	13	99.5	-0.7

The dryer is configured with a 1/16 inch O.D. Nafion tube inside a 1/4 inch O.D. tube; both of which are 24 inches long and can be coiled to a minimum diameter of 6 inches. In the POM the dryer is configured in a counter-current flow scheme in which sample air first passes through the Nafion tube before entering the sensor housing. After exiting the housing the sample air is then routed through the larger outside tube. As the dry air flows through the larger tube it collects the water molecules that passed from the inside to the outside of the Nafion tube. In the counter-current flow scheme the return

flow in the outer tube must be pulled at a vacuum of at least 15 inches of Hg relative to the sample air in the Nafion tube.

After the sample air passes through the particle filter and the dryer it is split equally between the two inlets on the sides of the sensor housing. The rate at which air flows through the inlets is controlled by a critical orifice installed between the housing exit and the dryer return inlet. The sample air flow rate can be varied by installing the desired critical orifice. The critical orifice is a 1/4 inch O.D. stainless steel tube that is 5 cm long and open at one end and nearly closed at the other. The nearly closed end has a small opening with a diameter proportional to the desired flow rate. When air is pulled through the orifice at a vacuum of at least 15 inches of Hg the flow rate of the air is constant. The flow rate is independent of the level of the vacuum as long as it is greater than 15 inches of Hg. The orifice control is positioned downstream of the housing to avoid leaks in both the housing and the upstream plumbing that may be caused by exerting a vacuum on those components.

Pump

For microenvironmental and personal monitoring a small, lightweight, quiet pump with low power consumption is desired. For this monitor application the pump must also be able to pull a vacuum greater than 15 inches of Hg. The POM uses a diaphragm pump (KNF Neuberger, Trenton, NJ) that measures 8 cm x 3.5 cm x 5.5 cm, weighs 180 g, and can pull a vacuum of at least 15 inches of Hg at flows up to 0.8 LPM. It operates on 12 VDC and can be powered with a battery. However, with its current draw of 250 mA, a large rechargeable battery would be needed for sampling times in the range of 10 hours. For this reason an AC to DC power supply was used for the microenvironmental ozone monitoring described later in this report.

Power Supply

The sensor circuit board (5 VDC, 50 mA) and the pump (12 VDC, 250 mA) are powered with a switching power supply (Condor DC Power Supplies, Oxnard, CA). The input to the supply can range from 100-240 VAC and 47-62 Hz. Therefore, the supply was fitted with a standard three prong

grounded power cord. The supply (with standoffs) measures 11 cm x 6 cm x 4 cm, weighs 100 g and has three outputs, +5.1 VDC (2.5A), +12 VDC (1.5 A), and -12 VDC (0.2 A). The power supply is isolated from the metal enclosure with rubber washers that are placed between the standoffs and the enclosure.

Datalogger

The frequency output of the ozone sensor is logged by a programmable datalogger (Campbell Scientific, Logan, UT). The datalogger measures 22 cm x 4 cm x 10 cm, weighs 420 g, and requires a 12 VDC power supply. To minimize sampling error the datalogger manufacturer recommended that a battery be used to supply power. Therefore, a 12 VDC rechargeable battery (Powersonic, San Diego, CA) measuring 10 cm x 4 cm x 5 cm and weighing 600 g was used. The battery has a capacity of 1.2 A-hr and the datalogger, as configured for this application, draws about 1 mA. Thus, data can be logged for about 1200 hours on a single battery charge. The datalogger has two 8 bit pulse counters that can be used separately to measure frequencies up to 2 kHz or they can be used together to measure frequencies up to 250 kHz. The datalogger is programmed by the user with a PC running the manufacturer's PC208W software. A program was written that instructs the datalogger to measure the sensor output frequency every 5 sec. Each minute the average of the frequency measurements is stored to a register log with the date and time. The register has a capacity of 12000 entries which means the logger can store one minute frequency data for about 3 days before it is overwritten.

Component Cost

The part number, cost, and manufacturer of each of the components described above is provided in Appendix B. The total cost of the major monitor components was $1645 when purchasing for six monitor assemblies (five monitors and one set of spare parts). Miscellaneous parts such as Teflon and Tygon tubing, electrical contacts, connectors, and wire increase the cost per assembly by approximately $20. Additional equipment necessary for operating the piezoelectric ozone monitor

includes polybutadiene ($35 per 100 mL), a brush ($5), and a fixture to hold crystals during coating application. This fixture consists of a platform containing two sets of crystal sockets ($20) and the circuit board ($275). The coating fixture circuit board requires a 5 VDC power supply and a frequency counter, both of which should be standard laboratory equipment. Communicating with the datalogger via a personal computer requires the PC208W software ($275) and an optically isolated RS-232 interface ($140). To summarize, the total cost of one monitor is $1665 which is well below the project goal of $2500. The cost of additional equipment needed to operate one or more monitors, not including 5 VDC power supply, frequency counter, and personal computer, is $750.

2.1.8 Other Test Equipment

Sensor development and evaluation of the final monitor design required the use of additional experimental equipment. The typical equipment configuration used for testing the parallel flow and impactor flow test fixtures is shown in Figure 2.9. The POM test configuration is shown in Figure 2.10. Known levels of ozone were produced by a UV lamp in a multi-gas calibrator (Thermo Environmental Instruments model 142). Pollutant-free air was provided to the multi-gas calibrator by a zero-air supply (Dasibi model 5011-B) equipped with an activated carbon canister, a Purafil II chemisorbent canister, and a heated palladium/alumina catalyst. The ozone levels were monitored with a UV photometric ozone analyzer (Dasibi model 1008-AH).

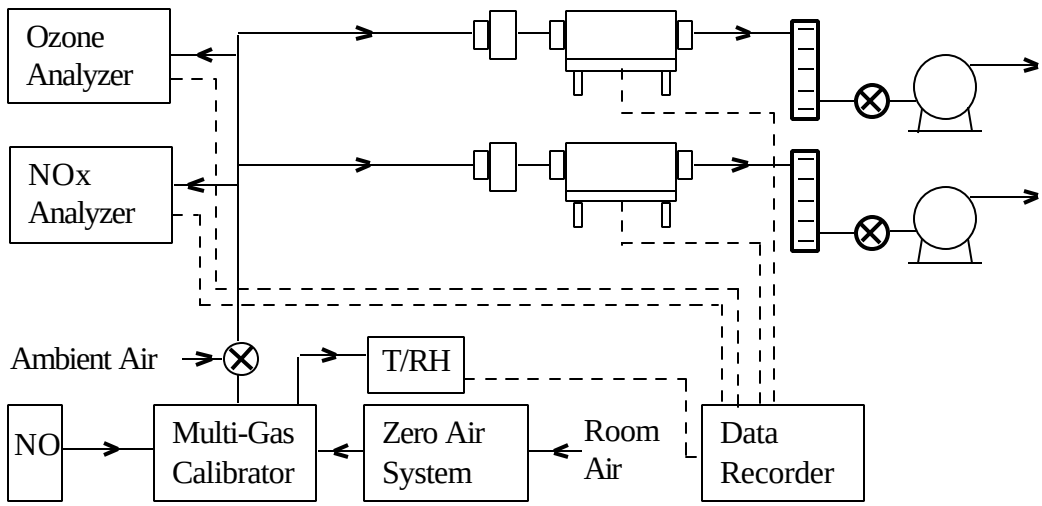


Figure 2.9. Laboratory equipment configuration for parallel and impactor fixtures.

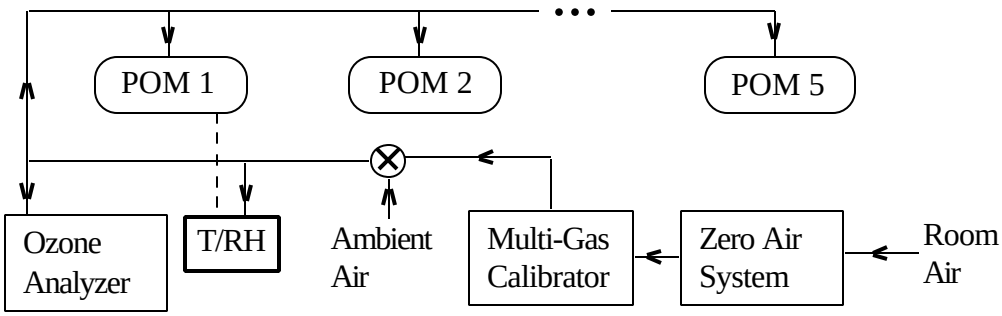


Figure 2.10. Laboratory equipment configuration for POM testing.

The multi-gas calibrator also provided controlled levels of potential interference gases. Nitric oxide (NO) was produced by diluting NO from a Scott-Marin gas cylinder. Ozone created by the calibrator's UV lamp was mixed with NO to produce nitrogen dioxide (NO_2). Permeation tubes containing nitric acid (HNO_3) and toluene produced controlled levels of these gases when placed in a 35 °C oven.

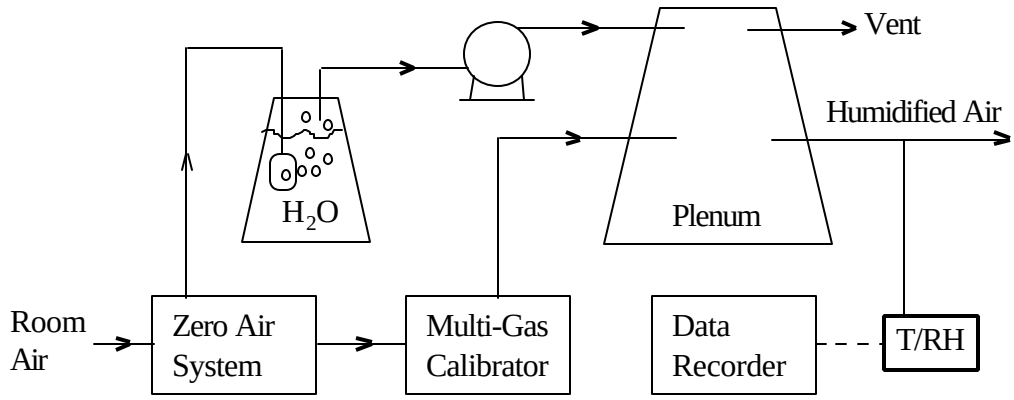


Figure 2.11. Laboratory equipment configuration for water vapor interference testing.

Water vapor was generated by pumping pollutant-free air provided by a zero-air unit through a ground glass bubbler submerged in de-ionized water (Figure 2.11). Sample air containing various levels of water vapor and ozone was generated by combining ozonated air from the multi-gas calibrator with humidified air from the bubbling flask in a glass plenum (Figure 2.11). Losses of water vapor and ozone to the glass surface were not a concern because humidity and ozone levels were monitored downstream of the plenum. Relative humidity (RH) and temperature were measured by pumping the sample air through a glass Erlenmeyer flask fitted with a temperature/RH meter (Cole-Parmer thermohygrometer probe model no. 37950-10).

2.1.9 Quality Control/Quality Assurance

The multi-gas calibrator (TECO 146) used in this research was calibrated by the Bay Area Air Quality Management District (BAAQMD) in Richmond, CA. The ozone output was calibrated using an ozone analyzer that had been calibrated with an EPA-approved ozone transfer standard.

Two UV photometric ozone analyzers (Dasibi 1008-AH) used in this study were calibrated at UC Berkeley using the calibrated multi-gas calibrator and five ozone settings. Calibrations were repeated every three months. The ozone analyzers were also calibrated at the California Air Resources Board (CARB) in Sacramento, CA on October 3, 1997 and at the BAAQMD in Vallejo, CA on December 1, 1998. Both calibrations were performed with an EPA-approved ozone transfer standard.

Calibration of the multi-gas calibrator was repeated after the ozone analyzers were calibrated at CARB and BAAQMD.

2.1.10 Sensor Performance Parameters

Parameters that can be used to characterize the performance of an ozone sensor/monitor include limit of detection, lifetime, precision, bias, and accuracy. These parameters were used during the development of the polybutadiene-coated quartz crystal sensor to compare and evaluate various sensor configurations. The performance of the final monitor design was also characterized by measuring these parameters.

Sensor Response

The sections of this report that discuss the development and performance of the sensor refer to the sensor response, defined as the rate of change of sensor beat frequency output in units of Hz min^{-1}. The sensor response was converted to ozone concentration by multiplying by a calibration factor that had units of ppb min Hz^{-1}.

Limit of Detection

The limit of detection (LOD) of a sensor is often defined to be three times the noise level of the sensor response. In the case of the quartz crystal ozone sensor presented in this study the noise level was measured as the average of the sensor response to pollutant-free air and had units of Hz min^{-1}. To provide a more useful description of sensor performance, the LOD in Hz min^{-1} was converted to an ozone concentration by multiplying by an appropriate calibration factor. Recall that the calibration factor is a function of the sensor's flow geometry, air flow rate, electrode diameter, and type of polybutadiene coating.

Sensor Lifetime

The reaction of ozone with polybutadiene is irreversible; therefore, the coating has a limited lifetime. The effective lifetime of the sensor was measured as the period over which the sensor response to ozone was linear. More precisely, it was calculated as the amount of time in which the sensor measurement was within ±10% of the actual ozone concentration. The lifetime of the sensor is reported in units of ppb-hr.

Precision, Bias, and Accuracy

The precision of the ozone measurements was determined with data from two POMs operated side-by-side. Precision was calculated by dividing the difference between the two POM measurements by the average of those two measurements. The bias of the ozone measurements was calculated with data from a POM and a UV photometric ozone analyzer that were operated side-by-side. Bias was determined by dividing the difference between the POM and UV measurements by the UV measurement. Accuracy was calculated in a similar manner to bias except that the absolute value of the difference between the POM and UV measurements was divided by the UV measurement. By using the absolute value the accuracy figure represents both positive and negative errors. With the bias statistic positive and negative errors can cancel each other and result in a deceptively low bias figure.

2.1.11 Sensor Design Parameters and Testing

During development of the polybutadiene-coated quartz crystal ozone sensor numerous experiments were conducted to examine the relationship between sensor design parameters and performance. The parameters included type and amount of polybutadiene coating, crystal electrode diameter, sample air flow rate and flow geometry. The temperature and relative humidity in the laboratory in which this testing was conducted ranged from 20 to 30 °C and 20 to 70%, respectively.

Coating Type

As described earlier, there were two types of polybutadiene that were examined—80% 1-4 addition and 99% 1-4 addition (coating A and B, respectively). Tests were conducted with each type

of polybutadiene in which 6 kHz (~20 μg) of the coating was applied to a crystal with a 9.5 mm diameter electrode. The crystals were installed in the parallel flow test fixture with a sample air flow rate of 0.2 LPM. Some of the earliest testing of the sensor was conducted with potentially interfering gases as described below in section 2.1.12. The initial goal of this testing was to determine if coating A and B responded differently to ozone in the presence of other common ambient gases. Whichever coating exhibited the least interference would be selected as the sensor coating and used for subsequent sensor parameter development.

Crystal Electrode Diameter

Experiments were conducted with the parallel flow test fixture, sample air flow rate of 0.2 LPM, 6 kHz of coating A, and crystal electrode diameters of 5, 9.5, and 11.5 mm. The goal of this testing was to determine if there was any relationship between electrode diameter and sensor lifetime and use that relationship to maximize the lifetime.

Sample Air Flow Rate

At a constant concentration of ozone, the number of ozone molecules that come in contact with the coated surface of the crystal is proportional to the sample air flow rate. Therefore, sensor response to ozone should be related to sample air flow rate. Several experiments were conducted with the parallel flow fixture and the impactor fixture. The crystals in each test had 9.5 mm diameter electrodes and were coated with 6 kHz of coating A. Sample air flow rate through the parallel flow fixture was controlled by a needle valve and a rotameter. Various flow rates from 0.1 to 1 LPM were examined while the ozone concentration was held constant at 80 ppb. Experiments with the impactor configuration used ozone concentrations of 30 and 50 ppb and sample air flow rates of 0.13 and 0.25 LPM. The flow rate through the impactor fixture was controlled by a critical orifice.

Coating Amount

Coating quantity was varied from 6-20 kHz to examine the relationship between the amount of coating applied to the crystal and the lifetime of the sensor. Experiments were conducted with the parallel flow fixture, the impactor fixture, the final monitor (POM) and crystals with 9.5 mm diameter electrodes. Sample air flow rate through the parallel flow fixture was 0.2 LPM. A 0.13 LPM critical orifice was used to control flow through the impactor fixture and the POM.

Flow Geometry

Coated crystals can be positioned in the sample air flow stream in two ways. In the parallel flow configuration the face of the crystal is parallel to the direction of the air flow. The stream of air splits when it hits the edge of the crystal and flows over both sides of the crystal. In the impactor flow configuration each of the crystal faces is exposed to a perpendicular jet of sample air. Each of these flow configurations was tested with 9.5 mm diameter electrode crystals and coating A. The sample air flow rate, coating amount, and ozone concentrations were varied during several experiments, and the performance of each sensor flow configuration was compared.

Sensor Response Testing

Both the parallel flow configuration and the POM (using impactor flow) were exposed to various levels of ozone in the range of 0 to 300 ppb. The parallel flow configuration used a coating amount of 6 kHz and a sample air flow rate of 0.2 LPM. The POM used coating amounts ranging from 8-14 kHz and a sample air flow rate of 0.13 LPM. Tests with the parallel flow configuration consisted of two test fixtures sampling side-by-side. Two to five POMs would sample laboratory-generated ozone simultaneously.

Coated Crystal Storage

As described in section 2.2.1, the sensing crystal must be coated and conditioned with ozone before the POM can be used. Field studies conducted with the POM would be simplified if a batch of crystals could be coated, conditioned, and stored prior to the study. Multiple experiments were

conducted with several POMs fitted with a 0.13 LPM critical orifice and 9.5 mm diameter electrode crystals coated with 8, 12, and 14 kHz of coating A. After being coated, some crystals were conditioned with 300 ppb of ozone for 40 minutes, and others were not conditioned before being capped and placed in a zip-lock bag. Storage periods of 24 hours, 4 days, and 24 days were examined. After the storage period the crystals were installed in POMs that were placed side-by-side with POMs containing freshly coated and conditioned crystals, and were exposed to 30 to 300 ppb of ozone. The POM measurements made with the freshly coated and stored crystals were compared. The lifetimes of the stored and freshly coated crystals were also compared.

2.1.12 Interference Testing

Laboratory

For the ozone monitor to be effective it is important that any change in the mass of the polybutadiene coating on the sensing crystal be caused only by ozone and not by any other constituent of ambient air. Interference testing was conducted in the laboratory with the following compounds: water vapor, nitric oxide (NO), nitrogen dioxide (NO_2), nitric acid (HNO_3), and toluene. All interference tests, unless otherwise indicated below, were conducted with the parallel flow test fixture, 6 kHz of coating, and a sample air flow rate of 0.2 LPM.

A previous study using a quartz crystal coated with polybutadiene showed a slight hygroscopic effect (Fog and Reitz 1985). Water vapor was therefore examined in this study as a potential interference. Relative humidity (RH) of the sample air was rapidly varied from 25 to 75% and 75 to 25% while the ozone concentration was held constant at 100 ppb.

As described in section 2.1.7, the POM uses a Nafion dryer to remove water vapor. Tests were conducted with five POMs configured side-by-side to determine if rapid changes or high levels of RH would interfere with POM ozone measurements. Each POM was tested using 9.5 mm diameter electrode crystals coated with 12 kHz of 80% 1-4 addition polybutadiene. The POMs were exposed to varying levels of ozone and RH levels of 20 and 80%. Also, RH levels were rapidly changed from 20 to 80% and 80 to 20%.

NO and NO_2 were chosen for interference testing because their levels in outdoor air are related to ozone levels, and because NO and NO_2 concentrations are typically higher in indoor environments containing gas appliances (Wilson et al., 1986). An NO concentration of 200 ppb and NO_2 concentrations of 200 and 900 ppb were chosen for testing in this study. Measurements of NO_2 made in museums located in Southern California indicated peak levels of ~100 ppb (Hisham and Grosjean, 1991), while measurements made in homes showed peak levels up to 1000 ppb when gas appliances were operated (Brauer et al., 1990).

HNO_3 was evaluated as a potential interference because, like ozone, it is an oxidant and is commonly measured in ambient air (Hisham and Grosjean, 1991). An HNO_3 concentration of 40 ppb was generated using a permeation tube. This concentration is approximately double the concentration measured in museums in Southern California (Hisham and Grosjean, 1991).

Toluene was used as a surrogate for a class of organic solvents that are commonly found in indoor environments. The toluene test level of 50 ppb was generated by a permeation tube and exceeded the combined indoor concentrations of several common volatile organic compounds measured in Woodland, CA (Sheldon et al., 1992).

Outdoor Air

The objective of measuring outdoor air with the polybutadiene-coated quartz crystal ozone sensor was to compare its performance against a UV photometric ozone analyzer under real-world conditions and to screen for other interferences that might be present in ambient air. The parallel flow test fixture was the only prototype design available at the time, therefore, it was used to evaluate the sensor in the field at the Azusa, CA air monitoring station from Oct. 18-20, 1997. The Azusa site is located at the foot of the San Gabriel mountains northeast of Los Angeles, and was chosen due to its historically high ozone levels. The sensors and related equipment were set up inside the monitoring facility where temperature was constant at ~22°C. Outdoor air was sampled through a Teflon tube that ran 20 ft. from the interior to 3 ft. above the edge of the rooftop. Outdoor ozone levels during field sampling at Azusa ranged from 20 to 100 ppb.

The test equipment assembled in Azusa was similar to that used in laboratory testing and shown in Figure 2.9. Two parallel flow test fixtures using 9.5 mm diameter electrode crystals coated with 6 kHz of coating A were evaluated simultaneously at sample air flow rates of 0.2 LPM. Ozone levels were measured upstream of the prototype sensors with a UV photometric ozone monitor, while temperature and RH were measured downstream with a temperature/RH probe (Vaisala model 50Y). Data from the prototype ozone sensors, the UV photometric ozone analyzer, and the temperature/RH probe were recorded at 20 second intervals with a laptop computer equipped with a Labview data acquisition system. Data were also recorded by hand in a logbook. An ozone generator (TECO 146 multi-gas calibrator), UV photometric ozone monitor (Dasibi 1008-AH), and pollutant-free air source (canisters of Dri-rite and activated carbon) were configured at the site to generate calibration points. Calibrations were performed before and after each sampling period by exposing each ozone sensor to 30 and 100 ppb of ozone for 25 minute intervals each.

2.2 Results

2.2.1 Sensor Design Parameter Optimization and Testing

The goal of the sensor development phase of this research was to determine the optimal combination of coating type and amount, crystal electrode diameter, sample air flow rate and flow geometry. The impact of varying each of these design parameters is described below. It should be noted that all figures presented in this section show measured quantities as ten minute running averages.

Coating Type

In general, sensor response to ozone did not depend on the type of polybutadiene coating—80% or 99% 1-4 addition—that was applied to the crystal electrode. Coating behavior was dramatically different, however, in the presence of NO_2. A sensor using the 99% polybutadiene exhibited measurements of ozone ~50 ppb higher than actual levels when ~100 ppb of NO_2 was present (Figure 2.12). A similar sensor coated with 80% polybutadiene measured 105 ppb of ozone in

the presence of 100 ppb of ozone and 200 ppb of NO_2 (Figure 2.13). The same sensor measured 20 ppb of ozone in the presence of no ozone and 900 ppb of NO_2.

Crystal Electrode Diameter

Two similarly configured sensors were repeatedly run side-by-side and exposed to a constant ozone concentration of 50 ppb. Each of the sensors used a different crystal electrode diameter and was exposed to ozone until the polybutadiene coating was exhausted. The 5 mm and 9.5 mm diameter electrode crystals exhibited lifetimes of 250-300 ppb-hr and 500-600 ppb-hr, respectively. Sensing crystals with 11.5 mm diameter electrodes did not produce a stable output.

Sample Air Flow Rate

The parallel flow configuration of the sensor was exposed to a constant ozone concentration of 80 ppb while the flow rate was varied. The sensor response increased from 0.7 to 1.9 Hz min^{-1} as the flow rate increased from 0.1 to 1.0 LPM (Figure 2.14). The relationship between sensor response and flow rate is not linear over the full 0.1 to 1.0 LPM range, but was approximately linear from 0.1 to 0.3 LPM. The relationship is described by the equation
$SR = 3.2 * Q + 0.41$ where SR equals the sensor response in Hz min^{-1} and Q equals the flow rate in LPM.

The impactor configuration of the sensor was exposed to a constant ozone concentration of 50 ppb at two flow rates—0.13 and 0.25 LPM. The relationship between sensor response SR and flow rate Q was $SR = 10.2 * Q - 0.44$. The difference in the value of the slopes indicates that sensor response is about three times more sensitive to changes in flow rate in the impactor configuration than in the parallel flow configuration.

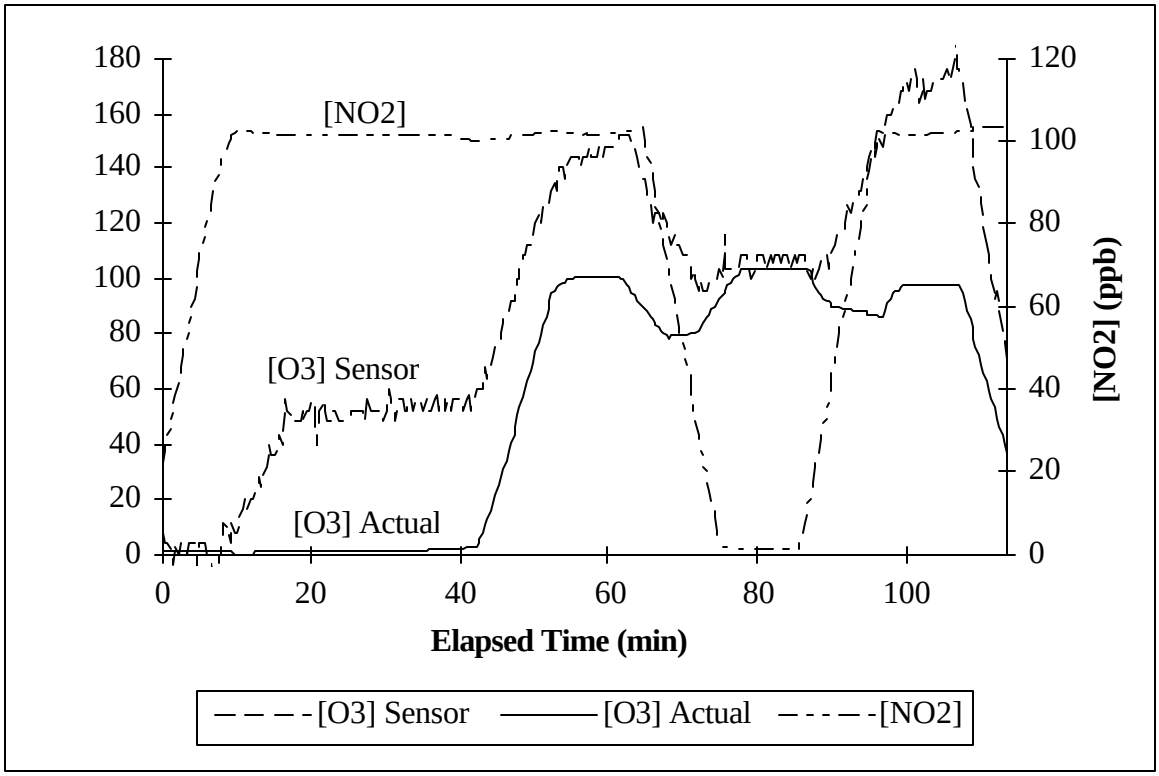


Figure 2.12. Sensor response (parallel flow at 0.2 LPM and 9.5 mm electrodes coated with 6 kHz of 99% 1-4 addition) when exposed to varying levels of ozone and nitrogen dioxide.

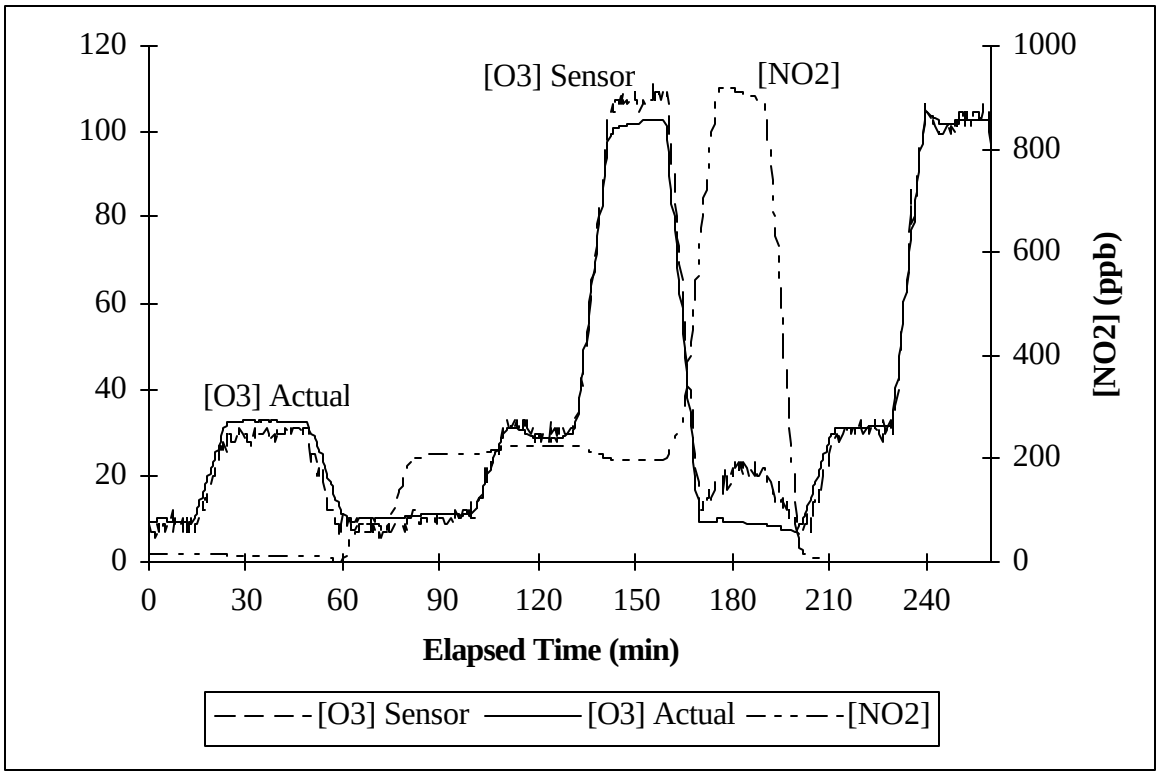


Figure 2.13. Sensor response (parallel flow at 0.2 LPM and 9.5 mm electrodes coated with 6 kHz of 80% 1-4 addition) when exposed to varying levels of ozone and nitrogen dioxide.

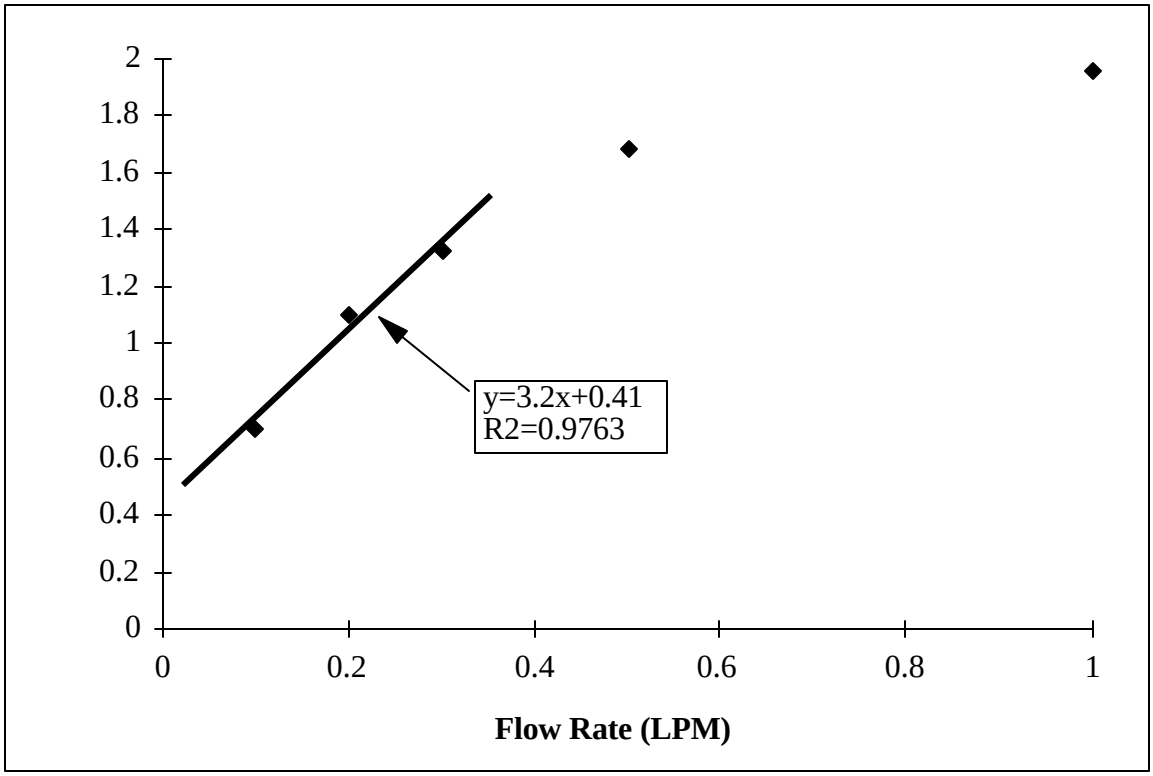


Figure 2.14. Sensor response vs flow rate with parallel flow and 9.5 mm electrodes coated with 6 kHz of 80% 1-4 addition polybutadiene. Ozone concentration was constant at 80 ppb.

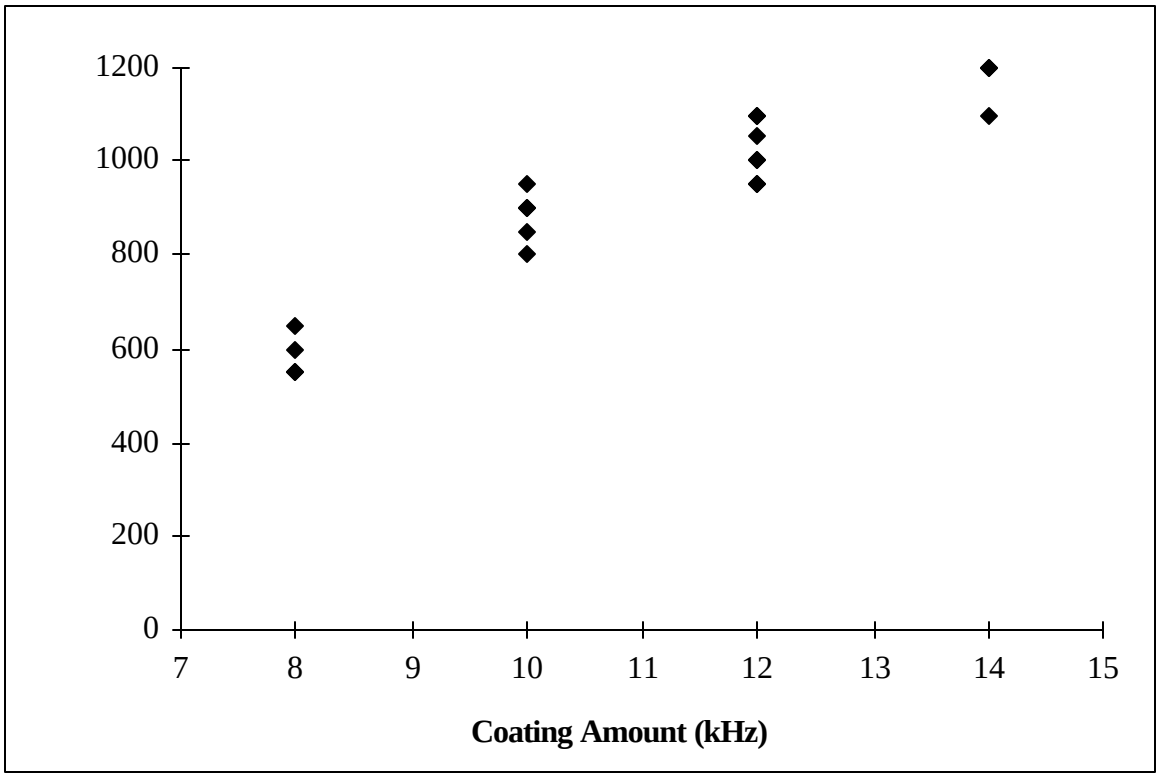


Figure 2.15. POM sensor lifetime with impactor flow at 0.13 LPM and 9.5 mm electrodes coated with 8 to 14 kHz of 80% 1-4 addition polybutadiene.

Coating Amount

The lifetime of the sensor in the parallel flow configuration showed no dependence on coating amount when the amount was varied from 6 to 20 kHz. Experiments with the final monitor design showed that sensor lifetime increased from 550 to 1200 ppb-hr when the coating amount was increased from 8 to 14 kHz (Figure 2.15).

Flow Geometry

Sensors in the parallel and impactor configurations performed comparably, for the most part. However, response of the parallel flow sensor to ozone varied by ±20% if great care was not taken to precisely align the sensing crystal parallel to the direction of sample air flow. The crystal is held in place by two thin electrical contact wires (Figure 2.1). The alignment of these wires can be changed slightly during the coating and cleaning procedures. A small change in the alignment of the crystal caused significant variation in the sensor response for the parallel flow geometry. Alignment of crystals parallel to air flow was achieved by gently bending the crystal electrical leads until the crystal was parallel to a line marked on the base of the test fixture. The impactor configuration proved to be less sensitive to precise alignment of crystals. Sensor response varied ±7% when little care was taken to align the sensing crystal.

Sensor Response to Ozone

In the laboratory the POM accurately measured ozone concentrations from 30 to 320 ppb (Figure 2.16). The initial response of the sensor was not linear. The non-linearity is shown between 1400 and 1500 hours in Figure 2.16; the POM measurement increased from 10 to 320 ppb while the actual ozone level was constant at 320 ppb. This delay is referred to here as the induction period of the sensor. To insure that the sensor responds linearly to ozone it must be conditioned with ~300 ppb of

ozone for at least 40 minutes. Following the conditioning period the ozone sensor responds rapidly to changes in ozone levels. The sensor responds linearly until the polybutadiene coating becomes saturated. Coating saturation was shown after 1130 hours when the sensor measurements steadily decreased even though the actual ozone levels were constant (Figure 2.16).

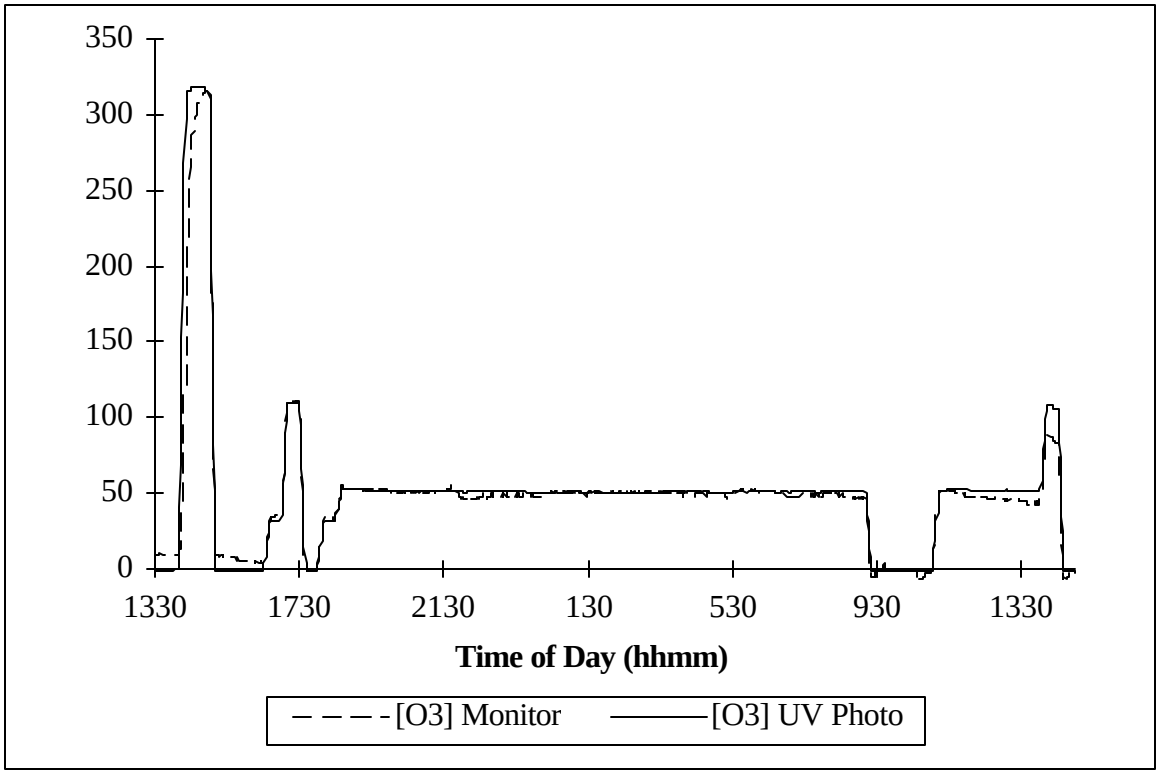


Figure 2.16. POM response (0.13 LPM flow and 9.5 mm electrodes coated with 8 kHz of 80% 1-4 addition polybutadiene) when exposed to laboratory generated ozone over 24 hours.

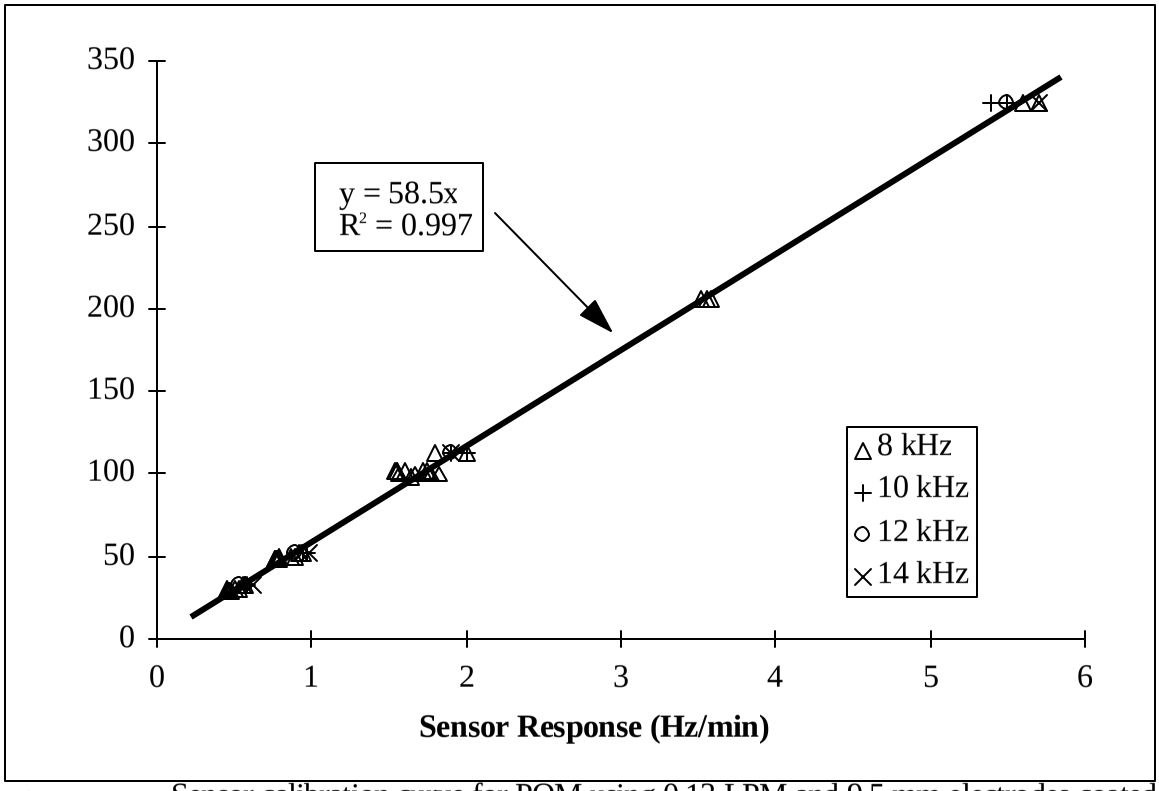


Figure 2.17. Sensor calibration curve for POM using 0.13 LPM and 9.5 mm electrodes coated with 8 to 14 kHz of 80% 1-4 addition polybutadiene.

Several laboratory experiments were conducted in which POMs were exposed to varying levels of ozone. Several different sensing and reference crystals were swapped between POMs and coating amounts varied from 8 to 14 kHz. A calibration curve was generated by plotting the actual ozone concentrations vs the sensor response in Hz min^{-1} (Figure 2.17). The sensor response was linear from 30 to 300 ppb.

Table 2.2. Sensor lifetime with freshly coated and stored coated crystals.

Storage Period (days)	Coating Amount (kHz)	Conditioned[a] Before or After Storage	Lifetime (ppb-hr)
0	8	n/a	600
1	8	After	400
4	8	Before	200
0	12	n/a	1000
24	12	Before	100
0	14	n/a	1200

4	14	After	400

[a]Coated crystal was conditioned by exposing to 300 ppb of ozone for 40 minutes. Coated crystals that were not stored were conditioned in the same manner immediately before the lifetime test.

Coated Crystal Storage

When crystals were coated in advance and stored prior to use, those conditioned with ozone before or after storage, exhibited the same sensor response to various ozone levels as freshly coated crystals. This was true for coating amounts of 8, 12, and 14 kHz. While initial sensor response to ozone was unaffected by storage, the useful lifetime of coated crystals deteriorated during storage. For example, the lifetime of crystals with 8 kHz coatings conditioned after 24 hours of storage was 400 ppb-hr compared to 600 ppb-hr with freshly coated crystals. Crystals with 8 kHz coatings that were conditioned with 300 ppb of ozone for 40 minutes before four days of storage exhibited an even shorter lifetime of 200 ppb-hr. The lifetime of crystals with 14 kHz coatings conditioned after four days of storage was 400 ppb-hr compared to 1200 ppb-hr with freshly coated crystals. Crystals with 12 kHz coatings and conditioned with 300 ppb for 40 min before 24 days of storage exhibited a lifetime of 100 ppb-hr. This lifetime was about an order of magnitude lower than that exhibited by freshly coated and conditioned crystals.

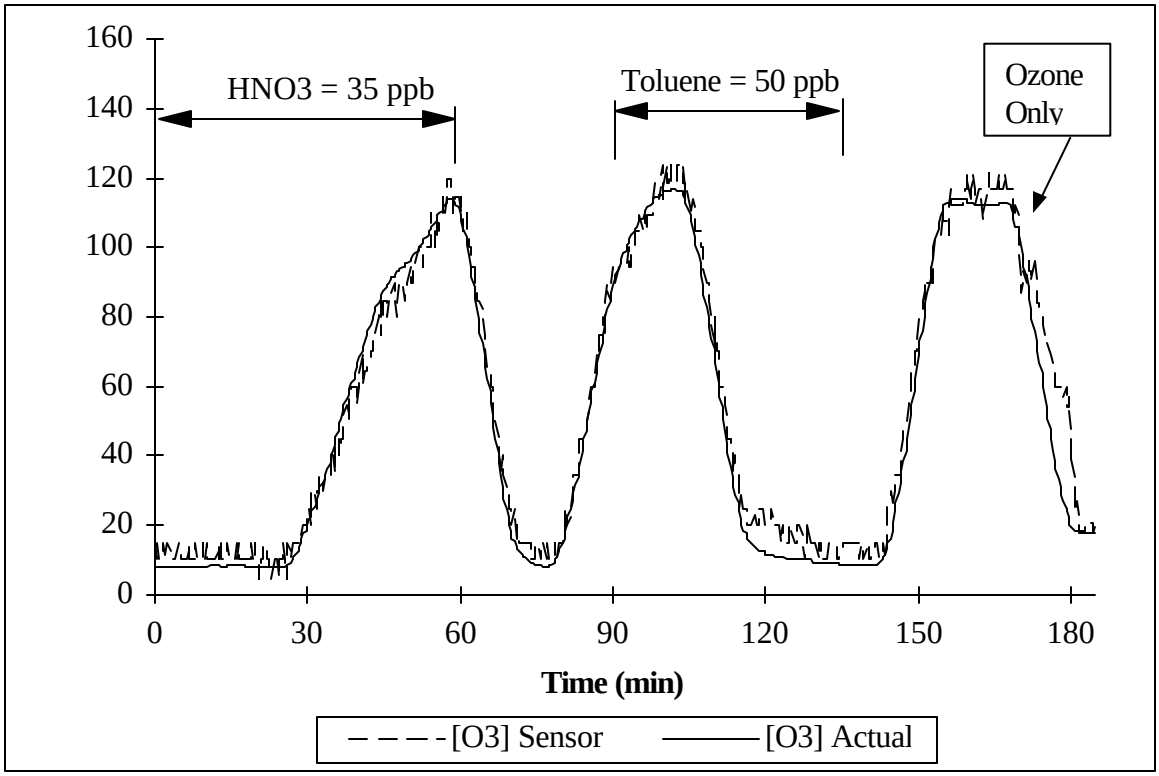


Figure 2.18. Sensor response (parallel flow at 0.2 LPM and 9.5 mm electrodes coated with 6 kHz of 80% 1-4 addition) when exposed to nitric acid (HNO_3) and toluene.

2.2.2 Interference Testing

Laboratory

Whereas 99% 1-4 addition polybutadiene (coating B) reacted significantly with NO_2, sensors using 80% 1-4 addition polybutadiene (coating A) exhibited minimal interference by NO_2 (Figure 2.13). Sensors using coating A or B exhibited no change in response to 100 ppb of ozone with or without the presence of 200 ppb of NO (data not shown). Sensors using coating A or B exhibited no change in response to 100 ppb of ozone with or without the presence of 35 ppb of HNO_3, or 50 ppb of toluene (Figure 2.18). Sensors using coating A measured 100 ppb of ozone within ±5% when the relative humidity (RH) was constant either at 25% or 75% (Figure 2.19). Rapid changes in RH cause transient shifts in the sensor ozone measurements as shown in Figure 2.19.

When the POMs were exposed to rapidly changing RH levels the transient spikes were not observed (Figure 2.20). Figure 2.20 shows ten minute running average data from one of the five

POMs, a Dasibi UV photometric ozone analyzer, and an RH probe. Discrete ten minute average data of all five POMs is shown in Table 2.3.

A summary of the laboratory testing for each of the potential interference gases is provided in Table 2.4. Error was calculated by dividing the difference between the sensor measurement and the actual ozone level by the actual ozone level.

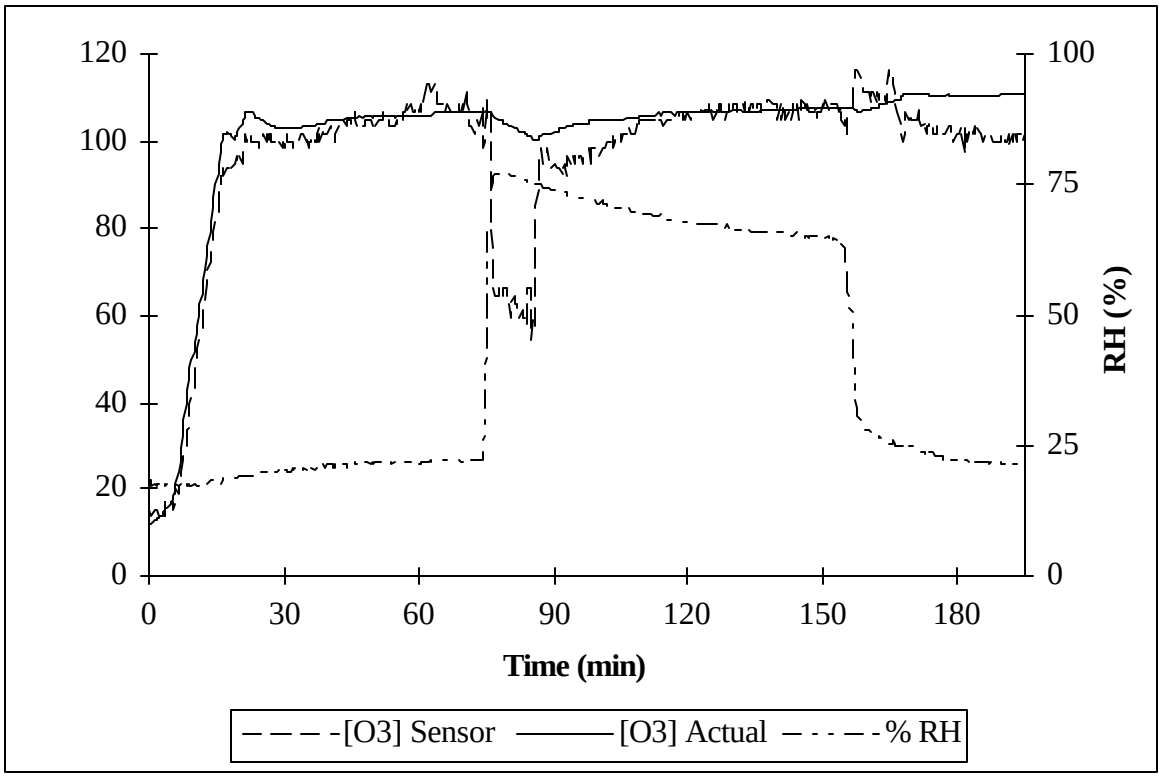


Figure 2.19. Sensor response (parallel flow at 0.2 LPM and 9.5 mm electrodes coated with 6 kHz of 80% 1-4 addition) when exposed to varying levels of relative humidity.

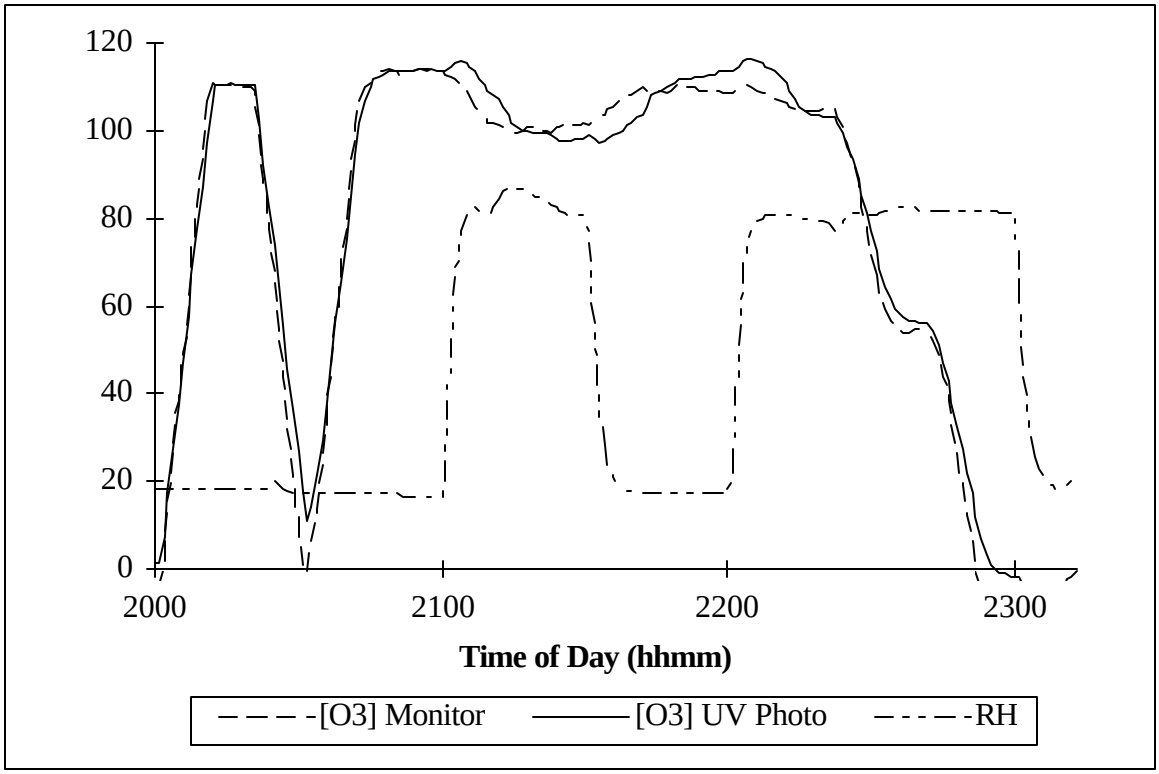


Figure 2.20. POM response (0.13 LPM flow and 9.5 mm electrodes coated with 12 kHz of 80% 1-4 addition polybutadiene) when exposed to ozone and water vapor.

Table 2.3. Water vapor interference test data for all five POMs (each using 0.13 LPM flow and 9.5 mm electrodes coated with 12 kHz of 80% 1-4 addition polybutadiene).

Time of Day (hhmm)	RH (%)	Dasibi (ppb)	POM1 (ppb)	POM2 (ppb)	POM3 (ppb)	POM4 (ppb)	POM5 (ppb)
2000	18	1	5	6	7	1	4
2010	18	87	99	95	93	97	95
2020	18	111	115	111	112	113	110
2030	17	27	8	10	9	14	10
2040	17	75	82	82	79	80	80
2050	17	113	117	114	115	114	113
2100	17	113	115	114	114	114	113
2110	80	109	105	102	102	102	102
2120	85	99	100	97	96	99	100
2130	81	98	103	100	99	101	102
2140	18	102	108	107	107	108	108
2150	17	111	111	107	110	108	110

2200	17	113	111	108	111	109	109
2210	80	113	107	104	104	104	107
2220	79	103	105	100	102	102	105
2230	81	77	71	70	70	71	72
2240	82	56	54	53	52	55	55
2250	82	22	14	12	13	16	12
2300	81	2	10	7	8	6	9

Table 2.4. Summary of laboratory testing with each potential interference gas.

Potential Interference Gas	**Sensor Configuration[a]**	**Actual $[O_3]$[b] (ppb)**	**Measured $[O_3]$[c] (ppb)**	**Error (%)**
100 ppb NO_2	parallel (99% 1-4 addition PBD)	0	50	-
"		100	150	50
200 ppb NO_2	POM	30	30	0
"	"	100	105	5
900 ppb NO_2	POM	10	20	100
35 ppb HNO_3	parallel	118	118	0
50 ppb Toluene	parallel	118	120	2
65% RH	parallel	108	108	0

25-75% RH Transition	parallel	105	60	-43
80% RH	POM	98	100	2
"		56	54	-4
20-80% RH Transition	POM	109	105	-4
80-20% RH Transition	POM	102	108	6

[a]All polybutadiene (PBD) used was 80% 1-4 addition unless otherwise noted.
[b]Actual ozone concentration measured with UV photometric analyzer.
[c]Measured ozone is that measured with the piezoelectric crystal ozone sensor.

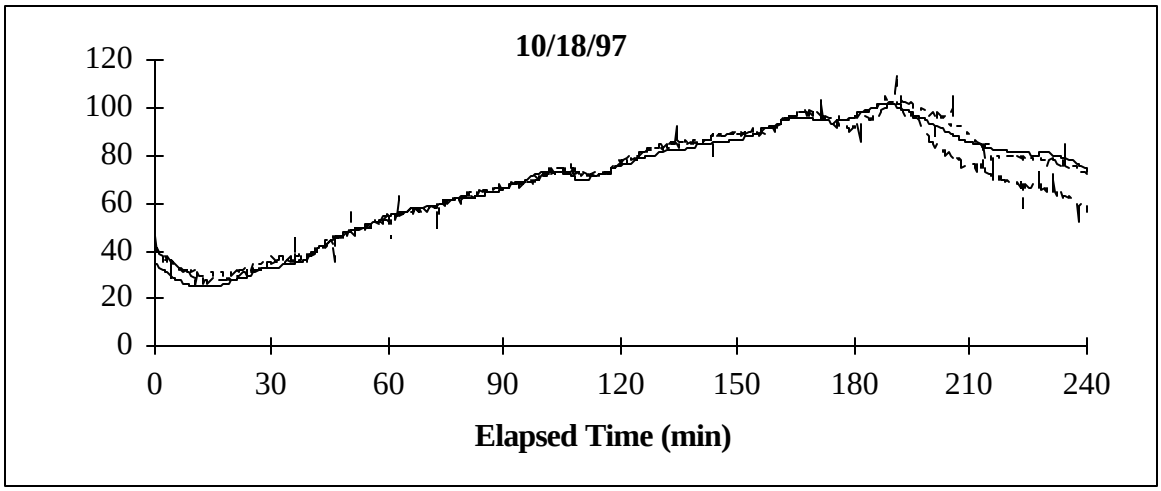
Outdoor Air

Outdoor ozone levels ranged from 5 to 90 ppb during the three days of sampling conducted in Azusa, CA during October 1997 (Figure 2.21, Table 2.5, and Appendix C). Calibration of two sensors was conducted before sampling. Six different calibration factors, one for each sensor on each day, were determined. The calibration factors ranged from 56 to 68 ppb of ozone per Hz min^{-1}. Separate calibration factors were used for each sensor in each run. The sensors responded accurately and rapidly responded to varying ozone levels (Figure 2.21). The side-by-side precision ranged from 4 to 7% and exhibited bias ranging from –6 to 3% when compared to UV photometric ozone

measurements. The spikes on the sensor measurements seen in Figure 2.21 were caused by datalogging errors that were associated with the Labview system.

Table 2.5. Hourly average ozone measurements (ppb) recorded by Azusa monitoring station (UV photometric ozone analyzer) on 10/18/97-10/20/97.

Time	10/18/97	10/19/97	10/20/97
0800	8	12	30
0900	12	18	42
1000	23	29	46
1100	32	58	44
1200	63	66	44
1300	84	68	40
1400	87	63	36
1500	75	67	35
1600	62	51	23
1700	39	33	24
1800	15	20	24
1900	24	14	21
2000	5	8	21



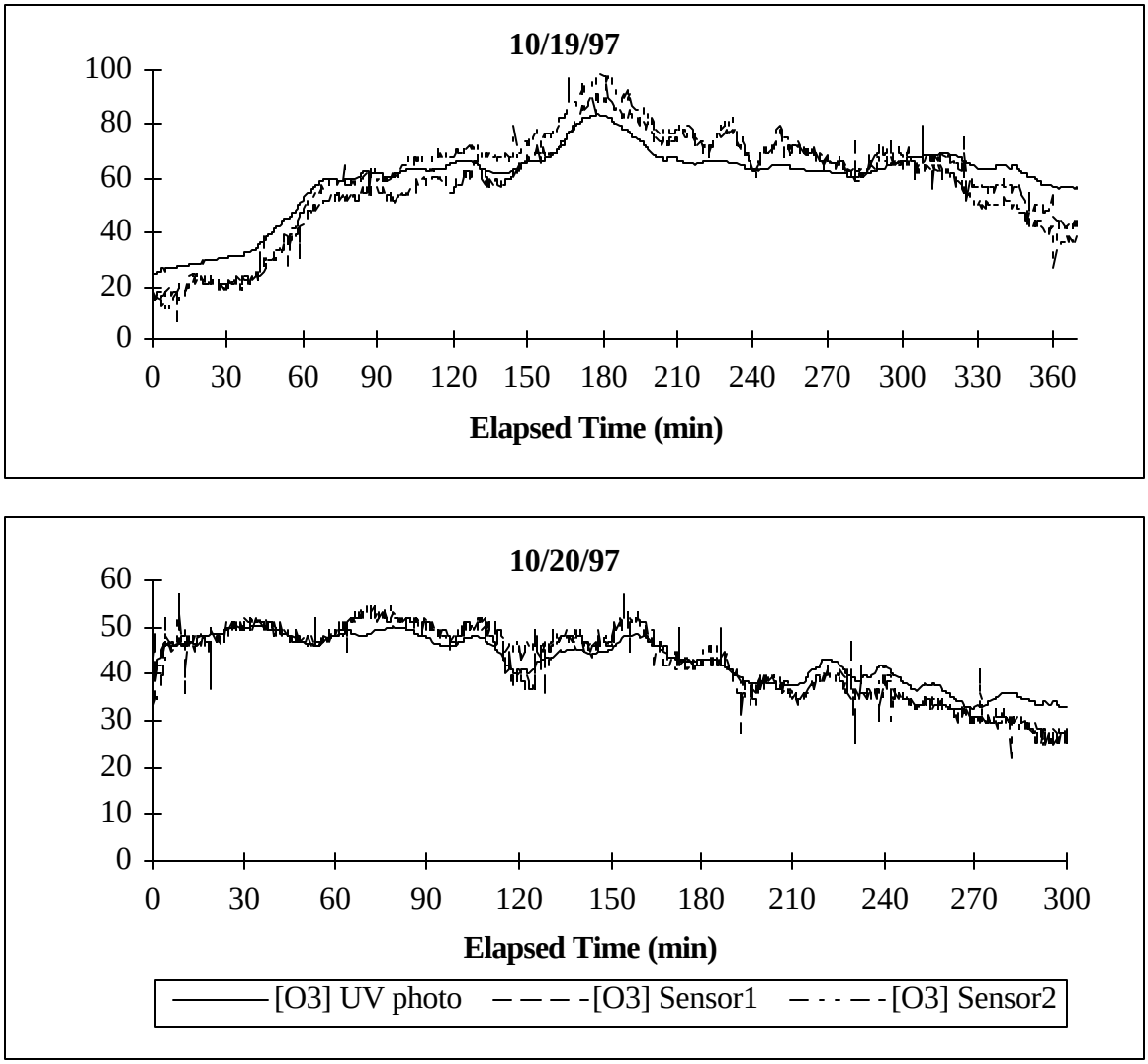


Figure 2.21. Sensor measurements of outdoor air made in Azusa, CA on 10/18-10/20/97. Sensor was configured with parallel flow at 0.2 LPM and 9.5 mm electrodes coated with 6 kHz of 80% 1-4 addition polybutadiene.

2.3 Discussion

2.3.1 Sensor Design Parameter Optimization and Testing

Coating Type

The 99% 1-4 addition polybutadiene (coating B) was originally considered as possibly superior to the 80% 1-4 addition polybutadiene (coating A) because it was thought that the higher proportion of 1-4 addition monomers would increase the sensor's sensitivity and, in turn, increase lifetime. Products

formed by the ozone reaction with the branched 1-2 addition monomers were expected to be more likely to volatilize than those formed by reaction with the long chain 1-4 addition monomers (Figure 2.2). If the products of the ozone/polybutadiene reaction volatilized there would be a smaller mass increase on the crystal electrode surface and, in turn, a decreased sensor response. After testing the sensor response in the presence of NO_2 it was determined that coating B was not suitable for use in the ozone sensor. Similar tests with coating A indicated minimal response to NO_2 and only a small decrease in sensitivity and lifetime. Conversations with the polybutadiene supplier (Aldrich Chemical Co.) revealed that coatings A and B are produced by separate manufacturers. The supplier claimed any further information was proprietary. It was inferred, however, that coating A was produced with a stabilizer or anti-oxidant and that coating B was not. This was supported by the fact that the manufacturer of coating B instructed the user to keep the polybutadiene stored under nitrogen. The manufacturer of coating A did not require the user to employ any special storage procedures. Having to store coating B under nitrogen meant that a nitrogen source, such as a cylinder, had to be present when crystals were coated. Use of coating A therefore required less equipment compared to coating B.

Chemical manufacturers produce polymers in large batches or lots. Aldrich printed the manufacturer's lot number on each container of polybutadiene that was supplied. The majority of sensor testing and development was conducted with coating A from the same lot. However, the POM was evaluated with coating A from two separate lots. No difference in the POM ozone measurements was observed when coating from the different lots was tested side-by-side. Containers of polybutadiene of the same lot were opened on different dates. Again, no difference in monitor performance was observed when coating of different "ages" was used.

Crystal Electrode Diameter

Experiments confirmed that the lifetime of the sensor configured in parallel flow was related to the diameter of the sensing crystal electrode. It was expected that in the parallel flow configuration the sensor coating would be consumed as the sample air moved across the crystal. Therefore, the more coating there was in the direction of the sample air flow the longer the coating would last. The only way

to put more coating in the direction of the flow was to increase the diameter of the crystal electrode. Fortunately, the crystal supplier was able to provide crystals with 9.5 mm diameter electrodes at the same cost as those with 5 mm diameter electrodes. Electrodes larger than 9.5 mm could not be reliably produced.

Sample Air Flow Rate

As expected, sensor response was proportional to sample air flow rate in both parallel and impactor flow configurations. The slope of the relationship between sample air flow rate and sensor response was nearly three times greater for sensors using impactor flow compared to those using parallel flow. Since the linear relationships were derived over about the same range of sample air flow rate it was inferred that the response of sensors using impactor flow was about three times more sensitive to changes in flow than those using parallel flow. Careful control of sample air flow rate was, therefore, necessary when using the impactor flow geometry. To minimize flow variation in the POM a critical orifice was used. The critical orifice produced a constant flow rate; a variety of different-sized orifices can be used to provide a wide range of flow rates.

The optimal flow rate for the POM with critical orifice flow control was found to be 0.13 LPM. This flow rate provided the optimal trade-off between limit of detection (LOD) and lifetime. With a flow rate of 0.13 LPM and coating of 12 kHz, the LOD surpassed design objectives (<30 ppb) and lifetime was ~1000 ppb-hr. Ozone levels below 30 ppb could be measured by substituting a critical orifice that provides a higher flow rate, although this would reduce sensor lifetime.

Coating Amount

Experiments with the parallel flow geometry did not indicate a relationship between the amount of coating applied to the sensing crystal and sensor lifetime. Therefore, the majority of the laboratory testing, and all the field testing, of the POM was conducted with only one coating amount, 8 kHz. Further laboratory experiments conducted with the POM showed that sensor lifetime was proportional to the amount of polybutadiene applied to the sensing crystal. However, the relationship between

coating amount and lifetime was not linear. The absolute increase in lifetime decreased as coating amounts increased. Also, the variability of the sensor response was greater at higher coating amounts. A coating amount of 12 kHz appears to be optimal. This amount of coating provides ~1000 ppb-hr of sensor lifetime.

Flow Geometry

Initially the impactor flow configuration was selected over the parallel flow configuration because preliminary tests indicated that there was no induction period with impactor flow. This would have meant that the conditioning of the crystal coating with a brief exposure to a high ozone concentration would not be necessary. Later testing with the POM indicated that while the induction period was greatly decreased by using the impactor flow geometry, it was not eliminated. Nevertheless, there are two major advantages to using impactor flow geometry:
(i) the sensor response was not as sensitive to the alignment of the sensing crystal, and (ii) larger amounts of coating could be applied while still maintaining reliable sensor operation and thus, lifetimes in the range of 1000 ppb-hr were achieved.

Sensor Response to Ozone

The POM sensor response was linear from 30 to 300 ppb of ozone. The line generated when the actual ozone concentration was plotted against the sensor response (SR) was described by the equation $[O_3] = 58.5 * SR$. Therefore, the calibration factor was 58.5 ppb of ozone per Hz min^{-1}. Recall that the monitor's limit of detection (LOD) was described as a function of the monitor's calibration factor and its noise level (the average response when no ozone was present). More precisely, the LOD equals the product of the calibration factor and three times the noise level. The noise level of the POM SR was 0.15 Hz min^{-1}, so therefore the LOD was 26 ppb.

Coated Crystal Storage

The ability to store coated and conditioned crystals would improve the ease of use of the POM in field sampling. All of the crystals necessary for a particular field study could be coated, conditioned, and stored prior to the field work. This would save time during field sampling and eliminate the need to have ozone generating equipment at the field site. Experiments with the POM showed that the crystals could be coated and stored from 24 hours to four days and perform comparably to freshly coated crystals when all of the crystals were conditioned immediately before sampling. However, tests also showed that crystals that were coated, conditioned, and stored for 24 hours, 4 days, and 24 days had much shorter lifetimes than freshly coated and conditioned crystals. Possible remedies to this storage problem are considered below.

2.3.2 Interference Testing

Laboratory

A sensor using the parallel flow geometry and 80% 1-4 addition polybutadiene exhibited ~3% interference in the presence of 200 and 1000 ppb of NO_2. This was determined by dividing the difference between the measured and actual ozone concentrations by the NO_2 concentration. In other words, sensor response to NO_2 is 0.03 times that for ozone. Therefore, even extreme indoor NO_2 levels (1000 ppb) would give a signal corresponding to <30 ppb of ozone. Please refer to section 2.3.1 for further discussion of NO_2 and polybutadiene. No interferences were observed when a sensor using the parallel flow geometry and 80% 1-4 addition polybutadiene was exposed to ozone and either NO, HNO_3, or toluene. Therefore, NO, NO_2, and HNO_3 are not of concern as interferences to sensors coated with the 80% 1-4 addition polybutadiene. Toluene, and by extension other organic solvents, are also unlikely to interfere with ozone measurements.

Water vapor could cause an interference if it adsorbs to the surface of the sensing and reference crystals at different rates. Since the two surfaces are different–the reference electrodes are gold and the sensing electrodes are gold coated with polybutadiene–it is possible that these two surfaces would not adsorb water at the same rate. In fact, gold is more hygroscopic than polybutadiene and this is illustrated by the fact that the sensor response decreased when water vapor content was abruptly increased (Figure 2.19).

The Nafion dryer used in the POM greatly reduces water vapor interference as shown in Figure 2.20 and Table 2.3. Both the POM and the UV photometric measurements indicate that ozone levels decreased when RH levels increased and vice versa. The changes in ozone concentration were caused by variations in the mixing ratios of ozonated air and air containing water vapor. Different amounts of each gas stream were needed to create the various combinations of ozone and RH levels. The POM measurements were within 10% of the Dasibi readings when RH varied from 20 to 80 to 20 to 80% and ozone was maintained at ~100 ppb. The POM measurements were also within 10% of the Dasibi readings when ozone varied from ~100 ppb to 50 ppb and RH was maintained at ~80%. These test

results indicate that ambient levels and variations in water vapor should cause only minimal interference to the POM ozone measurements.

Outdoor Air

Separate calibration factors were used for each sensor in each run because the goal of the study was to determine if any constituents of outdoor air caused significant interference. If an average or composite calibration factor were used variations in the sensor response could have been misinterpreted as response to interferences. Interferences would have been indicated if the sensor measurements had all been higher or lower than the actual levels. No such bias was observed over the three days of sampling.

3 Field Evaluation

3.1 Experimental

3.1.1 Offices and Residences

The final design of the piezoelectric ozone monitor (POM) was evaluated under real-world sampling conditions between Oct. 27 and Nov. 3, 1998 in Southern California. Sampling was conducted on one day each at two offices located in Riverside, CA and on two days each at two residences in Pasadena, CA. Hourly average ozone measurements made at the Riverside and Pasadena-S Wilson Ave monitoring stations is shown in Table 3.2. Indoor measurements were made inside each location on each day with two POMs and a UV photometric ozone monitor. A temperature and humidity probe (Vaisala 50Y) was placed near the monitors and T/RH data were recorded using one of the POM's dataloggers. Measurements of outdoor ozone concentrations were made with one POM and a UV photometric ozone monitor at the residential locations only. Both monitors were placed indoors with Teflon sample lines running out a window. The sample line inlet was positioned about 30 cm from the outside wall. A temperature and humidity probe was positioned near the sample line inlet and was recorded by the POM datalogger. Indoor and outdoor measurements were made simultaneously on each day of sampling at each residence. All sampling was conducted from 9 AM to 5 PM each day at each location. Although both residences had gas stoves with pilot lights, the stoves were not operated during our field sampling.

One of the offices was located at the University of California at Riverside, College of Engineering Center for Environmental Research and Technology (CE-CERT) and will be referred to as office 1. Office 1 was a cubicle (2.5 m x 3.5 m) located within a room (32m x 42 m x 5 m). The monitors were placed on a cart with their sample inlets facing the center of the cubicle at a height of 1 m.

The room did not have windows that could be opened. The room air was conditioned by a swamp cooled ventilation system controlled by the building operator.

The other office was a small office (2.7 m x 4.3 m x 3.7 m) located on the second floor of Pierce Hall on the main UC Riverside campus and will be referred to as office 2. Monitors were placed on the floor along the back wall with their sample air inlets facing away from the wall. Two narrow windows were located near the ceiling, but these could not be opened. The air inlet and exhaust of a mechanical ventilation system were located in the ceiling; the air inlet was covered with a fabric filter. Air flow in the room was increased when the door was left open.

One of the residences in Pasadena was a two story 65 m^2 (700 ft^2) apartment. The apartment was located in the back of the building and its windows faced away from the residential street located about 50 m away. All monitors were placed in the living room of the apartment on the first floor. The monitors measuring indoor air were placed on chairs in the center of the room with their sample air inlets facing away from the backs of the chairs. The monitors sampling outdoor air were placed on the floor with sample lines running out a nearby window. Ventilation was controlled by opening and closing the window in the living room and two sliding glass doors in the kitchen. A 2 m wide patio that adjoined the walls containing the window and sliding glass doors was enclosed by a 2 m high wooden fence. About 50% of the patio area was shaded by a large tree.

A second residence was a single story 75 m^2 (800 ft^2) duplex house located in Pasadena near the foothills of the San Gabriel Mountains. The indoor monitors were placed on the dining room table with the sample air inlets facing the center of the living/dining room. The living/dining room windows faced and were perpendicular to the residential road about 20 m away. The road was in the process of being resurfaced and on the second day of sampling diesel-powered construction equipment was operated in front of the house. The monitors measuring outdoor air were positioned in a back room beneath a window facing a yard with little tree cover. Strong airflow was generated in the living/dining room when windows and doors in this room were opened. The windows and doors were opened and closed periodically to cause changes in indoor ozone levels.

All sampling was conducted using three POMs with 9.5 mm diameter electrode crystals coated with 8 kHz of coating A and sample air flow rates of 0.13 LPM. The POMs were operated as described in Appendix A. An ozone generator (TECO 146 multi-gas calibrator), UV photometric ozone monitor (Dasibi 1008-AH), and pollutant-free air source (canisters of Dri-rite and activated carbon) were configured at a laboratory near the sampling sites to condition the coated crystals and generate calibration points. POMs were calibrated at the beginning and at the end of each sampling day (Table 3.1). Calibrations were made with ozone levels of 30, 50, and 100 ppb except those for the offices which did not include the 100 ppb calibration point.

3.1.2 Photocopy Room

Ozone measurements were made from 9 AM to 5 PM on Dec. 12, 1998 in the 7th floor photocopy room of Davis Hall on the UC Berkeley campus with two POMs and a UV photometric ozone monitor. Sample lines for each monitor were positioned at typical breathing height (1.5 m) and about 0.3 to 0.6 m behind where the photocopier operator would stand. Operators were asked to record the time of day and the number of copies made on a log sheet attached to the copier. The room had a volume of 40 m^3, was mechanically ventilated and contained one Kodak Imagesource 85 photocopier. The copier was about one year old, copied at a rate of 85 per minute, and was not fitted with an exhaust filter. The copying mechanism consisted of a three wire corona primary charger, dual component dry toner, magnetic roller developer, and a heated roller fuser.

3.2 Results

3.2.1 Offices and Residences

One of the goals of the study was to evaluate the performance of the POM under real-world sampling conditions using a single pre-determined calibration factor. Use of a single calibration factor greatly decreases overall sampling time and effort by eliminating the need for individual calibrations. Field calibration data (Table 3.1) were combined with laboratory test data (Figure 2.17) to determine a calibration factor of 58 ppb of ozone per Hz min^{-1}. This calibration factor was used to interpret all but

one day of data collected during field sampling. At office 1, a higher flow rate orifice (0.25 LPM) was used to increase sensitivity to ozone, and a calibration factor of 24 ppb of ozone per Hz min^{-1} was used to interpret data collected at this site. This calibration factor was determined with laboratory data.

Ozone levels in office 1 did not exceed 12 ppb (Figure 3.1). Since the detection limit of the monitor was 30 ppb, objectives for sensor performance are not applicable to office 1 measurements. Even small differences between ozone levels can lead to large relative errors when the measured ozone concentrations in the denominators of the precision and accuracy calculations are less than 30 ppb. The POMs did track the ozone levels fairly well in office 1 despite operating below the detection limit most of the time (Figure 3.1). Ozone levels in office 2 were typically below 25 ppb and only exceeded 30 ppb for 90 minutes (Appendix C). The
30 ppb limit of detection is designated as a thick dashed line on each field sampling figure.

Indoor ozone levels at the two story apartment (residence 1) did not exceed 30 ppb on either day (Appendix C). Again, the POMs tracked the low ozone levels fairly well (Figure 3.2). Outdoor ozone levels at residence 1 exceeded 30 ppb for about 4 hours on one day and for nearly the entire sampling period on the second day (Figure 3.3). The accuracy of POM outdoor ozone measurements was within 3% of UV photometric measurements on each day (Table 3.2).

At the duplex house (residence 2) both indoor and outdoor ozone levels reached 60 ppb. POM measurements of ozone in indoor and outdoor air are shown in Figures 3.5 and 3.6, respectively. The indoor measurements also show the POM's rapid response to the changes in ozone concentration that occurred when windows were opened and closed. Until about noon on 11/3/98 indoor ozone levels were less than 10 ppb. At noon the windows were opened and, due to the high air exchange rate, indoor ozone levels rapidly approached outdoor levels (Figure 3.5). When the doors and windows were closed at 1430 hours the indoor ozone levels rapidly decreased from ~50 ppb to <10 ppb.

The precision of the indoor measurements made at residence 2 was 4% on day one and 9% on day two (Table 3.3). The bias and accuracy of the indoor POM measurements made at residence 2 ranged from -17 to -1% and 2 to 17%, respectively (Table 3.3). The outdoor POM measurements

exhibited a bias and accuracy of -11% and 11%, respectively, on the first day of sampling and -3% and 4%, respectively, on the second day (Table 3.3).

Outdoor ozone measurements made with UV photometric analyzers at the Pasadena residences (Appendix C) agreed well with those recorded at the nearest monitoring station (Table 3.2). The daily average difference between the hourly measurements made at the residences and the nearest monitoring station ranged from –2 to 5 ppb and the bias ranged from –2 to 13%. The maximum difference between hourly measurements made at either residence and the nearest station monitor was 23 ppb.

3.2.2 Photocopy Room

Ozone levels in the copy room were typically below 20 ppb during the sampling period. When the hourly average number of copies approached 50 ozone levels increased proportionately with a maximum observed ozone level of 40 ppb (Figures 3.7 and 3.8). The POMs accurately measured the rapid changes in ozone concentration that coincided with higher numbers of copies. Specifically, the accuracy of each POM was 12% and the precision of the two POM measurements was 5% (Table 3.3). The bias of POM1 and POM2 was 2.4% and -3.7%, respectively (Table 3.3).

Table 3.1. POM calibration factors determined on each day of the 1998 field study.

Calibrated	Calibration Factor (ppb of ozone per Hz min^{-1})

Location	Date	Before/After Sampling?	Indoor POM1	Indoor POM2	Outdoor[a] POM
Office 1[b]	10/27/98	Before	24.1	23.3	—
“	“	After	24.8	25.0	—
Office 2	10/28/98	Before	57.0	55.2	—
“	“	After	57.2	56.5	—
Residence 1	10/30/98	Before	56.5	56.0	56.5
“	“	After	58.3	57.6	56.0
“	10/31/98	Before	56.4	58.0	55.8
“	“	After	59.0	60.9	57.6
Residence 2	11/2/98	Before	56.8	55.5	58.1
“	“	After	57.0	56.1	57.5
“	11/3/98	Before	55.8	57.2	56.5
“	“	After	56.3	56.0	57.0
Photocopy Rm	12/10/98	Before	55.7	58.0	—
“	“	After	56.0	58.3	—

[a]No outdoor POM at office and photocopy room sites.
[b]POMs equipped with 0.25 LPM orifice at this location only. All other days were 0.13 LPM.

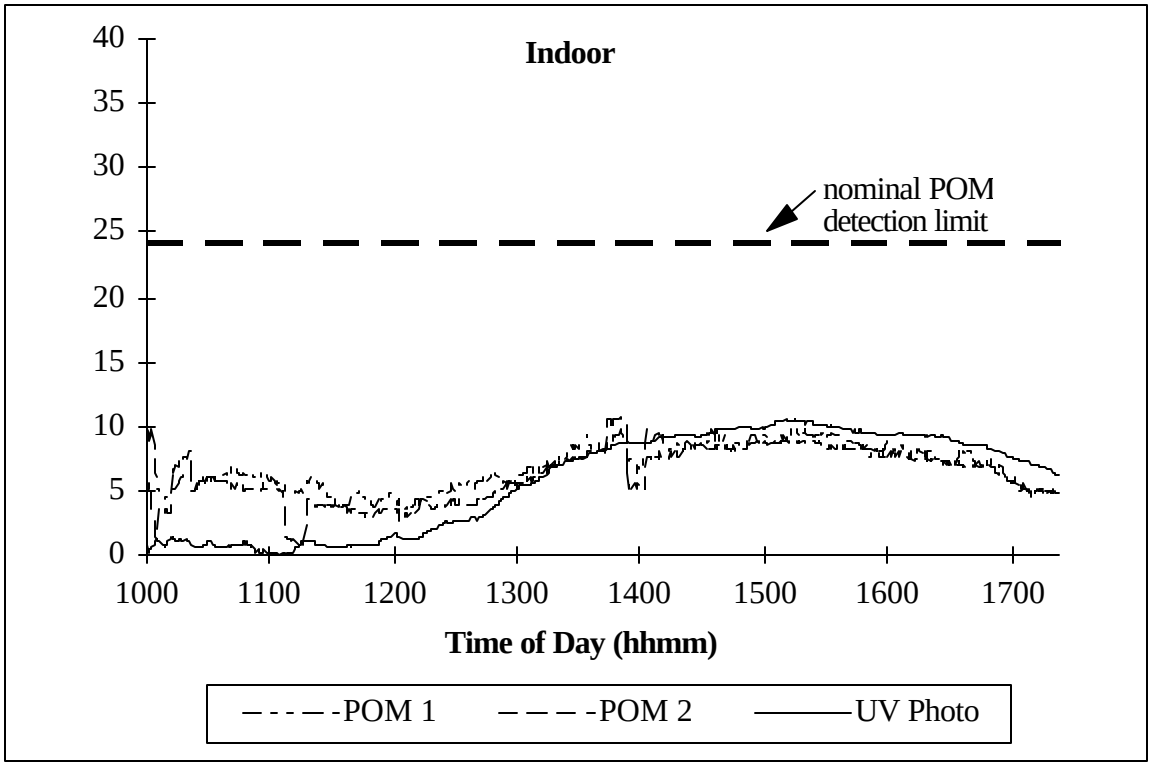


Figure 3.1. Indoor POM measurements made at office 1 on 10/27/98. POM using flow of 0.25 LPM and 9.5 mm electrodes coated with 8 kHz of 80% 1-4 addition polybutadiene.

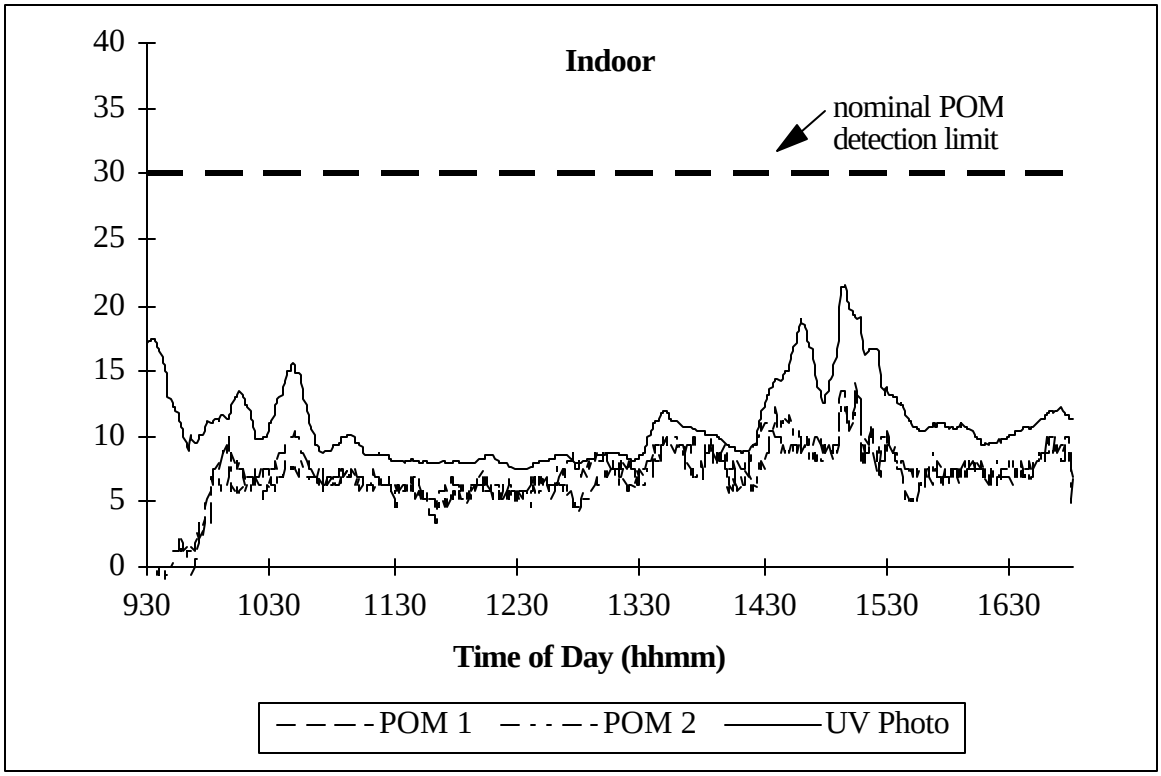


Figure 3.2. Indoor POM measurements made at residence 1 on 10/31/98. POM using flow of 0.13 LPM and 9.5 mm electrodes coated with 8 kHz of 80% 1-4 addition polybutadiene.

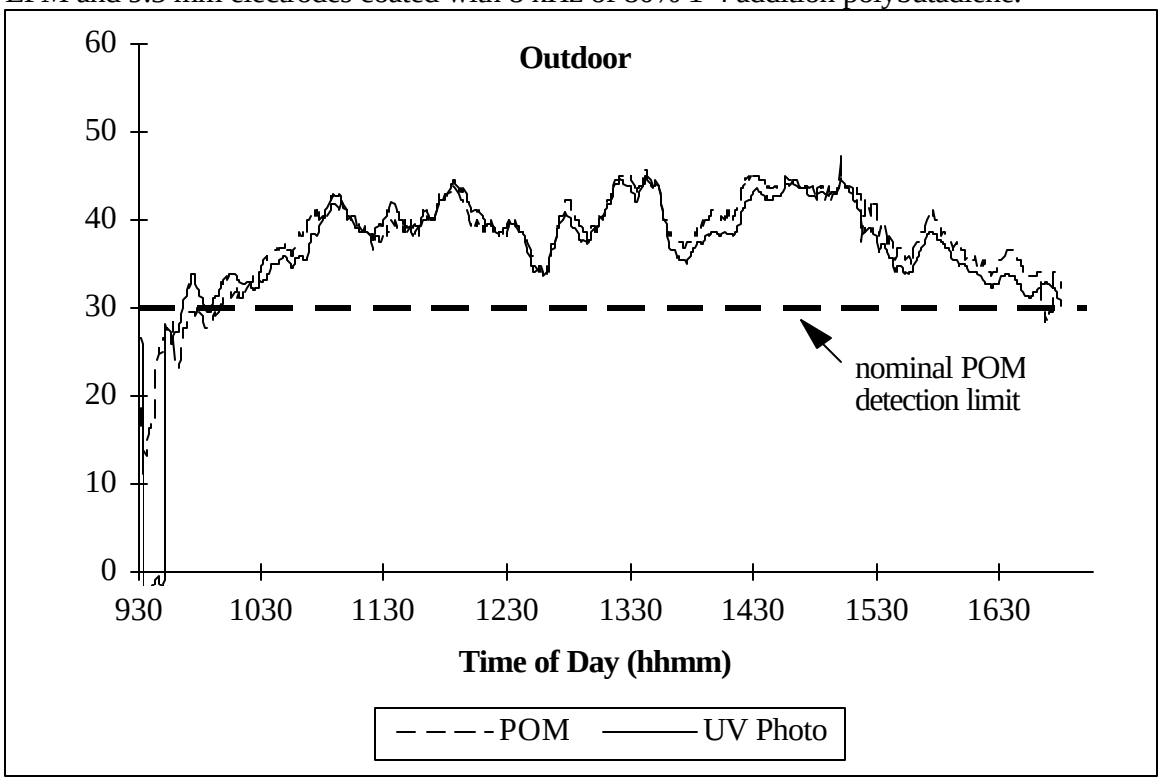


Figure 3.3. Outdoor POM measurements made at Residence 1 on 10/31/98. POM using flow of 0.13 LPM and 9.5 mm electrodes coated with 8 kHz of 80% 1-4 addition polybutadiene.

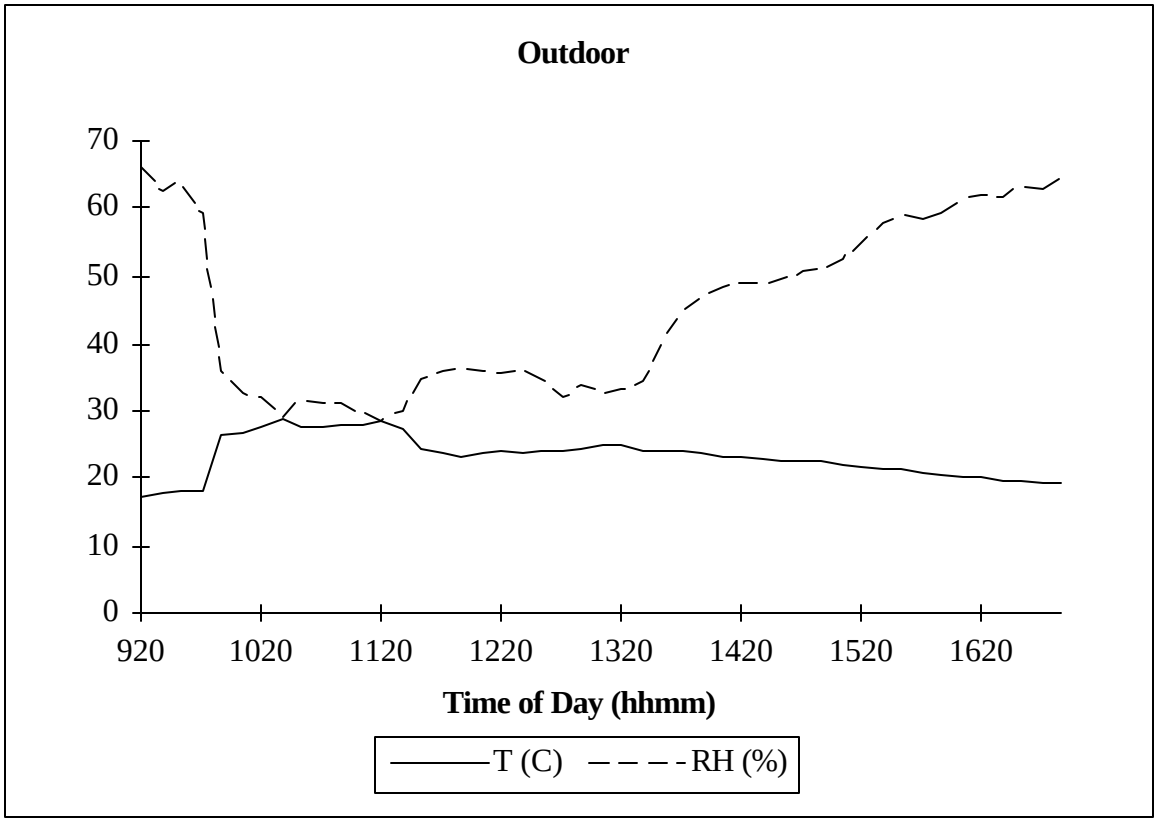


Figure 3.4. Outdoor temperature and relative humidity at Residence 1 on 10/31/98.

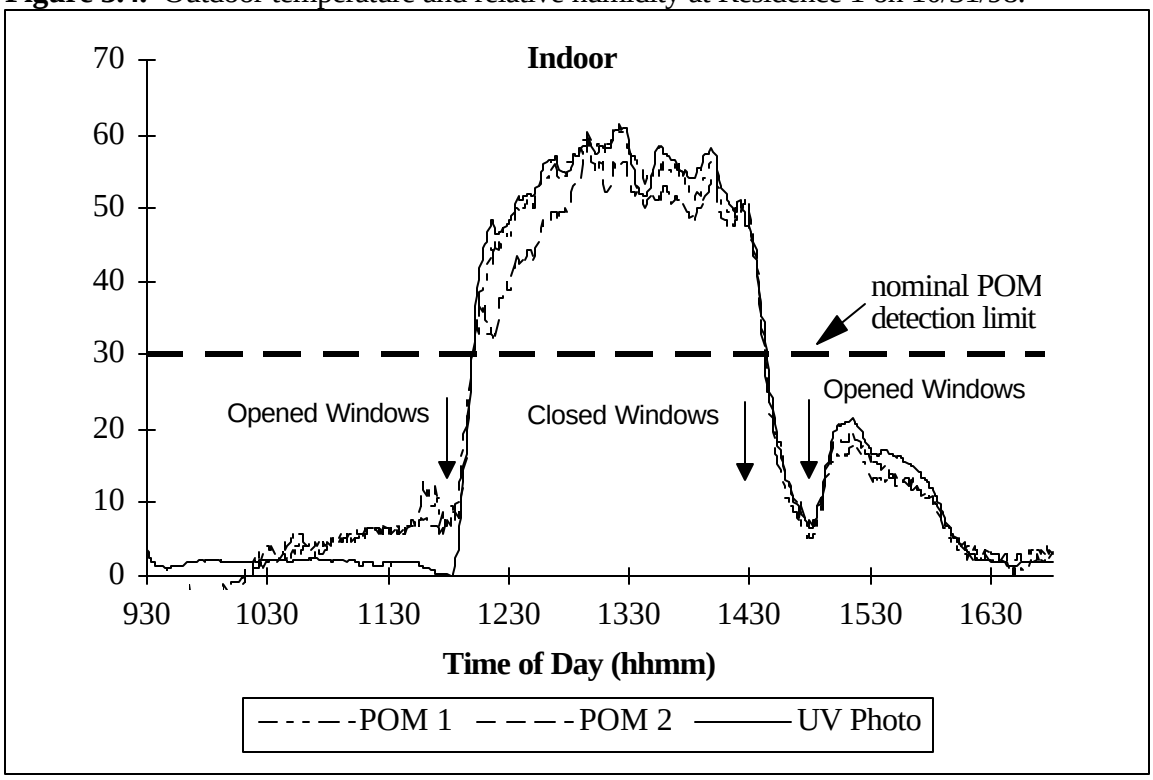


Figure 3.5. Indoor POM measurements made at Residence 2 on 11/3/98. POM using flow of 0.13 LPM and 9.5 mm electrodes coated with 8 kHz of 80% 1-4 addition polybutadiene.

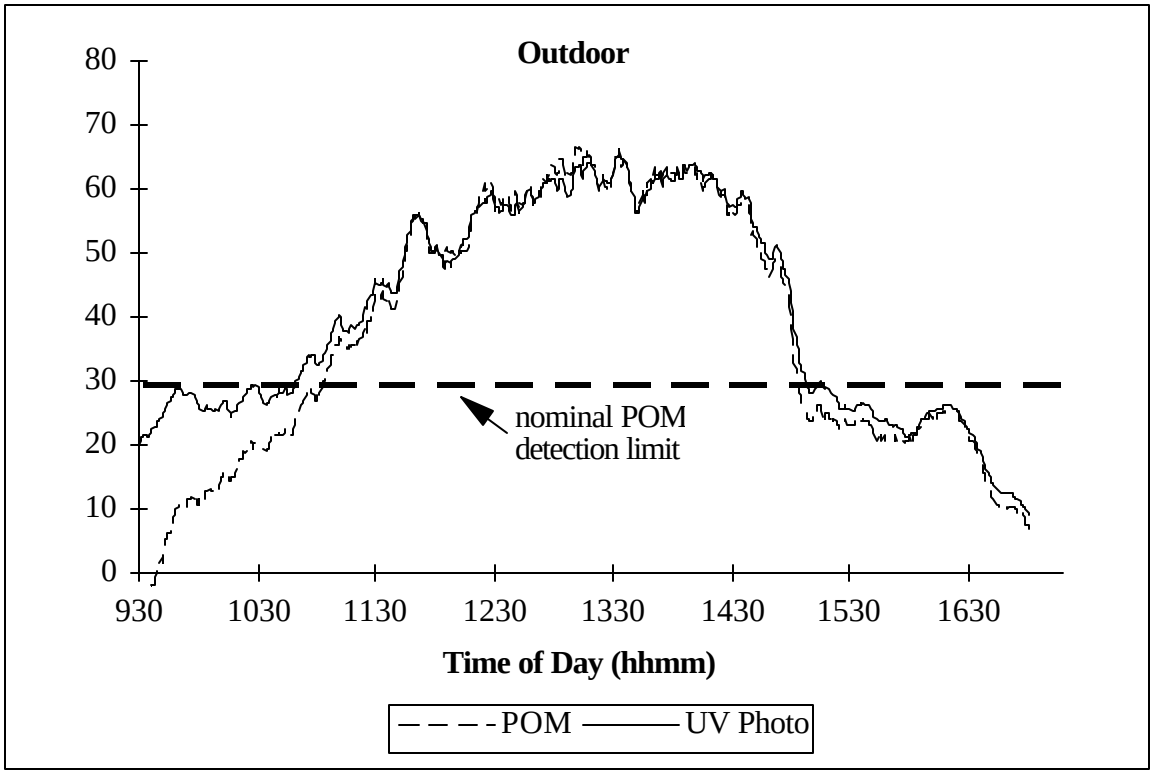


Figure 3.6. Outdoor POM measurements made at Residence 2 on 11/3/98. POM using flow of 0.13 LPM and 9.5 mm electrodes coated with 8 kHz of 80% 1-4 addition polybutadiene.

Table 3.2. Hourly average ozone measurements (ppb) recorded at monitoring stations closest to each sampling location.

Time	10/27/98[a]	10/28/98[a]	10/30/98[b]	10/31/98[b]	11/2/98[b]	11/3/98[b]
0800	4	4	10	21	11	6
0900	5	11	15	33	29	24
1000	29	23	18	35	47	44
1100	43	50	20	39	57	57
1200	59	62	19	39	63	66
1300	58	49	28	45	46	58
1400	56	52	31	40	34	43
1500	51	43	33	40	34	23
1600	50	52	24	32	29	19
1700	40	32	6	16	8	1
1800	23	10	0	8	2	0
1900	14	4	0	1	0	0

2000	6	3	0	0	0	0

[a]Measurements from the Riverside monitoring station.
[b]Measurements from the Pasadena-S Wilson Ave monitoring station.

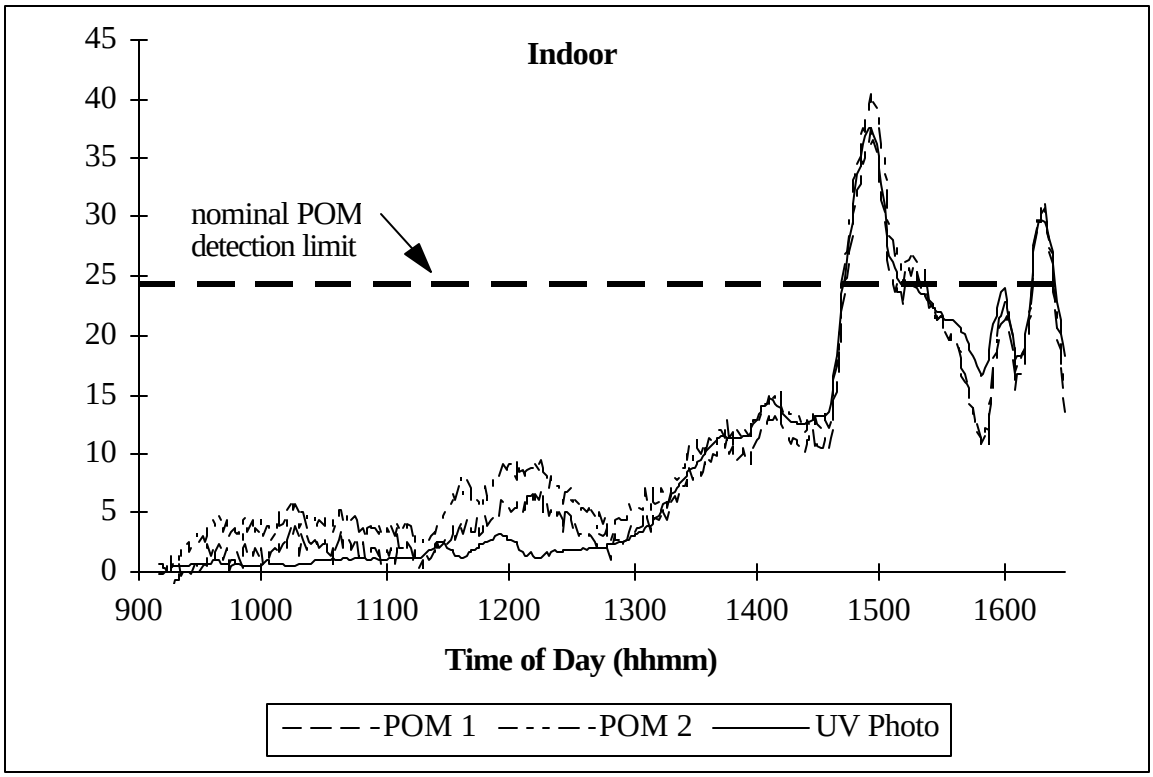


Figure 3.7. Measurements made in photocopy room with two POMs (each using flow of 0.13 LPM and 9.5 mm electrodes coated with 8 kHz of 80% 1-4 addition polybutadiene) and a UV photometric ozone analyzer.

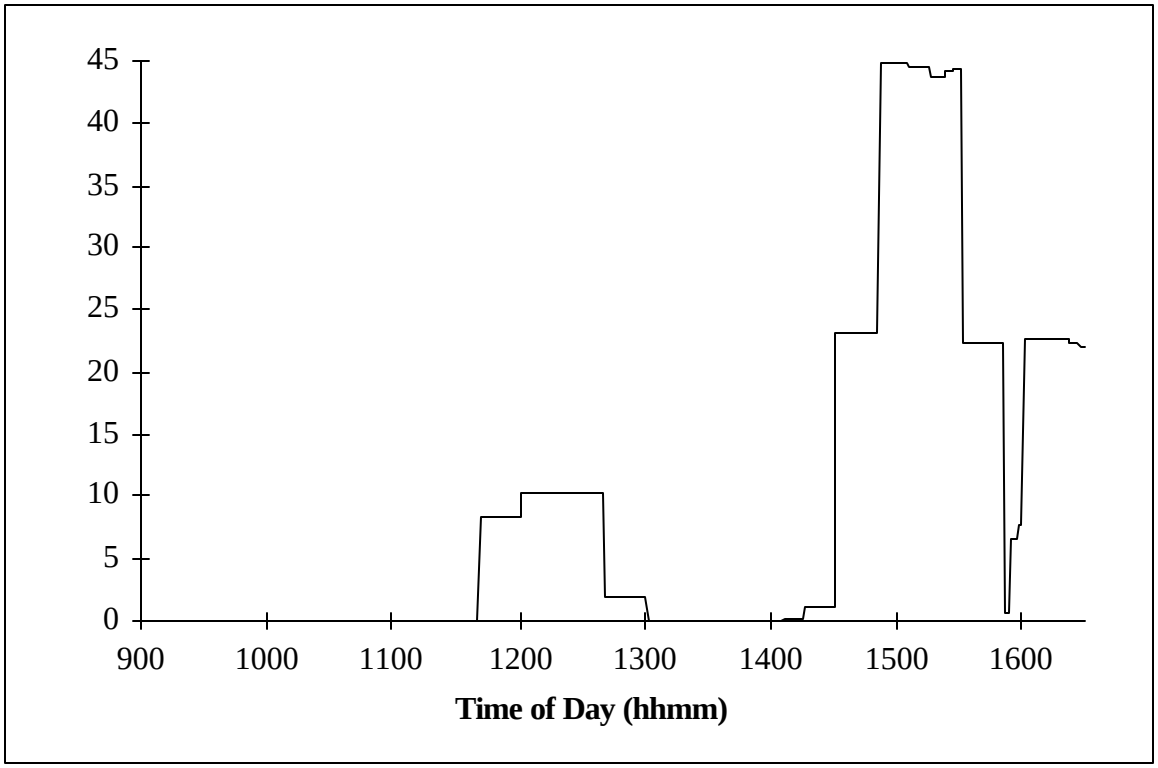


Figure 3.8. Hourly average number of photocopies made during ozone sampling.

Table 3.3. Precision and accuracy statistics for microenvironmental sampling.

Location	Precision[a] (%)	Bias1 (%)	Bias2 (%)	Accuracy1 (%)	Accuracy2[b] (%)
CE-CERT Office Indoor[c]	—	—	—	—	—
Pierce Hall Office Indoor[d]	5.7	-22.6	-26.9	22.6	26.9
Residence 1 Indoor[e]	—	—	—	—	—
Residence 1 Outdoor	—	3.0	—	3.0	—
Residence 1 Indoor[c]	—	—	—	—	—
Residence 1 Outdoor	—	2.0	—	2.6	—
Residence 2 Indoor	4.2	-13.9	-17.3	13.9	17.3
Residence 2 Outdoor	—	-10.8	—	10.8	—
Residence 2 Indoor	9.1	-1.0	-9.5	1.7	9.5
Residence 2 Outdoor	—	-3.0	—	3.9	—
Photocopy Room[f]	5.1	2.4	-3.7	12.3	11.9

[a]Only indoor measurements were made with two POMs side-by-side to estimate precision.
[b]One POM was used to sample outdoor air, thus, only one accuracy statistic is provided for outdoor measurements.
[c]Ozone levels <30 ppb for entire sampling period.
[d]POM measurement noise was caused by repeatedly connecting a PC to the datalogger.

[e]Ozone levels >30 ppb for ten minutes during sampling period.
[f]Ozone levels >30 ppb for twenty minutes during sampling period.

3.3 Discussion

3.3.1 Microenvironmental Measurements

The precision and accuracy of the POM field measurements were within 10 and 20%, respectively, and thus met the study goal (Table 3.3). It should be noted that the study goal was to meet these criteria at ozone levels greater than 80 ppb. Differences between ozone measurements lead to larger relative errors when the measured ozone concentrations in the denominators of the precision and accuracy calculations are low. Thus, the POM met a higher standard of performance by achieving the precision and accuracy goals at ozone levels lower than 80 ppb.

The consistent performance of the POM is shown in the calibrations conducted at the beginning and end of each sampling day (Table 3.1). The calibration factors determined for the 0.13 LPM flow rate had a mean of 57.0 ppb of ozone per Hz min^{-1} and a relative standard deviation of ±2.1%. The small standard deviation indicates how consistent the response of all three POMs was over five days of field sampling. Furthermore, the calibration factor varied on average by only 2% between the beginning and end of any individual sampling day for all POMs.

Each POM used at office 1 was equipped with a 0.25 LPM flow control orifice instead of the standard 0.13 LPM orifice because low ozone levels were expected. The higher flow rate was used to increase the sensitivity of the POM sensor. Ozone levels measured in office 1 were well below 30 ppb, but the POM measurements still tracked the low levels (Figure 3.1). The POM flow rate was easily changed in the field because the orifice is held at one end by a threaded Swagelok fitting and by Tygon tubing on the other. The higher flow rate was not used on other sampling days because (i) higher ozone levels were expected and (ii) there is a trade-off between increased sensor sensitivity and decreased sensor lifetime.

Temperature (T) and relative humidity (RH) varied during the microenvironmental sampling (Appendix C). During one day of sampling at residence 1 the RH of the outdoor air varied from 30 to

65% (Figure 3.4). In fact, RH fell quite rapidly (65 to 30% over a 20 minute period) when sunlight first illuminated the patio area at about 10 AM. This rapid change in RH did not interfere with the POM measurements. Use of the Nafion dryer has significantly reduced earlier concerns of water vapor-induced interference.

Real-time measurements enable correlation of ozone levels to other changes in the microenvironment. For example, the measurements made inside and outside of residence 2 show how rapidly indoor ozone levels changed when windows were opened or closed (Figures 3.5 and 3.6). When windows were opened the air exchange rate increased and indoor ozone levels approached outdoor levels. When windows were closed the ozone levels decayed nearly as rapidly as they increased when windows were opened, but the air exchange rate was much lower. Therefore, rapid ozone loss occurred indoors due to reactions with indoor surfaces. The indoor measurements can be combined with outdoor measurements to determine indoor/outdoor (I/O) concentration ratios for specific ventilation conditions.

In addition to changes in ventilation conditions, use of indoor ozone sources can cause changes in indoor ozone levels. The electric wire corona used by most photocopy machines can produce ozone (Leovic et al., 1996). This was seen in the measurements made in the photocopy room (Figures 3.7 and 3.8). When the photocopier was not in use the ozone levels were very low. However, when photocopies were made ozone levels increased rapidly. The magnitude of the peaks in ozone concentration were proportional to the number of photocopies made. Measurements made in this study indicate that ozone exposure may be significant when the number of copies being made is very large, although higher volume photocopiers are sometimes equipped with activated carbon filters to scrub ozone from machine ventilation air.

The transient noise exhibited in some of the POM measurements (e.g. steps at 1000, 1100, and 1400 in Figure 3.1 and at 0930 in Figure 3.3) was caused by electrical noise interference. This electrical noise was exacerbated by connecting and disconnecting the PC to the datalogger. The PC connection was made to monitor the POM measurements and was done infrequently on most days of sampling. During sampling in office 2 the POM measurements were monitored often and the resulting

noise in the stored frequency data was such that the accuracy of the POM readings was compromised (Table 3.2). Investigation in the laboratory conducted after the field study revealed that the noise was caused by a short between the circuit board and the metal enclosure. This short and, in turn, the electrical noise was eliminated by isolating the circuit board from the metal enclosure with rubber stand-offs.

Overall the POM ozone measurements agreed well with those made by the UV photometric analyzer when ozone levels were greater than 30 ppb. The POM responded rapidly to even small changes in ozone levels (Figures 3.3 and 3.6). However, when ozone levels were below 30 ppb at the beginning of the sample period the POM measurements appear to lag below those of the UV photometric analyzer (Figures 3.2 and 3.6). The POM measurements did reach those of the UV analyzers when ozone levels exceeded 30 ppb. This lag was not observed during laboratory testing with the POM conducted before the field study. One difference between the laboratory and field testing was that during the field testing the POM was conditioned and calibrated in a different location away from where the sampling took place. As a result, the POM was turned off, with no flow through the sensor, for about 30 to 60 minutes during transport between POM conditioning/setup and sampling locations. A suitable conditioning and storage procedure is needed that would allow installation and immediate use of coated crystals at the sampling location.

3.3.2 Sensor Response and Temperature

Before the 1998 field study some experiments indicated that the sensor response was related to the temperature inside the sampler enclosure. The sensor beat frequency output would vary 2 Hz for 1°C change in temperature. This was only observed in the Hz min^{-1} sensor response when the temperature changed very rapidly over time. In other words, the temperature-induced interference was usually below the sensor noise level. No temperature related interference was observed during the 1998 field study. Nevertheless, the issue is of potential concern in microenvironments with rapidly-changing temperatures, or for future personal monitoring applications where sudden temperature changes may occur as the subject moves from one microenvironment to another.

3.3.3 Ease of Use and Cost of POM

The POM is relatively easy to use for anyone familiar with gas analyzing equipment. Preparation time before each use of the POM requires about one hour. The only skill necessary to prepare the POM that could be considered "special" would be the application of the polybutadiene coating. The coating application procedure is easily mastered with some practice. The POM does not require attention from the operator during sampling. After sampling is concluded only 15 minutes is required to download the data and clean the sensing crystal. The POM preparation and maintenance steps are described in detail in Appendix A, and the estimated time for each procedure is summarized in Table A.1.

A parts list including cost is provided in Appendix B. The cost of parts for one POM is less than $1700, and the time for assembly is about one hour.

4 Summary and Conclusions

This research has demonstrated the use of polybutadiene-coated piezoelectric quartz crystals for real-time measurement of ozone concentrations. A compact and portable sampler has been developed that is suitable for microenvironmental monitoring.

Major phases of this project included (i) investigation of sensor design parameters such as coating type, methods of coating application, air flow and sensor configuration, (ii) assessment of potential interferences via laboratory and field testing, (iii) design, fabrication, and testing of five piezoelectric ozone monitors, and (iv) field evaluation of the monitors under real-world sampling conditions in two residences, two offices, and a photocopy room.

The sensor consists of two 10 MHz piezoelectric quartz crystals with gold electrodes. One crystal is coated with polybutadiene which reacts irreversibly with ozone and causes a mass increase on the crystal electrode which is sensed as a shift in crystal oscillation frequency. A second crystal oscillation frequency is used as a reference signal to compensate for changes in temperature. In their optimal configuration, sensing crystals are coated with polybutadiene on both sides and exposed to jets of sample air in an impactor flow geometry. Two different types of polybutadiene coating were evaluated, and only one was found to be suitable for use in ozone sensing applications. The second coating was susceptible to oxidation by O_2 and NO_2, and this interfered with specific detection of ozone. A Nafion membrane was used to dry the sample air without removing ozone. This was necessary because the rate of uptake of water from the sample air stream by the coated sensing crystal differed from the rate of uptake by the uncoated reference crystal. Preconditioning of the sampler by exposure to 300 ppb of ozone for ~40 minutes was necessary to obtain a linear relationship between sensor response and ozone concentration.

The ozone monitor has a detection limit of 30 ppb and a useful lifetime of about 1000 ppb-hr, with a time resolution of 10 minutes. In side-by-side testing of ozone monitors in the field, precision ranged from 4 to 9% (6% on average), bias ranged from -17 to 3% (-5% on average), and accuracy ranged from 2 to 17% (9% on average) when compared to a reference method (UV photometric detection) for real-time ozone measurement. The ozone monitors responded rapidly to changes in indoor ozone levels induced by (i) deliberately altering air exchange rate and (ii) operating a photocopier during field sampling.

Laboratory testing indicated a possible temperature related interference. This is a potential concern in microenvironments with rapidly-changing temperatures, or in future personal monitoring applications where sudden temperature changes may occur as the subject moves from one microenvironment to another.

This study is the first demonstration of a portable, affordable, real-time ozone monitor. The monitor provides new capabilities to measure diurnal variations in human exposure to ozone, and represents a major advance in the state of the art in techniques for ozone exposure assessment.

5 Recommendations

Further Interference Testing

The results of the interference testing conducted in this study are promising, but they do not address the questions of all indoor and outdoor interferences likely to be encountered in the field. Further laboratory and field interference testing should examine indoor pollutants such as cleaners, solvents and emissions from indoor combustion sources (e.g. gas stoves). The effects of rapid temperature change should also be examined.

Further Sensor and Monitor Refinements

As described in section 2.2.1, the sensing crystal must be coated and conditioned with ozone before the POM can be used. Field studies conducted with the POM would be simplified if a batch of crystals could be coated, conditioned, and stored prior to the study. Further investigation of storage methods should be conducted. One possible method may be to continuously pass filtered air over the coated crystals during the storage period. This could be accomplished with an appropriate container, an activated carbon filter, and a small battery-operated pump.

The POM performed well during the microenvironmental sampling conducted in this study. However, as discussed in section 3.3.1, an initial POM measurement lag was observed during some sampling sessions. This initial lag should be examined further in laboratory and field testing. A possible remedy may include refining the conditioning procedure; this may include changing the ozone concentration and/or the duration of conditioning. A suitable storage scheme as described above may also eliminate the lag by allowing the installation and immediate use of coated crystals at the sampling location.

The ability to sample for more than one day with the same coated sensing crystal would greatly improve the POM's ease of use. This could be accomplished by incorporating a partial duty cycle sampling scheme in which the sensor would only be exposed to sample air containing ozone for a fraction of the total sampling time and, thus, only a fraction of the coating would be exhausted compared to full duty cycle sampling. Sample air could be directed through the sensor for a period of time and then re-routed, via an automated valve, through a charcoal filter to remove ozone before reaching the sensor. For example, sample air could be monitored for 10 minutes every 30 minutes to provide an ozone concentration reading every 30 minutes. This would diminish the time resolution of the data compared to the current sampling scheme, but would improve sampler lifetime by a factor of three.

The POM performance described in this report can only be expected when Aldrich part no. 38-369-4 polybutadiene is used. If any other polybutadiene formulations are used calibration and interference testing must be repeated.

Further Field Testing

The field testing of the POM conducted in this study should be repeated for other microenvironments during other seasons. Sampling should be conducted both indoors and outdoors during the Spring and Summer in order to evaluate the performance of the POM at higher ambient ozone levels. Microenvironments to examine include residences and offices with different ventilation characteristics than those used in this study, schools, hospitals, and inside vehicles. To use the POM inside a vehicle would require that the POM be converted solely to battery power; this would require some simple re-wiring and a larger capacity rechargeable battery. Microenvironments with rapidly changing humidity levels should also be examined.

Microenvironmental Monitoring

One suggested approach to estimating personal ozone exposure involves real-time monitoring of ozone concentrations in all microenvironments in which an individual spends time. The sensor developed in this project is well-suited to this task, and its capabilities should be demonstrated during an

upcoming “instrumented house” study in California. Further development of the sensor will be needed to allow for larger-scale deployments in field studies designed to assess ozone exposure. Eliminating the need for sensor preconditioning at the beginning of each sampling day would reduce the set-up time and costs of using the sensor.

Personal Monitoring

We believe an exciting future application of piezoelectric crystal-based sensing will be in real-time personal ozone monitoring. This application should be pursued and compared with results of ozone exposure assessment that are based on microenvironmental monitoring and time-activity diaries. Further reductions in the weight, size, and energy demand of the sensor will be required for use as a personal monitor.

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Appendix A

Ozone monitor operating procedures

Operating and maintaining the POM consists of several procedures that include monitor preparation, crystal coating, crystal installation, monitor operation, data downloading and converting, and crystal removal and cleaning. How often each operating and maintenance procedure must be performed and the time required and difficulty of each procedure is shown in Table A.1.

1. POM Preparation

These operating instructions assume that the datalogger has been properly programmed. If programming is necessary the instructions provided by Campbell Scientific's PC208W software should be followed.

Each time the POM is used the voltage of the battery powering the datalogger should be measured with a standard multimeter. If the battery voltage is less than 11 VDC, replace the battery with a freshly charged one. When the battery is disconnected the datalogger storage memory and operating program are retained, but the date and time are lost. The date and time are set by connecting a PC running the Campbell Scientific PC208W software to the 9 pin RS-232 connector on the back of the POM via Campbell's SC23A optically isolated interface. Follow the instructions in the software's "Connect" window to set the datalogger date and time to the PC date and time.

The sample air flow rate should be measured periodically with a rotameter or bubble flowmeter at the inlet on the back of the POM. The sensor housing should be secured with its four retaining bolts when the flow is being measured. If the flow measurement is higher than expected there may be a leak in the system, and if it is lower than expected the orifice may be clogged. The orifice can be removed and cleaned with a solvent and lint free tissue.

2. Crystal Coating

The POM has been designed to use two 14 mm diameter AT-cut quartz crystals with 9.5 mm diameter gold electrodes supplied by International Crystal Manufacturer, Inc. (Oklahoma City, OK). The sensing and reference crystals are installed in a coating fixture that contains the oscillator and mixing electronics. The fixture is powered by a 5 VDC power supply and its frequency output is connected to a standard multimeter. The sensing crystal electrodes are coated with a total of 12 kHz of 80% 1-4 addition polybutadiene. Using a fine-bristled artist brush an amount of coating greater than

desired is applied to one electrode and spread evenly. Excess coating is then removed by wiping the brush with a lint-free tissue between brush strokes that are made in an even pattern. When the desired amount of coating is applied to one electrode the process is repeated for the other electrode. After coating is complete the crystals should be covered with metal caps that snap onto the base of each crystal.

3. Crystal Installation

The crystals can be installed when the POM is powered, but it is recommended that the POM be unplugged during crystal installation. To install the crystals first take off the POM enclosure cover. Then, after loosening all four retaining bolts, lift the sensor housing off the base and set it on the datalogger. The sensor housing can not be completely removed from the enclosure because it is connected to the various tubing and hardware that direct sample air flow. The sensing and reference crystals are installed in the sockets labeled "S" and "R", respectively. The crystal caps are removed and the sensor housing is then placed over the crystal platform and secured with its four retaining bolts. The enclosure lid is then replaced and secured with four screws. The POM is now ready to operate.

4. POM Operation

The sensor electronics are powered when the POM power cord is plugged into a standard 120 VAC, 60 Hz outlet. The flow of sample air through the ozone sensor housing does not begin until the pump is powered with the switch on the front of the POM enclosure. Recall that the flow rate of the sample air is regulated by the critical orifice chosen by the user; a 0.13 LPM orifice is recommended. The sensing crystal must now be conditioned before ozone measurements can be made.

To condition the crystal it must be exposed to a high level of ozone for a short period of time or a low level of ozone for a long period of time. Exposure to 300 ppb of ozone for 40 minutes is suitable when a 0.13 LPM critical orifice is installed. The crystal is exposed to ozone by connecting the POM air inlet to an ozone generator.

Place the POM wherever ozone measurements are desired. For best results the POM should be operated in a shady, cool location. To sample in sunny areas a Teflon sample line can be connected to the 1/4 inch Swagelock connector on the rear of the POM.

5. Data Download and Conversion

At the end of the sampling period the POM pump should be switched off and the unit can be unplugged. To download the time and frequency data from the datalogger connect a PC running the PC208W software to the 9 pin RS-232 connector on the back of the POM via the SC32A isolator. The data is downloaded to a user selected file by following instructions in the "Connect" window. The user can choose to download all of the data in memory or just the data recorded since the last download. The data is stored in a comma delimited text format that can be opened by a spreadsheet program. The date, time, and frequency columns can be copied to a template file that converts the frequency data to ozone concentration measurements. This is done by programming a column to calculate the ten minute running average of the rate of change of the frequency and multiply that rate of change by a calibration factor. When the POM is operated with a sample air flow rate of 0.13 LPM, the calibration factor has been found to equal 58 ppb of ozone per Hz min^{-1}. The time resolution can be set lower than ten minutes, but this increases the noise level of the measurements.

6. Crystal Removal and Cleaning

To remove the crystals first take off the POM lid and separate the sensor housing from the base as described above in the Crystal Installation section. Then, after placing caps over the crystals, take a small screwdriver and gently lift each crystal out of its respective set of sockets. The sensing crystal should be cleaned with a solvent-soaked swab. Examine each cleaned crystal for scratches or worn spots and replace the sensing crystal when necessary. To be temperature matched the new sensing crystal and the reference crystal should have AT cut angle values within 0.1 degrees. The reference crystal should only need occasional cleaning and should rarely need to be replaced.

7. POM Calibration and Maintenance

The POM should be calibrated whenever components (including crystals) are replaced. If the same pair of crystals is used with the same POM repeatedly, calibrations should only be necessary about every two weeks. A three point calibration should be performed over the range of ozone concentrations expected during sampling. Known ozone concentrations should be generated with suitable gas calibration equipment.

To maintain the POM the Teflon particle filter should be replaced after each month of use. Also, the orifice flow control should be cleaned after each month of use or whenever the sample air flow rate decreases by 10%. The stainless steel flow control orifice can be cleaned with a swab and isopropyl alcohol.

Table A.1. POM preparation, operation, and maintenance procedures.

Activity	Frequency	Time (minutes)	Difficulty (1-5; easy to hard)
POM Preparation			
-check battery voltage	before each use	5	1
-check flow rate	before each use	5	1
Crystal Coating	before each use	10	3
Crystal Installation	before each use	5	2
Crystal Conditioning	before each use	40	1
Data Downloading			
-download logger	after each use	5	1
-convert raw data	after each use	5	1
Crystal Cleaning	after each use	5	2
Calibration and Maintenance			
-calibration	every 10 uses	60	2
-replace particle filter	every 30 uses	10	1
-clean flow orifice	every 30 uses	10	1

Appendix B

Ozone monitor parts list

Table B.1. POM parts numbers, costs, and manufacturers.

Part	Part Number	Cost ($)	Manufacturer
Battery	PS-1212	15	Powersonic Corp.; San Diego, CA
Battery Recharger	PS-12300A	40	Powersonic Corp.; San Diego, CA
Circuit Board	QCM CKT BD (no center pins)	275	California Measurements, Inc.; Sierra Madre, CA
Crystal	131361	30/pr.	ICM Co., Inc.; Oklahoma City, OK
Datalogger	CR500	660	Campbell Scientific, Inc.; Logan, UT
Datalogger PC Software	PC208W	275	Campbell Scientific, Inc.; Logan, UT
Datalogger Interface Cable	SC32A	140	Campbell Scientific, Inc.; Logan, UT
Enclosure	1401P	65	Hammond Manuf. Co. Inc.; Cheektowaga, NY
Filter Holder	4-25-4	50	Savillex Corp.; Minnetonka, MN
Flow Cell Mat'l and Machining	N/A	180[a]	PEDCO, Inc.; Berkeley, CA
Orifice	K4-5-SS	15	O'Keefe Controls Co.; Monroe, CT
Polybutadiene	38-369-4 (100mL)	35	Aldrich Chemical Co.; Milwaukee, WI
Power Supply	GSC25A	50	Condor DC Power Supplies, Inc.; Oxnard, CA
Pump	UNMP50KNDC	100	KNF Neuberger, Inc.; Trenton, NJ
Sample Air Dryer	MD-110-24FP	115	Perma Pure Inc.; Toms River, NJ
SS Hardware	SS-400-1-2 SS-400-9 SS-400-3 SS-400-61 SS-4-TA-1-OR	90	Swagelok, Co.; Solon, OH

a. The flow cell material and machining cost per assembly was determined by dividing the total cost of machining six assemblies.