LAB DOCUMENTATION

MEASUREMENT OF OZONE EMISSION AND PARTICLE REMOVAL RATES FROM PORTABLE AIR PURIFIERS

Stephen A. Mang,[1] Maggie L. Walser,[1] John M. Laux,[2] Sergey A. Nizkorodov[1*]

1. Department of Chemistry, University of California, Irvine, Irvine CA 92697

2. Department of Chemistry, Orange Coast College, Costa Mesa CA 92626

** Corresponding author: nizkorod@uci.edu, 949-824-1262*

INSTRUCTOR NOTES

Required Chemicals

The following chemicals are used and/or generated in this project:

- Ozone (O_3, gas; CAS 10028-15-6)
- Sodium chloride (NaCl, solid; CAS 7647-14-5)
- Water (H_2O, liquid; CAS 7732-18-5)

Required Supplies

The following supplies must be purchased before setting up the experiment. The manufactures, part numbers (p/n), and prices are listed only for supplies that are not commonly available from chemistry stockrooms or hardware stores.

- Four ¼" feed-through fittings; Altech, Inc.; p/n 4105 A; $12 each.
- Roll of Teflon film; Professional Plastics; p/n FEP-200A; $57 per pound.
- 10' of ¼" Teflon PFA tubing; McMaster-Carr; p/n 5773K13, $4.50 per foot.
- 10' of ¼" ID conductive silicon tubing; TSI, Inc.; p/n 3001788; $6.60 per foot.
- One particle HEPA filter; Pall, Inc.; p/n 12144; $67 each.
- 50' of ¼" polyethylene or polypropylene tubing.
- 50 medium sized binder clips and/or bulldog paper clips for sealing access opening(s) in the measurement chamber.
- Ring stands and clamps for mounting hardware inside the measurement chamber.
- Miscellaneous ¼" Swagelok fittings and valves. Preferably, they should be made of Teflon for ozone lines and of stainless steel for particle lines.

Required Instruments and Appliances

The following instruments must be available.

- Several ozone-emitting air purifiers, including refrigerator and personal (worn around-neck) models. A list of air purifiers known to emit ozone can be found on the California Air Resources Board website: http://www.arb.ca.gov/research/indoor/ozone.htm
- A low concentration ozone monitor. These instruments are regularly used to monitor the air quality in major cities, and many different models are currently available on the market. Two examples of current models are Thermo Scientific model 49i and InUSA model IN-2000. They are generally expensive but working models can be purchased from a surplus equipment vendor for a small fraction of the cost. For example, the model used in the experiments described below (Ebara Jitsugyo EG-2001) was purchased as lab surplus for $125 in relatively new condition. We subsequently purchased two additional ozone monitors in working condition (InUSA model IN-2001 and Dasibi model 1003-PC) for less than $300 each. Ozone's absorption cross section at 253.65 nm Hg-line is well know, $\sigma_{253.65nm}=1.136\times10^{-17}$ cm^2, and can be used for absolute calibration of the zone monitors against a UV/Vis spectrometer.
- An optical particle counter. Similarly to the case of the ozone monitors, latest models of particle counting instruments (such as TSI model 3321 or Particle Measuring Systems model LAS-X II) are quite expensive. However, many adequate instruments can be

purchased from surplus suppliers. We acquired a used Particle Measurement Systems model Lasair 1510 for $1000 and had it re-calibrated by Particle Measurement Systems. This project does not require the counter to have absolute calibration with respect to the particle number concentration. However, linearity of detection (measured vs. actual concentration of particles) and quick time response (< few seconds) are essential.

- A personal computer (PC) with appropriate software and hardware for interfacing with the ozone monitor and particle counter. Experiments described below used National Instruments SCB-68 data acquisition board to read voltages from the ozone monitor, and a LabView program to display and store the data. However, the same tasks could have been accomplished with Vernier LabPro analog-to-digital converters, which gained popularity in school and university labs in recent years. In the absence of the computer and software, the data collection can be done manually by periodically writing down the outputs from the front panels of the ozone monitor and particle counter. In this case, students should be provided a stopwatch.
- An atomizer for generation of aerosol particles. An inexpensive aerosol dispenser will work. For example, we used a medicinal model SPAG-2 that is used to administer aerosolized drugs to patients (http://www.virazole.com/spag.jspf), which we got for free. If no source of aerosol particles is available, soot particles can be produced from smoldering wood. It is very difficult to control the absolute amount of particles introduced by this method, however, and this should be considered a last resort.
- A small refrigerator for testing refrigerator air-purifiers in realistic conditions. The best approach is to find a sacrificial refrigerator and have the inlet and outlet holes drilled in the top of the refrigerator for the sample lines. Stainless steel or Teflon tubes should be inserted through the holes, and spaces around the tubes should be filled with epoxy to prevent leaks.
- Small fan for circulating air in the measurement chamber. We used a computer processor fan powered by an AC/DC adapter.
- *Optional*: Air humidifier for setting a desired level of relative humidity in the chamber.
- *Optional*: Humidity and temperature probe (such as Vaisala HMP233).

Setting up the Measurement Chamber

A Teflon chamber with a known volume (at least 500 L) must be constructed. The chamber should have at least 4 feed-through ports for connecting ¼" sampling tubes. The chamber can be fabricated by taking a rectangular frame and surrounding it with Teflon film on all sides as shown in Figure 1a. The film is then carefully sealed with a thermal sealer. If a thermal sealer is not available, Teflon film can be attached directly to the chamber frame with packaging tape and/or heavy duty paper clips. The chamber does not have to be completely leak free but all significant openings (> 1 mm^2) must be eliminated. The chamber must have an access port for installing air purifier(s), fan, ring stand(s), humidity probe, and other necessary components inside. One possible solution is to leave a 50 cm opening in one of the seams. The opening can be sealed with packaging tape or clips after placing the components inside.

Alternatively, an inflatable Teflon bag can be used as shown in Figure 1b. It is in fact easier to fabricate than a fixed-volume chamber. First, one prepares a rectangular Teflon sheet of a desired size. Next, four feed through ports for ¼" tubing are installed in the sheet. Finally, the sheet is folded upon itself and its edges are sealed with a thermal sealer except for a 50 cm opening on one side. This opening is necessary so that air purifiers and equipment can be placed inside the bag, and it can be sealed with packaging tape and or clips. The bag can be suspended above a work surface on a horizontal rod. The height of the rod should be adjusted so that the bottom of the bag is still in contact with the work surface when the bag is fully inflated (Figure 1b). The main disadvantage of a bag as opposed to the fixed-volume chamber is that it is difficult to know precisely the volume of air contained inside the bag. Therefore, the bag must be filled with air through a calibrated flow-meter or a flow totalizer to accurately measure the volume of air added.

Sufficient length of ¼" Teflon PFA tubing must be available for ozone sampling. Two separate tubes are connected to the chamber's feed-through ports. One tube is connected to the inlet of the ozone monitor, and the other is connected to the outlet. Note that many other tubing materials are not suitable for handling ozone either because they are degraded by ozone (polyethylene, tygon, rubber) or they efficiently catalyze ozone destruction (copper). Stainless steel joints and valve may be used but the amount of metal areas exposed to ozone should be minimized.

It is necessary to use ¼" inner diameter conductive silicon tubing for particle sampling. This tube must connect one of the chamber's ports with the inlet of a particle counter. Non-conductive tubing such as polyethylene is generally not suitable because aerosol particles often carry charge and will be drawn to the walls of the tubing.

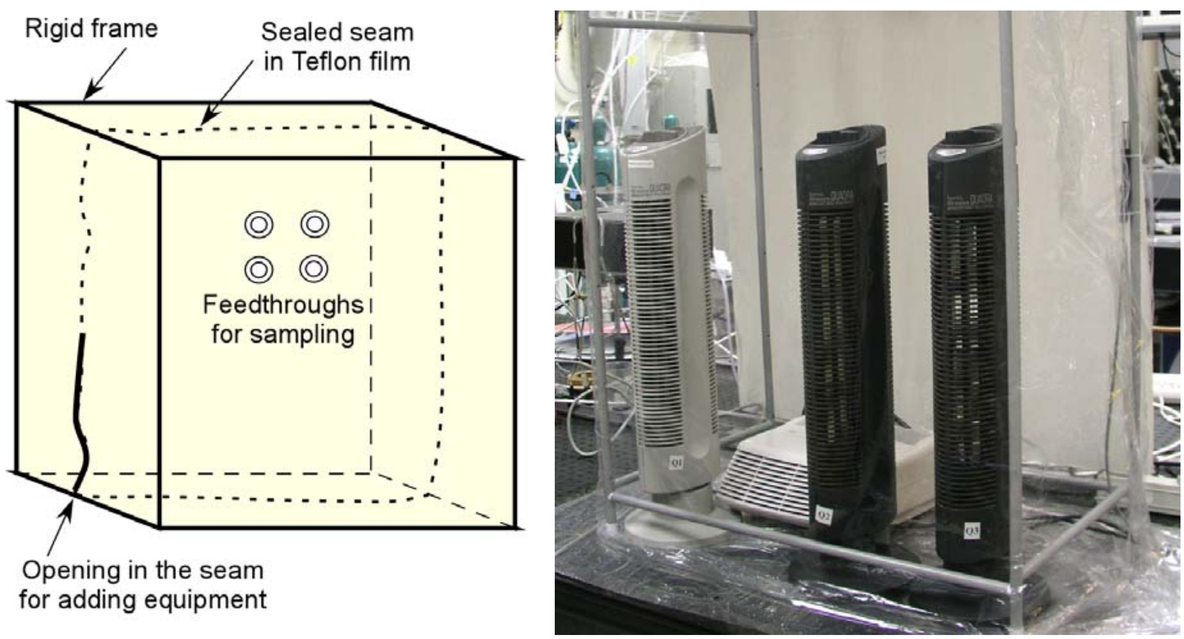

Figure 1a: Schematic diagram of a possible fixed-volume chamber design for this project and a photograph of an actual chamber with several air purifiers inside. The aluminum frame visible in the photo comes from an IKEA wardrobe. The Teflon film is thermally sealed on top and all sides of the frame. Loose ends of the Teflon film at the bottom are attached to another sheet of Teflon film on the table surface with tape.

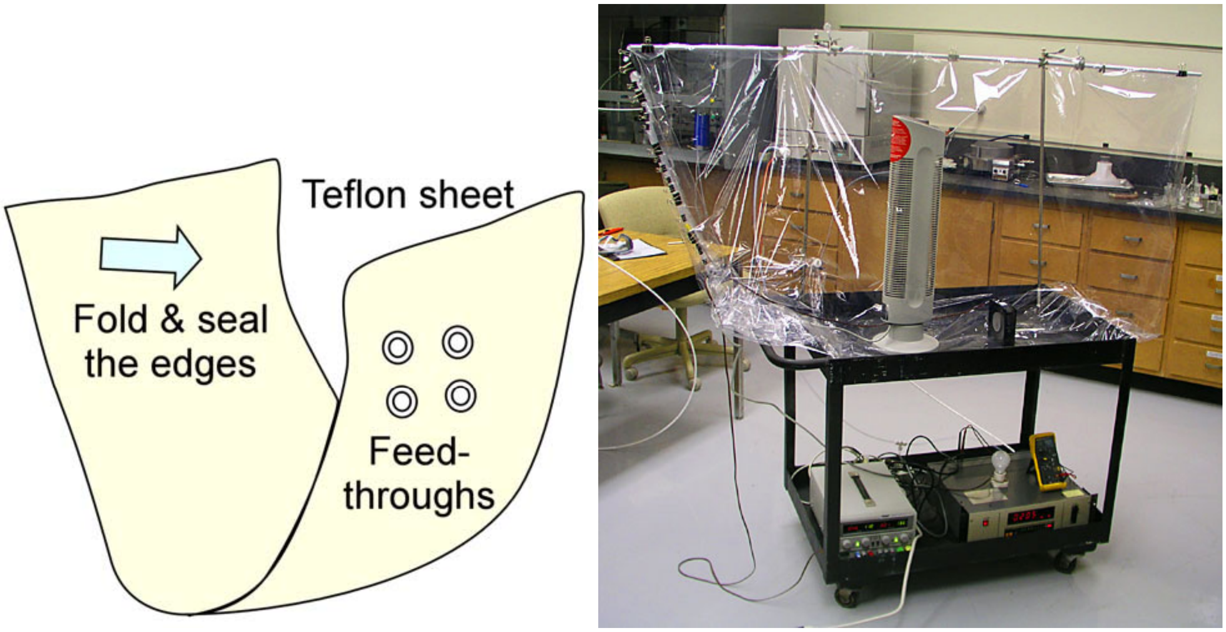

Figure 1b: Fabrication of a Teflon bag. A sheet of Teflon, with pre-installed feed-through ports is folded upon itself and its edges are sealed. The right side shows a photograph of an actual bag installed on a cart. The air purifier was added through an opening in the left side of the bag, and the opening was sealed with multiple paper clips.

The remaining inlet port on the chamber should be used for purging it with clean air, for adding aerosol particles, and for pumping on the chamber. Lab air and vacuum lines should be available in the room. Lab air supply should deliver dry (<5% relative humidity) and filtered (particle free) air, and it should have at least 50 SLM (standard liters per minute) capacity to be able to purge the chamber reasonably quickly.

The specific connections between the chamber, instruments, air supply, and vacuum supply will be shown in the experimental description.

Safety

Ozone is a known air pollutant capable of inducing adverse health effects in people even at relatively small exposure levels. Therefore, do not operate powerful ozone generators in open spaces. Turn them on only when they are placed inside a sealed Teflon chamber as described below. If students smell ozone during the experiment they should turn off all ozone generators, notify the instructor immediately, and leave the laboratory for at least 15 minutes (typical air recirculation time for a college laboratory).

The students must be instructed in compressed air safety, electrical safety, and general laboratory safety before starting on this project. Goggles must be worn at all times. Protective clothing is recommended.

INTRODUCTION

Due to escalating air pollution issues in the U.S. and worldwide, indoor air purification has gained widespread popularity in recent years *(1,2)*. A large variety of portable air purifiers can be purchased in retail stores and on the internet. Indoor air purifiers are designed for removal of odorous molecules, dust, pollen, and airborne particles from the air. From an operational standpoint, there are several basic types of air purifiers including air filtration, air ionization followed by electrostatic precipitation of air pollutants, oxidative treatment of air with gaseous ozone, and UV radiation treatment of air. Household use of certain air purifiers has raised serious concerns because they produce ozone, a criteria air pollutant, either intentionally or as a byproduct of air ionization.

Ozone is a colorless molecule with the chemical formula O_3. It has a characteristic pungent odor commonly noticed around electrical transformers or photocopiers used for extended periods. As opposed to molecular oxygen, which is a major component of air, ozone is present in tropospheric air in trace amounts. In fact, scientists prefer to measure ozone concentration in units of parts per million (ppm) and parts per billion (ppb), defined as follows:

1 ppm = 1 molecule of ozone per 1,000,000 molecules or other gases
1 ppb = 1 molecule of ozone per 1,000,000,000 molecules or other gases

The concentration of ozone in clean air is around 0.02-0.04 ppm (or 20-40 ppb). Smoggy air can contain considerably more ozone. For example, 0.1 ppm is quite typical for the Los Angeles area. In the past, ozone concentrations in LA could reach values as high as 0.7 ppm.

Table 1. Health-protective standards for ozone mixing ratio in air established by US government agencies. NIOSH = National Institute for Occupational Safety and Health; OSHA = Occupational Safety and Health Administration; CARB = California Air Resources Board; EPA = Environmental Protection Agency; IDHL = Immediately Dangerous to Life or Health Concentrations; PEL = Permissible Exposure Limit; STEL = Short-Term Exposure Limit; NAAQS = National Ambient Air Quality Standard.

Agency	Standard	Exposure time	Mixing ratio (ppm)
US EPA	NAAQS	1-hour average	0.12
US EPA	NAAQS	8-hour average	0.080
CARB	California AAQS	1-hour average	0.090
CARB	California AAQS	8-hour average	0.070
NIOSH	IDLH	-	5.0
NIOSH	PEL	15-min	0.10
OSHA	PEL	8-hour average	0.10
OSHA	STEL	15-min	0.30
CARB	Stage 1 smog alert	-	0.20
CARB	Stage 2 smog alert	-	0.35
CARB	Stage 3 smog alert	-	0.50

Ozone is known to have a number of adverse health effects on humans and animals, even at small concentrations *(3,4)*. Several health-protective standards for ozone have been established by various U.S. agencies (Table 1). The standards are defined as the average concentration of ozone that should not be exceeded during a given interval of time. For example, the U.S. Environmental Protection Agency (EPA) has classified ozone as a criteria pollutant and established national ambient air quality standards (NAAQS) of 0.120 ppm for a 1-hour exposure and 0.080 ppm for an 8-hour exposure. The new California 8-hour standard is 0.070 ppm *(5)*. In

California, a stage-one smog alert is issued whenever the ambient concentration of ozone is in excess of 0.20 ppm. Ozone levels of 0.35 ppm and 0.50 ppm correspond to stage-two and stage-three smog alerts, respectively. The establishment of these standards has been reasonably successful in protecting the public from ozone exposure. It has to be understood, however, that there is no scientific evidence for existence of a threshold concentration below which ozone can be regarded as safe *(4)*.

Ozone is transferred indoors though air exchange. The normal indoor-to-outdoor concentration ratio for ozone is in the range of 0.2-0.7 *(6)*. However, much higher levels of ozone can occur indoors if ozone is generated intentionally, e.g., by ozone-emitting air purifiers. Once generated, ozone is removed by ventilation and by reactions with various indoor surfaces. In a standard home, the lifetime of ozone is generally about 20 minutes *(6)*. The lifetime of ozone is the characteristic time ozone will remain in the air before it is removed by chemical reaction or physical processes.

Ionic (a.k.a., ionization or ionizing) air purifiers are available in a broad spectrum of designs including large units for household use, smaller units for use in bathrooms, refrigerators and closets, units intended specifically for cars, personal wearable units, ionic brushes, shoe cleaners, toothbrush disinfectors, etc. Most ionic devices work by charging airborne particles in a discharge and electrostatically precipitating them on metal electrodes. The electrical discharge that is meant to produce ions is also capable of splitting molecular oxygen into oxygen atoms, and creating ozone as a by-product:

$$O_2 + \text{discharge} \rightarrow O + O$$

$$O_2 + O + M \rightarrow O_3 + M \quad (M = \text{any gas-phase molecule})$$

Although not all ionic air purifiers emit ozone, certain models can easily produce a few milligrams of ozone per hour (mg/hr) during their operation *(7,8)*. Some of them are not efficient in cleaning the air *(1)*. Ironically, many users of ozone-emitting ionic air purifiers mistakenly confuse the smell of ozone with the "smell of clean air".

Ozone generators use a more powerful electrical discharge to produce several hundred mg/hr of ozone *(7,9)*. The rationale for generating lots of ozone is to use its oxidizing power to destroy VOCs (Volatile Organic Compounds) in indoor air and kill bioorganisms such as bacteria. However, reactions of most household VOCs with ozone are too slow to be efficient *(6)*. Furthermore, the level of ozone required to efficiently kill bacteria is detrimental to humans. Indeed, the U.S. EPA provided a comprehensive assessment of the effectiveness and health consequences of ozone generation indoors stating that “at concentrations that do not exceed public health standards, ozone is generally ineffective in controlling indoor air pollution” *(10)*. The California Air Resources Board dubbed ozone-generating air purifiers “insidious machines” *(11)*. In a recent report to the California Legislature entitled “Indoor Air Pollution in California” the board officially recommended that the public avoid using these devices indoors *(12)*. Recent California Assembly Bill 2276 (2006) authorized the California Air Resources Board to develop a regulation to limit the ozone emissions from indoor air cleaning devices. This important regulation will go into effect in 2008, and it will make it illegal to sell air purifiers that generate more than 50 ppb of ozone in the purified air stream to the general public.

PROJECT OBJECTIVES

The amount of ozone emitted by an air purifier can be characterized by its ozone emission rate, E_{ozone} (measured in mg/hr). Once emitted, ozone undergoes loss as a result of chemical decomposition on indoor surfaces and physical removal by ventilation. Competition between emission and loss leads to a steady state,

$$[\mathrm{O_3}]_{ss}(\mathrm{ppm}) = \frac{E_{ozone}(\mathrm{mg/hr}) \times \tau(\mathrm{min})}{118 \times V(\mathrm{m^3})}$$

where $[O_3]_{ss}$ is the ozone mixing ratio at steady state, V is the room volume, τ is the lifetime of ozone (typically ~20 minutes), and 118 is a unit conversion factor calculated at 1 atm and 25 ^{o}C. This equation can be used to estimate the steady state mixing ratio of ozone produced by an air purifier once its ozone emission rate is known.

The key parameter characterizing an air purifier is its clean air delivery rate, $CADR = \gamma F$, where F is the air flow rate through the purifier (measured in m^3/hr) and γ is the probability of capture for a given contaminant. The latter ranges from γ=0 for a plain fan that does not remove any contaminants to γ=1 for a purifier that removes all contaminants from the air. A given air purifier is characterized by different values of γ, and hence *CADR*, for different contaminants. For example, HEPA (high efficiency particulate air) filters efficiently remove particulate matter while having almost no effect on molecular contaminants.

The overall goal of this project is to quantify E_{ozone} and *CADR* for selected portable air purifiers. Results of these measurements are then used to predict whether these air purifiers can generate ozone levels in typical residential environments that are in excess of the health-protective standards listed in Table 1. The procedures described here are based on the following publications *(7,13)*.

EXPERIMENTAL APPROACH

Measuring Ozone: Ozone concentrations in the air can be sensitively measured with a UV photometer (Figure 2). Ozone photometers typically measure optical absorbance by air at the 253.7 nm Hg line in a cell of known length, *L*. In relatively clean air, ozone is the dominant absorber at 253.7 nm, and the absorption coefficient of ozone at this wavelength is well-known, $\sigma = 1.136 \times 10^{-17}$ cm^2/molecule *(14)*. The concentration of ozone is calculated using the Beer-Lambert law:

$$Absorbance = \ln\left(\frac{I_0}{I}\right) = \sigma \times L \times [O_3]$$

where I_0 and I are radiation intensity without and with ozone in the sample cell, respectively.

In this project, students use an Ebara Jitsugyo EG-2001 high-accuracy ozone monitor, which measures the ozone mixing ratio in ppm (referenced to 1 atm and 25 °C conditions) with a 0.001 ppm resolution. This monitor uses the Beer-Lambert law to calculate the ozone mixing ratio (as do all other commercial ozone monitors) and the mixing ratio is continuously displayed on the front panel. During operation, the instrument automatically re-zeroes itself every several minutes by sending air through the scrubber (Figure 2).

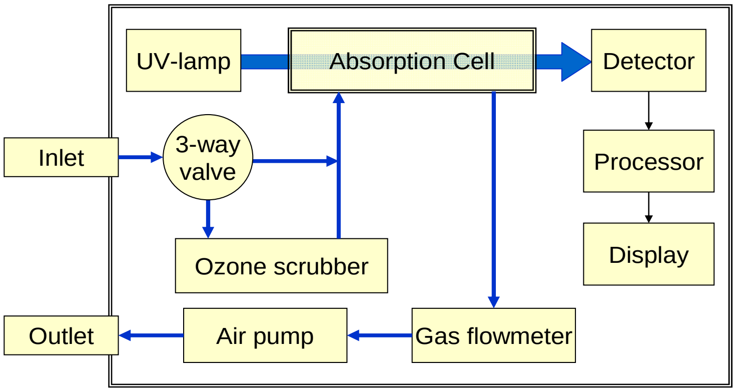

Figure 2: Layout of a typical ozone photometer. The air is drawn into the instrument by a pump through a flowmeter. In sample measurement mode, the air is sent into the absorption cell directly to measure *I*. In reference mode, which measures I_0, the air first goes through a scrubber that catalytically removes all ozone from the air flow. The data processor controls the three way valve and calculates the ozone mixing ratio.

The EG-2001 is connected to a computer that used a custom LabView program to read data from the instrument and save it on disk. However, measurements can also be done manually by periodically copying the ozone concentrations from the front panel in the laboratory notebook. The Ebara Jitsugyo EG-2001 instrument needs to warm up for 2-3 hours to achieve maximum stability, as do many other commercial ozone monitors. Therefore it should be turned on by the instructor before the class starts, and should not be turned off until all work is finished.

Measuring Particles: The concentration of aerosol particles in the air is measured with an aerosol particle counter. It works by sending a laser beam through a fast flow of sampled air. If there is a particle in the flow, it scatters the laser beam in all directions. The burst of scattered light is detected by a sensitive light detector. The instrument calculates the concentration of particles from the frequency of the bursts of light. The most common units for particle concentration are either particles/cm^3 (number of particles in a cubic centimeter of air) or $\mu g/m^3$ (combined weight of all particles in cubic meter of air).

The instrument used in this project is Lasair 1510 particle counter manufactured by Particle Measurement Systems. It is fully controlled by a computer running a custom LabView program, which records particle number concentrations in seven separate particle size channels ranging from 0.15 – 5 μm (particle diameter). The Lasair 1510 requires about 15 minutes of warm up time, as do most optical particle counters.

PROJECT DESCRIPTION

I. Ozone Emission Rates from Ionization Air Purifiers

The goal of this part of the project is to measure the ozone emission rate, E_{ozone}, from a relatively weak ozone generator such as an ionization air purifier. To do so, the air purifier is placed in a chamber with known volume, and turned on. The increasing ozone concentration inside the chamber is measured in real time with an ozone monitor. The ozone emission rate is obtained by fitting the resulting data and performing simple calculations.

Setting up the Experiment

Note: If the class is aimed at students who are preparing for graduate school or careers in research, the students should be encouraged to set up the experiment themselves. To save instructional time, the instructor can set up the chamber and connect the gas lines before instruction starts and ask the students to verify the setup at the beginning of the experiment.

Figure 3 shows the connections between the ozone monitor and the test volume (600 L Teflon chamber). Connect all the lines as shown. In Figure 3, ⊗ represents a shut-off valve and FM stands for "Flow Meter". The lines connecting to the EG-2001 ozone monitor should be made of Teflon PFA tubing. In this example, three identical ionization air purifiers are placed in the chamber along with one small HEPA/charcoal air purifier.

The chamber should be filled with air from the dry, particle-free air supply. For fixed-volume chambers, the chamber can be slightly over-filled with one of the sampling ports open to flush out any room air. For inflatable (bag-style) chambers, the flow should be controlled with a calibrated flow controller so that the volume of the added air is known. The bag should be completely deflated before it is filled; a vacuum line connected through Valve 3 is used for this purpose in Figure 3.

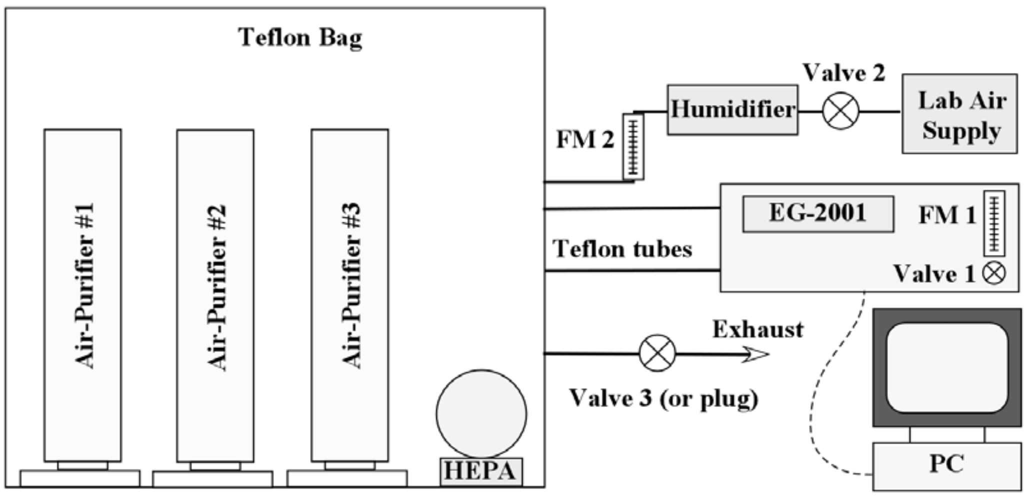

Figure 3: Sample set-up for measurements of ozone emission rates from ionization air purifiers.

If desired, a humidifier can be installed between Valve 2 and FM 2 in the lab air supply line to regulate the relative humidity in the Teflon chamber. If possible, the humidity should be set before the students arrive, since it can take a while to stabilize. The students should record the initial humidity and temperature at which the experiment is performed, and any changes that occurred during the experiments

Most air purifiers are designed to circulate air by themselves, making it unnecessary to use a separate fan. However, certain ozone-emitting air purifiers have no fan. If this is the case, a fan must be added to the chamber to circulate the air inside.

Performing the Measurements

Note: The following are the step-by-step instructions that were provided to students in our laboratory classroom. The names of instruments and computer programs used in our lab have been retained, and should be replaced as appropriate. The same applies to the instructions in parts II, III and IV of this manual.

1. Open Valve 1 and adjust it so that FM 1 (on the ozone monitor) reads 1.5 SLM. (The ozone monitor will not work correctly if the flow rate is lower than 0.5 SLM.) Make sure that the exhaust line for the ozone monitor is attached to one of the ports on the Teflon

chamber. The ozone monitor is now reading the ozone concentration inside the Teflon chamber.

2. Open the Ebara Logger computer program that will log the data for you. Set the sampling interval to 5 seconds. Press “Start” to commence acquisition. The computer will display the ozone concentration in real time and store it in a file for later analysis. Write down the file name and other pertinent information in your lab book.
3. After recording the background ozone concentration for a few minutes, turn on air purifier # 1.
4. Measure the ozone concentration in the chamber for at least 15 minutes. Make sure the concentrations of ozone recorded by the computer match the ones displayed on the front panel of the ozone monitor. At the end of the 15 minutes, press “Stop” on the Ebara Logger program. Turn air purifier #1 off. Now that ozone is not being produced by the air purifier, the ozone concentration will start to decay. Record the decay of ozone from the chamber for 10-15 min (optional).
5. Repeat these steps with air purifier #2. It is OK to start at non-zero ozone levels still existing from using air purifier #1 as long as a relatively stable background level is being measured. If the ozone concentration is too high (> 0.2 ppm) you can remove ozone from the air by turning on the HEPA/charcoal filter air purifier for 10 minutes or so. Running the HEPA/charcoal filter is likely to change the relative humidity in the chamber; write down the new value if this happens.
6. Repeat for air purifier #3.
7. Open your data files in Excel. The columns you need are the ones containing time and ozone concentration. Plot the measured mixing ratio as a function of time. Figure 4 shows an example of such a plot.
8. The initial concentration rise should be approximately linear in time because ozone production by an air purifier is a zero-order process. Fit the initial rise to a straight line using least squares analysis. To do so, plot the appropriate section of data in a graph, then right-click on one of the data points and select "add trendline". In the trendline options select "display equation on chart". Write down the slope (which is equal to $\frac{d[O_3]}{dt}$; make sure that your graph is plotted in appropriate units) in the units of ppm/min. The intercept in your fit should correspond to the initial concentration of ozone in the chamber.
9. As well as doing the linear fit to determine the rate of increase in the ozone concentration, estimate $\frac{d[O_3]}{dt}$ as follows, and compare your results with the linear fit.

$$\frac{d[O_3]}{dt} \approx \frac{[O_3]_{\text{final}} - [O_3]_{\text{initial}}}{\text{on-time}}$$

10. Convert your measurements into the common units used for ozone generators (mg/hr) as follows (the volume of the chamber is 600 L):

$$E_{ozone}(\text{mg/hr}) = 0.118 \times V_{chamber}(\text{L}) \times \frac{d[O_3]}{dt}(\text{ppm min}^{-1})$$

The factor of 0.118 is a conversion factor used to convert between units of ppm min^{-1} and mg hr^{-1}. To get a better understanding of this equation, you should calculate this conversion factor for yourself from fundamental constants.

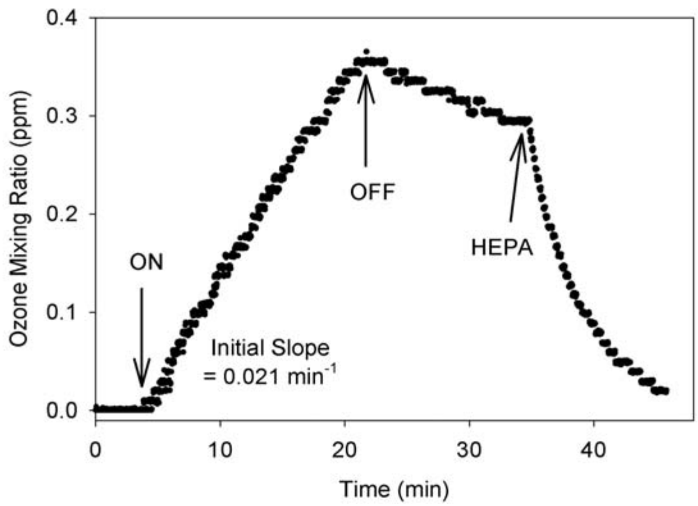

Figure 4: Sample ozone emission data for a Sharper Image Ionic Breeze air purifier, model SI627. As soon as the purifier is turned on, the ozone mixing ratio in the chamber starts to increase linearly. The ozone concentration slowly decays back to zero after the purifier is turned off (the more reactive surfaces available in the chamber, the faster the decay rate). The decay rate can be accelerated by turning on a HEPA/charcoal filter. This is useful for removing ozone between different runs.

II. Particle Removal Rates by Ionization Air Purifiers

Ionization air purifiers present an interesting dilemma. On one hand, they remove particles from the air by electrostatic precipitation, thus making the air cleaner with respect to particles. On the other hand, ozone emitted by certain ionization air purifiers can result in the production of new aerosol particles in the presence of unsaturated volatile organic compounds (VOC's) *(13)*. The main objective of this part of the project is to quantify the particle removal rate by an ionization air purifier. This can then be used to predict the clean air delivery rate (*CADR*) for the air purifier.*

Setting up the Experiment

The experimental configuration used to measure particle removal rates is largely the same as that used to measure ozone emission rates, with the addition of the Lasair 1510 particle counter and of a fan in the chamber. Figure 5 shows the required connections.

For this part of the experiment, an optical particle counter is used. The particle counter should be turned on several minutes before the experiment is to begin to give the instrument time to warm up. Ensure that the counter is hooked up correctly as shown below. Since most particle counters must pump 20-30 liters per minute through themselves in order to operate properly, filtered make-up air should be supplied to avoid substantially changing the bag volume during the experiment. This will also dilute the particle flow so that the counter does not become saturated. The ozone monitor may stay connected to the chamber as well, but it is best to turn it off to avoid unnecessary contamination of the absorption cell inside the ozone monitor by the particles. The fan inside the chamber must be on to ensure rapid mixing of air.

* The larger the CADR, the larger the chamber volume required for its measurement. The 600 L chamber used in this project is sufficient for measurements of CADR values below 30 ft^3/min (small ionization air purifiers).

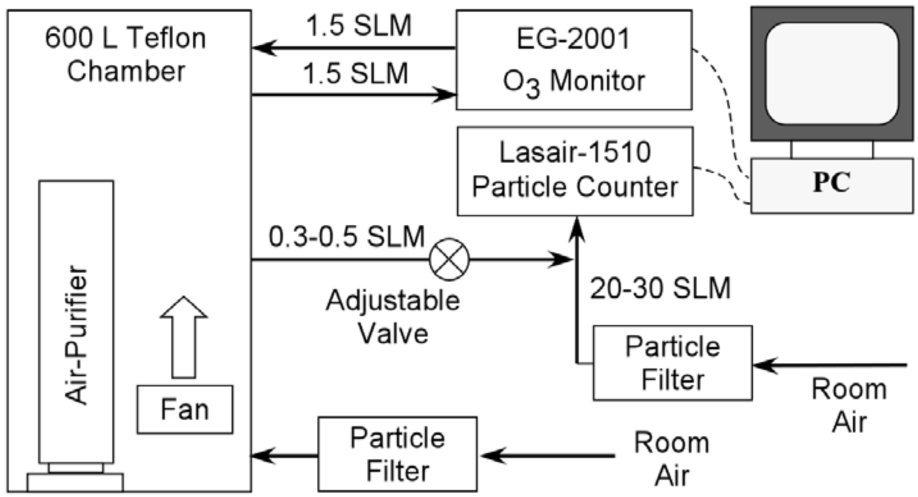

Figure 5: Sample set-up for measurement of particle removal rates from ionization air purifiers.

To avoid saturation of the particle counter, the air it withdraws from the chamber must be mixed with particle-free air. Carefully adjust the "adjustable valve" to make the flow through this valve equal to 0.3 SLM (measured by a separate flowmeter such as TSI model 4140). The rest of the flow needed by the particle counter will come from room air through the particle filter (Figure 5). This will correspond to dilution of the particle concentration by a factor of 100 for a particle counter that requires 30 LPM total flow.

Performing the Measurements

1. Start the program called Lasair. The data acquisition will start immediately when the program loads. The total particle concentration (uncorrected for dilution) will be displayed on the screen as a function of time. Record several cycles of particle size distributions with the air purifier off. This is your background particle count.
2. You will now have to add some aerosol particles to the chamber. Particles can be added by connecting an atomizer loaded with a NaCl solution to the chamber and running it for a very brief period of time. The relative humidity in the chamber may change during the injection. Write down the new value every time there is a change. When the aerosol flow starts, you will observe a burst in the particle count. After 10-15 minutes, the particle concentration will stabilize at a higher level compared to the background count (10^4-10^5 particles per cm^3, for example). An alternative method of adding particles, if no atomizer is available, is to insert a piece of smoldering wood briefly into the chamber. Take care to avoid damaging the chamber. This method of particle introduction should be considered a last resort, as it offer poor control over the particle concentrations.
3. Now turn on air purifier #1. The particle count will decrease exponentially. Keep recording until the particle counter readings become very small, indicating that almost all particles have been removed.
4. Stop data collection and turn air purifier #1 off.
5. Repeat this measurement for air purifiers #2 and #3.
6. Open the data files in Excel. The left panel of Figure 6 shows an example of a previous measurement. To get the particle removal rate you will need to do some data manipulation. We expect the particle number concentration to obey first order kinetics, so

that the particle concentration at a given time is described by the following integrated rate law:

$$[PM] = [PM]_0 \times e^{-k \cdot t}$$

where $[PM]_0$ is the particle concentration before the air purifier was turned on, and ***t*** is time elapsed since the air purifier was turned on. We are after parameter ***k***, the particle removal rate constant. Taking the natural logarithm of both sides of the integrated rate equation gives us a more straightforward equation for ***k***:

$$\ln([PM]) = \ln([PM]_0) - k \cdot t$$

As you can see, the natural logarithm of the particle concentration is a ***linear*** function of time. Therefore, we are going to do a linear fit of the natural logarithm of the particle concentration versus time. For a first order reaction, the slope of this plot will be equal to the negative of ***k***.

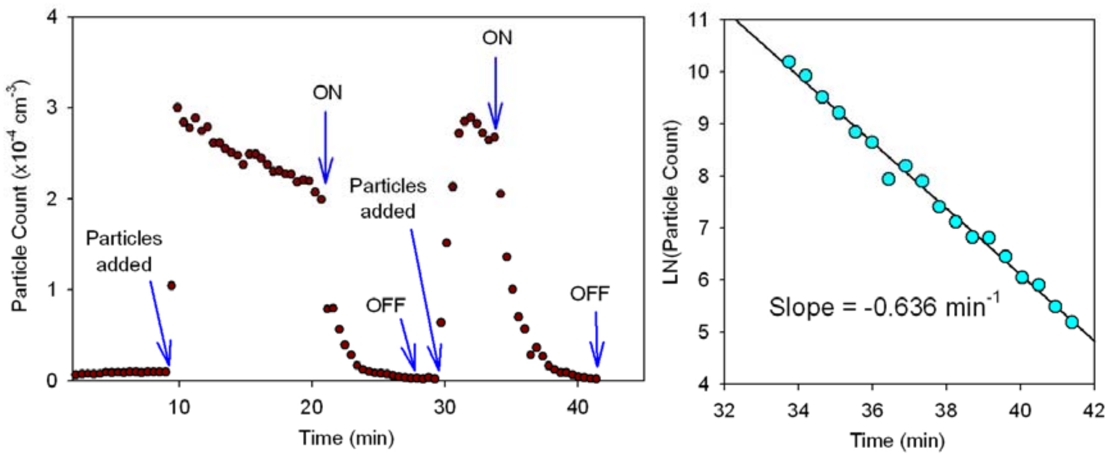

Figure 6: Sample particle concentration data for a Sharper Image Ionic Breeze air purifier, model SI637. The left panel shows two successive cycles of measurements. Particles are introduced and allowed to mix in the chamber for a certain period of time. Slow decline in the particle count during mixing is due to deposition of particles on the chamber walls. The particle concentration drops exponentially during the time the air purifier is on. The right panel shows a sample fit of this portion of the data on a log-linear scale.

7. To fit the data, plot the appropriate section of data in a graph (as shown in the right panel of Figure 6), then right-click on one of the data points and select "add trendline". In the trendline options select "display equation on chart". Write down the slope in units of inverse time (s^{-1} or min^{-1}).
8. Based on your slope, calculate *CADR* (the clean air delivery rate) for the air purifier. It can be calculated from the following formula:

$$CADR = k \times V_{Chamber}$$

Convert your result into units of m^3/hour. For example, for the data shown in Figure 6, *CADR* = 23 m^3/hour.

III. Ozone Emission Rates from More Powerful Ozone Generators

The goal of this part of the experiment is to characterize the ozone emission rate from fairly powerful (> 50 mg/hr) ozone generators. These devices generate ozone with a rate that is too large to measure by the above approach. Therefore, the strategy will be to turn the device on for a brief period of time and measure an incremental increase in ozone concentration during this time period.

Setting up the Experiment

This part of the experiment uses the same setup as the one shown in Figure 3 and described in part I. Some ozone generators are not equipped with fans, and in this case a small fan should be added to the chamber. All of the connections will be the same. Students will also need a stopwatch or some other way to keep time so that the exact length of the ozone additions can be measured.

Performing the Measurements

1. Fill the chamber with a fresh volume of air.
2. Turn the fan on to make sure air in the chamber is mixed rapidly.
3. Using the data table below, record the current level of ozone in the chamber, $[O_3]_{before}$.
4. Turn the air purifier on and start the stopwatch.
5. After a short period of time, e.g. 30 seconds, turn the air purifier off and stop the stopwatch. Write down the exact length of time for which the air purifier was on.
6. Wait 30-40 seconds for the ozone level in the chamber to become stable. Record the new level of ozone in the chamber, $[O_3]_{after}$.
7. Calculate the emission rate using the following equation

$$Rate(mg/hr) = 7.06 \times V_{Chamber}(L) \times \frac{[\mathrm{O_3}]_{\mathrm{after}}(\mathrm{ppm}) - [\mathrm{O_3}]_{\mathrm{before}}(\mathrm{ppm})}{\Delta \mathrm{t(seconds)}}$$

   The number 7.06 is a conversion factor used to convert the units of L ppm s^{-1} to mg hr^{-1}.
8. Repeat these steps three to four times for reproducibility and average the results of all of your measurements.

Δt (sec)	$[O_3]_{before}$ (ppm)	$[O_3]_{after}$ (ppm)	Rate (mg/hr)
		Average:	

IV. Refrigerator Air Purifiers

In this part of the project, ozone levels produced by air purifiers designed for use in refrigerators will be examined. Such appliances normally do not run continuously. Most of them only run 5-10 minutes per hour in order to conserve batteries. This produces periodic spikes in the ozone concentration inside the refrigerator. The goal is to record the magnitude of one such spike.

Setting up the Experiment

In this part of the experiment, the Teflon chamber is replaced by a small refrigerator. The air purifiers should be modified to run from a power supply located outside the refrigerator so that they can be turned on and off without opening the refrigerator door. In the case of air purifiers that run on a 9V battery, this modification is quite simple and involves attaching wires from the terminals of the battery to the air purifier's battery connection, with a switch in between. Relatively high gauge wire is suitable for this purpose and will not interfere with the closing of the refrigerator door.

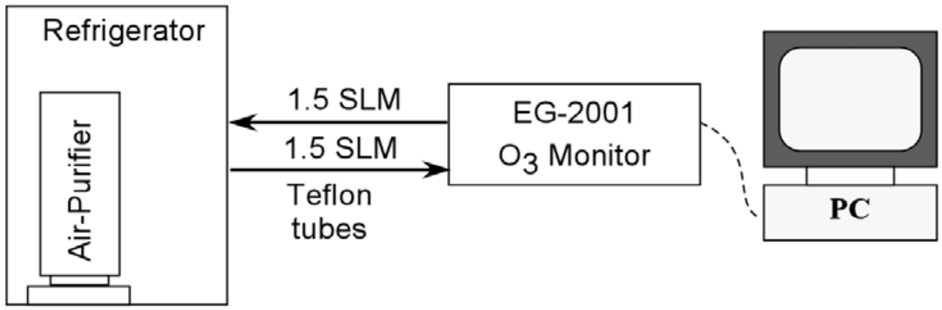

Figure 7: Sample set-up for measurement of refrigerator air purifiers.

Performing Measurements

1. Put a refrigerator air purifier inside the refrigerator.
2. Feed the inlet and outlet lines of the EG-2001 into the refrigerator as shown in Figure 7. The door of the refrigerator must be able to close fairly tightly during the measurement. A heavy item such as a lead brick may be used to keep the door from opening.
3. Start the ozone monitor program. Collect the background concentration of ozone for a few minutes. Normally, it will be close to zero in a closed refrigerator.
4. Turn the air purifier on without opening the refrigerator door. Most refrigerator air purifiers work on a cycle, e.g. 1 minute on per hour. The purifier will shut itself off after some amount of time (check the owner's manual for the exact time).
5. Collect data for about 20 minutes (or until the ozone concentration comes back to the background level) after the air purifier shuts itself off.
6. Stop the data acquisition.
7. Open the file in Excel. Use the data to measure the peak ozone concentration. Estimate the time-averaged ozone concentration assuming that such ozone spikes are produced once per hour. You can use the following formula:

$$[O_3]^{\text{long-time}}_{\text{average}} = \frac{1}{60\text{min}} \int_{\text{over spike}} [O_3](t)dt$$

   The above integral can be calculated in Excel by using the **SUM( )** function over a series of suitably small time steps.

V. Personal Air Purifiers

In this part of the project, a personal air purifier (PAP) will be tested. For this test, the EG-2001 ozone monitor will be outfitted with 2 alarms (EG-2001 has connections designed specifically for alarm switching). A yellow lamp will turn on when the concentration of ozone is larger than the U.S. EPA 8-hour ambient air quality standard (0.080 ppm). A red lamp will turn on whenever the concentration of ozone is larger than the EPA 1-hour ambient air quality standard (0.120 ppm). In addition, you will use a PC to record the ozone concentration as a function of time.

Setting up the Experiment

This part of the experiment can also be set up easily by students. The personal air purifier should be mounted from a ring stand or other support, and the inlet tube of the ozone monitor should be mounted directly above it, as shown in the left panel of Figure 8. In the past, we have set up this experiment with the personal air purifier hung around the neck of a large stuffed bear (mimicking the suggested usage of the device), and the sampling inlet was threaded through the mouth of the bear. This is not necessary by any means but did provide a nice visual demonstration of the potential personal exposure to ozone during the use of the air purifier.

Performing Measurements

1. Find a place on a bench that is free from strong air currents.
2. Suspend a personal air purifier (PAP) from a ring stand or other support.
3. Mount the inlet of the Teflon tube leading to the sample inlet of the EG-2001 ozone monitor 4" (10 cm) above the PAP. You can measure the distance between the PAP and the inlet with a ruler. For more stable results, mount a funnel at the sample line end.
4. Prepare the computer for data acquisition as described in Part I.
5. Turn the PAP on and watch what happens (for 10 minutes or so). Try to visually estimate the fraction of time during which the standards are exceeded by watching the light bulbs on the ozone monitor (if so outfitted) or by looking at the real-time graph of ozone concentration on the computer program. A sample measurement is shown in the right panel of Figure 8.

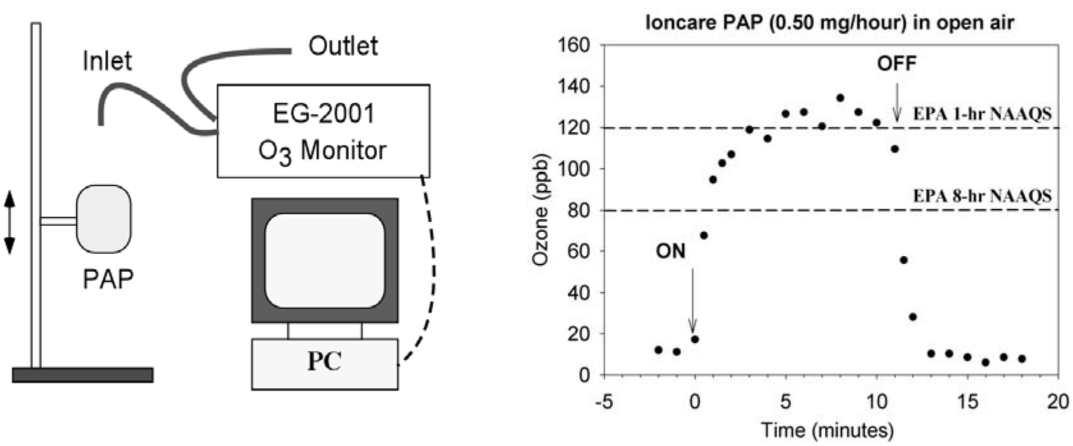

Figure 8: Setup and sample data for measurements with a personal air purifier.

6. Turn the PAP off and watch the level return to normal. Press stop on the computer program after 3-4 minutes.
7. Now, repeat the measurement for the same PAP but for a smaller PAP-inlet separation (e.g., 2"). Again, use the ruler to measure the distance between the PAP and the inlet.
8. Use the data to calculate the percentage of time during which the standards were exceeded. Compare the results for 2 distances to determine whether the wearer is exposed to more ozone when the PAP is held closer to the mouth (i.e. the sampling inlet).

REFERENCES

(1) *Consumer Reports* **2003**, *68*, 26-29.
(2) Shaughnessy, R.; Sextro, R. *J. Occup. Environ. Hygiene* **2006**, *3*, 169-181.
(3) McDonnell, W. F.; Kehrl, H. R.; Abdul-Salaam, S.; Ives, P. J.; Folinsbee, L. J.; Devlin, R. B.; O'Neil, J. J.; Horstman, D. H. *Adv. Environ. Health* **1991**, *46*, 145-146.
(4) Bell, M. L.; Peng, R. D.; Dominici, F. *Environ. Health Persp.* **2006**, *114*, 532-536.
(5) *California Adopts New Ozone Standard. Children's Health Focus of New Requirement,* (ARB Press Release 05-08), California EPA, 2005.
(6) Weschler, C. J. *Indoor Air* **2000**, *10*, 269-288.
(7) Britigan, N.; Alshawa, A.; Nizkorodov, S. A. *J. Amer. Waste Managm. Assoc.* **2006**, *56*, 601-610.
(8) Jakober, C.; Phillips, T. *Evaluation of Ozone Emissions From Portable Indoor Air Cleaners: Electrostatic Precipitators and Ionizers*, California Air Resources Board, February 2008 report, *http://www.arb.ca.gov/research/indoor/ozone.htm* (accessed Apr 2008).
(9) Phillips, T.; Jakober, C. *Evaluation of Ozone Emissions from Portable Indoor "Air Cleaners" That Intentionally Generate Ozone*, California Air Resources Board, May 2006 report, *http://www.arb.ca.gov/research/indoor/ozone.htm* (accessed Apr 2008).
(10) *Ozone Generators that are Sold as Air Cleaners: An Assessment of Effectiveness and Health Consequences* Environmental Protection Agency, 2005 report, *http://www.epa.gov/iaq/pubs/ozonegen.html* (accessed Apr 2008).
(11) *ARB Warns, Danger from Popular "Air Purifying" Machines*, ARB Press Release 05-02, California EPA, 2005.
(12) *Indoor Air Pollution in California: AB1173 Report to the California Legislature*, California Air Resources Board, 2005.
(13) Alshawa, A.; Russell, A. R.; Nizkorodov, S. A. *Environ. Sci. Tech.* **2007**, *41*, 2498-2504.
(14) Mauersberger, K.; Hanson, D.; Barnes, J.; Morton, J. *J. Geophys. Res. D* **1987**, *92*, 8480.

PRELAB QUESTIONS
Student Name: ____________________________________

1) What are the overall goals of this project?

2) What does the concentration unit “ppm” stand for? Convert a concentration of 0.50 ppm ozone to units of molecules/cm^3 and to $\mu g/m^3$..

3) What ozone levels correspond to stage 1, stage 2 and stage 3 smog alerts in California?

4) Do you use an indoor air purifier? If so, what type and model?

5) List several health effects attributed to the inhalation of ozone:

6) Define the term *lifetime*. What is the typical lifetime of ozone in a standard home?

POSTLAB QUESTIONS
Student Name: ___________________________________

I. Summary of Results

Part I: Ozone Emission by Ionization Air Purifiers

Air purifier	O_3 emission rate (ppm/min)	O_3 emission rate (mg/hr)	Humidity (%)
#1			
#2			
#3			

Part II: Particle Removal by Ionization Air Purifiers

Air purifier	Particle removal rate constant (min^{-1})	Clean Air Delivery Rate (*CADR*; m^3/hour)	Humidity (%)
#1			
#2			
#3			

Part III: Ozone Emission Rates by Ozone Generators

Generator Tested	O_3 Emission Rate (mg/hr)	Humidity (%)

II. Group Discussion Questions

People certainly don't spend much of their time in Teflon bags. The most common use of an air purifier is to run it continuously in a room, such as a bedroom or bathroom. In such a situation, the ozone concentration will reach a steady-state level in which the rate of production of ozone by the air purifier is exactly balanced by the rate with which ozone is destroyed by the room surfaces and removed by ventilation. It can be shown that the steady-state ozone concentration can be calculated from the following formula:

$$[O_3]_{\text{steady-state}}(ppm) = \frac{0.30 \times Rate\,(mg/hr) \times Lifetime(\text{min})}{V(cu.ft.)}$$

In this equation, *Rate* is the ozone emission rate that you measured above, *V* is the room volume, and *Lifetime* is the characteristic time ozone stays in the room before it is removed by chemical reaction and ventilation, and 0.30 is a conversion factor so that the steady-state ozone concentration is expressed in ppm. The lifetime of ozone has been measured in a number of homes in Southern California; its typical value can be taken as 20 minutes.

A) Take a typical bedroom with a volume of 1200 ft^3 and ozone lifetime of 20 min. Calculate the steady-state ozone concentration you would get from the weak ozone generator you characterized today (use the rate you measured). Compare it with the health standards for ozone.

B) Repeat this calculation for a strong ozone generator emitting 500 mg/hr. What do you conclude?

C) Repeat the calculations from parts A & B, but now for a small bathroom with a volume of 200 ft^3 and ozone lifetime of 60 minutes (larger than a typical value of 20 min because of the unreactive bathroom surfaces). What do you notice?

D) For the particle removal part of the project, compare your value of *CADR* with a typical rate of ventilation in an office building (50-200 m^3/hour). Based on your comparison, is the air purifier going to be effective in cleaning the air? (In order for the air purifier to be effective, *CADR* must be considerably larger than the ventilation rate).

E) Do you know anyone who uses an air purifier that produces O_3? If so, try to find the model, and see if there are O_3 generation rates or levels stated on the device. Does it mention any potential health hazards on the warning label?

III. Questions for Advanced Students

Consider a closed room. Assume that there is an air purifier in this room that produces ozone in the following zero-order process characterized by zero-order rate constant k_{source}.

$$\text{Air} \rightarrow \text{O}_3 \qquad \frac{d[\text{O}_3]}{dt} = k_{source}(cm^{-3}s^{-1}) \qquad (1)$$

Further assume that ozone is removed from the room in a first-order process, characterized by an effective loss rate constant k_{loss}.

$$\text{O}_3 \rightarrow \text{products} \qquad \frac{d[\text{O}_3]}{dt} = -k_{loss}(s^{-1})[\text{O}_3] \qquad (2)$$

Finally, assume that mixing of air in the room is fast enough to keep the ozone concentration uniform across the room volume.

Questions:

1. Show that k_{source} is related to the air purifier's ozone emission rate, E_{O3}, (expressed in mg/hr) and room volume V (expressed in cubic feet) as follows:

$$k_{source}(cm^{-3}s^{-1}) = 1.23 \times 10^{11} \times \frac{E_{O3}\ (mg/hr)}{V(cu.ft.)} \qquad (3)$$

2. Prove that after the air purifier is turned on, the ozone concentration builds up from zero to a steady-state according to the following equation

$$[\text{O}_3](\text{t}) = \frac{k_{source}}{k_{loss}}\left(1 - e^{-k_{loss}t}\right) \qquad (4)$$

3. Prove that after the steady-state is reached and the air purifier is turned off, the ozone concentration decays as follows

$$[\text{O}_3](\text{t}) = \frac{k_{source}}{k_{loss}} e^{-k_{loss}t} \qquad (5)$$

Now, let us consider a somewhat more advanced model for indoor ozone chemistry that accounts for the exchange of air between the outdoor and indoor environment. The following equation is normally used to describe concentrations of gaseous species in a single well-mixed indoor environment that exchanges air with the exterior atmosphere:

$$\frac{d[\text{X}]}{dt} = \kappa_X \lambda [\text{X}]_{out} + \frac{E_X(t)}{V} + R_X - \lambda[\text{X}] - k_{rX}[\text{X}] - \frac{S}{V}\upsilon_{dX}[\text{X}] \qquad (6)$$

$[\text{X}]$ and $[\text{X}]_{\text{out}}$ are concentrations of species X indoors and outdoors, respectively; λ is the whole air exchange rate; κ_X is outdoor-to-indoor penetration efficiency; V is the room volume; S is the interior surface area; E_X is the emission rate for X by all indoor sources; R_X is the combined rate of production of X by gas-phase chemistry; k_{rX} is an effective first-order rate constant for the removal of X by chemical reactions; υ_{dX} is the deposition velocity of X on indoor surfaces. The constants λ, k_{rX}, and $\frac{S}{V}\upsilon_{dX}$ all have units of inverse time, κ_X is unitless, and [X] has units of concentration. Ozone, the species considered in our model, is emitted indoors by the air purifier, and also penetrates from outdoors by means of air exchange. If the only chemical removal mechanism is ozone deposition on the room surfaces characterized by an effective rate constant $k_{dO3} = \frac{S}{V}\upsilon_{dO3}$, we can write:

$$\frac{d[\mathrm{O}_3]}{dt} = \lambda\kappa_{O3}[\mathrm{O}_3]_{out} + \frac{E_{O3}}{V} - \left(\lambda + k_{dO3}\right)[\mathrm{O}_3] \tag{7}$$

***Questions**:*

1. Show that the steady-state concentration of ozone depends on whether the air purifier is turned on or off as follows

$$[O_3]_{ss}^{ON} \cong \frac{E_{O3}/V + \lambda\kappa_{O3}[O_3]_{out}}{\lambda + k_{dO3}} \tag{8}$$

$$[O_3]_{ss}^{OFF} \cong \frac{\lambda\kappa_{O3}[O_3]_{out}}{\lambda + k_{dO3}} \tag{9}$$

2. The table below lists typical values for parameters found in the equations (7-9). Using these parameters, calculate the steady-state concentrations of ozone as a function of the air purifier's emission rate. Which emission rate is required to exceed the 1-hour NAAQS of 120 ppb?
Hint: You will need to make all units compatible before substituting values in.

Parameter	Definition	Assumed value
V	Room volume	50 m^3
$[O_3]_{out}$	Outside ozone level	30 ppb
λ	Air exchange rate	2.0 hr^{-1}
k_{dO3}	Ozone surface deposition rate constant	2.8 hr^{-1}
κ_X	Penetration efficiency	1.0
E_{O3}	Air purifier's ozone emission rate	0-100 mg hr^{-1}