

A Simple Method for Measuring Ground-Level Ozone in the Atmosphere

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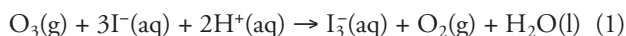
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Ozone is a key constituent of photochemical smog. Ozone is not released directly into the lower atmosphere, but instead is formed in situ by a complex series of chemical reactions involving sunlight, oxides of nitrogen, oxides of hydrogen, and hydrocarbons (1). The dynamic nature of ozone production leads to atmospheric concentrations that are highly dependent on a variety of factors including time, temperature, humidity, wind direction, and geographic location. The concentration of ozone in the lower atmosphere typically ranges from 10 to 120 ppb (by volume) (1). Higher concentrations of ozone are present in the stratosphere (i.e., the region of the atmosphere that is between an altitude of roughly 10 km to 50 km). Stratospheric ozone plays a vital role in shielding the Earth's surface from harmful UV radiation. In contrast, ground-level ozone is undesirable as it can damage biological matter.

We have attempted to create a simple method for measuring the concentration of ozone in the ground-level atmosphere. The main goal is to develop a technique that provides quantitative results without requiring expensive equipment. Qualitative colorimetric assays for atmospheric ozone have been employed for over one hundred years (2). Paper strips coated with potassium iodide and starch have been used to demonstrate the presence of ground-level ozone (3). Such strips, commonly known as Schoenbein paper, turn blue upon exposure to ozone. The response of the strips also depends on a variety of factors, especially relative humidity, and thus only serves as a rough indicator of ozone concentration (3). Improved iodometric assays were widely adopted by regulatory agencies in the latter half of the 20th century. Air is bubbled through an aqueous solution containing iodide and the atmospheric ozone oxidizes iodide to triiodide via the following reaction (4):



At the end of the sampling period, the triiodide concentration is determined with a UV-vis spectrophotometer. The moles of triiodide produced is not precisely equal to the moles of ozone bubbled through the solution because several trace atmospheric species can oxidize iodide (such as NO_2) or reduce I_3^- (such as SO_2), and other secondary reactions can occur that alter the stoichiometry between ozone and I_3^- (5). However, reaction 1 is the dominant source of I_3^- under normal atmospheric conditions (5). Iodometric assays for ozone were widely replaced in the 1970s by instrumental techniques that afforded greater accuracy and precision. The current state-of-the-art ozone-monitoring technique involves measuring the gas-phase absorbance of ozone at 254 nm in a specially designed instrument costing several thousands of dollars (5).

We have developed an iodometric assay that allows the ground-level ozone concentration to be determined with an inexpensive sampling apparatus and a homemade photometer. This protocol is sufficiently accurate to distinguish between low, moderate, and high ozone conditions. Simple apparatuses for sampling atmospheric SO_2 (6–8), NO (7), NO_2 (7, 8), formaldehyde (8), and particulates (8, 9) have been described in this *Journal*. Our sampling apparatus is most like that described by Rockwell and Hansen (9) and Ratna and Upadhyay (8). Several similar LED photometers have been used for different applications (10–13).

This laboratory experiment applies a variety of different fundamental concepts including oxidation–reduction chemistry, the ideal gas law, and spectroscopic analysis. In addition, students are provided with valuable experiences such as constructing simple instrumentation and collecting environmental samples. This experiment was designed to be conducted by high school teachers and their students, but could also easily be integrated into the laboratories for general, analytical, or environmental chemistry. It is important to note that atmospheric ozone levels are generally highest in hot weather conditions, so this experiment would be most appropriate for courses held in the late spring, summer, or early fall.

Experiment Procedure

Sampling System

A schematic of the air sampling system is shown in Figure 1. The sampling system was stationed at an outdoor location. Air was pulled through a 2.0-m Teflon tube (0.6-cm i.d.). The open end of the tube was suspended 1.5 m above the ground using a camera tripod. The air stream was bubbled through a 10.0-mL solution containing 0.06 M KI, 0.1 M boric acid, 0.3 μM hydrogen peroxide, and deionized water. The boric acid served to buffer the pH of the solution and the hydrogen peroxide removed any trace reducing contaminants. The bubbler was constructed from a 40-mL test tube fitted with a two-hole rubber stopper. The flow of air was maintained at 250 mL min^{-1} with a small vacuum pump and a needle valve.

Two pumping systems have been tested. The first configuration employed a vacuum pump, an electronic mass flow meter, and a stainless-steel metering valve. This system produced accurate flow rates that could be precisely adjusted and directly measured. However, the system cost approximately \$600 to construct. The second sampling configuration was much less expensive (approximately \$30). It employed a plastic needle valve and an air pump purchased from the aquarium section of a local pet store. A vacuum pump was

created by placing the air pump inside a plastic food container fitted with input and output ports (8). This inexpensive system produced stable gas flows; however, the flow rate had to be periodically checked using a soap-film meter. Similar ozone concentrations were determined using either vacuum system.

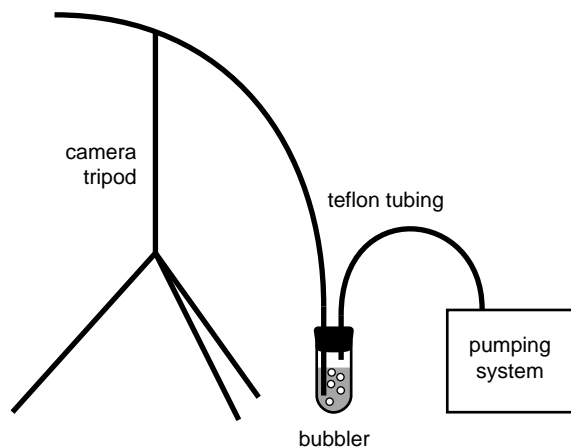


Figure 1. Schematic of the sampling apparatus.

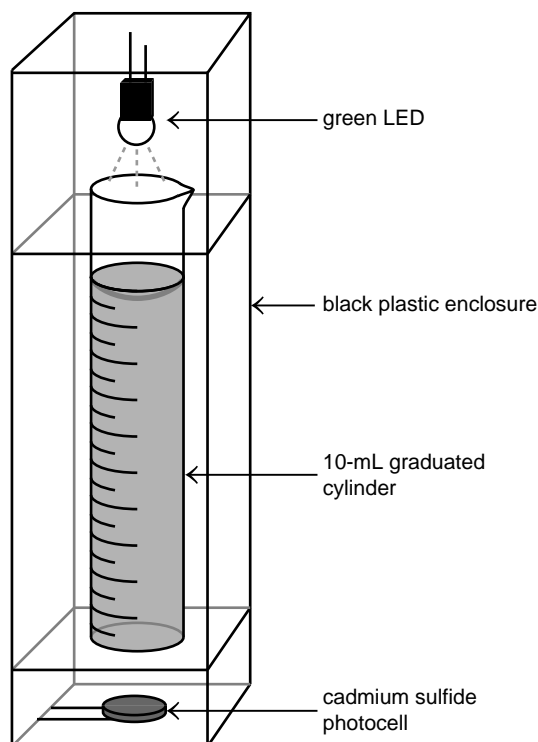


Figure 2. Schematic of the photometer.

Colorimetric Analysis

Air was bubbled through the buffered KI solution for 30 minutes. At the end of the sampling period, the KI solution was transferred to a test tube. Triiodide can be detected at micromolar concentrations with UV spectrophotometry (4, 14); however, we wanted to develop an assay that would not require costly instrumentation. Thus, starch was added (1.0 mL of a 2.0 g L⁻¹ soluble starch solution) to "shift" the absorbance into the visible region. Starch reacts with triiodide to form a violet colored complex (15). Our spectroscopic measurements found that this complex had a maximum molar absorptivity at 574 nm of 23,000 cm⁻¹ M⁻¹. After adding starch, the test tube was placed in ice water for 10 minutes and then placed in 25 °C water for 10 minutes. Immersion in ice water greatly reduced the time required to form the I₃⁻/starch complex. Incubation in room temperature water eliminated the problem of condensation on the glass surfaces of the photometer.

The concentration of the starch/I₃⁻ complex could be determined with a standard visible spectrophotometer, but we used a homemade photometer. This inexpensive instrument was developed so that multiple instruments could be constructed and distributed to local high schools. In addition, the homemade photometer provided a longer pathlength (11.5 cm) than most standard spectrophotometers; thus, increasing the sensitivity of the assay for low ozone concentrations. The photometer (a schematic is shown in Figure 2) is essentially a 10-mL glass graduated cylinder with a green light emitting diode (LED) that shines down the length of the tube toward a CdS photocell detector at the base of the tube. The photometer components are mounted inside a custom-machined black plastic block. The top piece was milled to hold the LED, the middle piece was bored out to hold the graduated cylinder, and the bottom piece was milled to hold the photocell. The middle and bottom pieces were bolted together, while the top piece was detachable so that the graduated cylinder could be removed, filled, and replaced. The green LED (Chicago Miniature Lamp Company, model 5100H5) emits a narrow range of wavelengths with a maximum at 562 nm. This is near the 574 nm absorbance maximum of the I₃⁻/starch complex. A 10.0-mL portion of each solution was analyzed in the photometer. The photometer response was given by the resistance of the CdS photocell. Resistance measurements were made with either a Wheatstone bridge circuit or a digital multimeter. The photocell resistance is inversely proportional to the light intensity. Thus, the absorbance of a sample, *A*, is given by

$$A = \log \frac{R_{\text{sample}}}{R_{\text{blank}}}$$

where R_{sample} is the resistance observed for the sample solution and R_{blank} is the resistance found for a blank solution (i.e., a solution not exposed to the atmosphere).

Calculations

The photometer response was calibrated by analyzing a series of standard I₃⁻ solutions. The standard solutions were generated by oxidizing iodide with iodate. A typical plot of solution absorbance versus triiodide concentration is shown

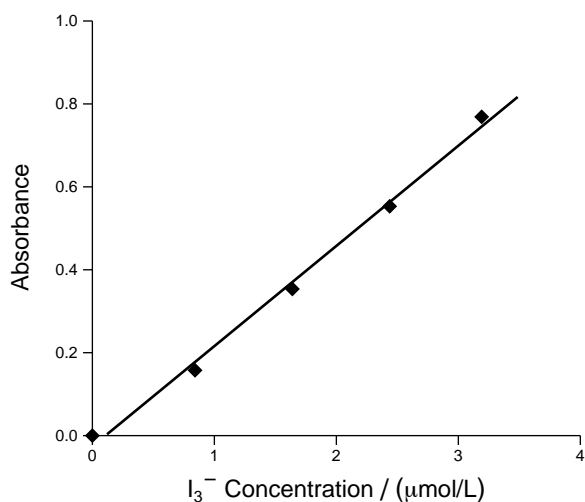


Figure 3. Photometer absorbance as a function of triiodide concentration for five standard triiodide solutions.

in Figure 3. The absorbance of the standard solutions was found to be a linear function of I_3^- concentration, indicating that Beers law is obeyed. The slope of the best-fit line was approximately $2.4 \times 10^5 M^{-1}$. For an 11.5-cm pathlength, this corresponds to an absorptivity coefficient of $2.1 \times 10^4 M^{-1} cm^{-1}$. This value is in good agreement with our spectroscopic measurements of the I_3^- /starch complex. The calibration curve was used to calculate the triiodide concentration in the solutions exposed to the atmosphere. We assumed that triiodide was produced exclusively by reaction 1. Using the stoichiometry of the reaction and the ideal gas law, the concentration of O_3 in the atmosphere was calculated as,

$$\begin{aligned} O_3 \text{ conc in air} &= \frac{n_{O_3}}{n_{air}} = \frac{V_{soln} [I_3^-]}{\left(\frac{P_{air} V_{air}}{RT}\right)} \\ &= \frac{0.0100 \text{ L} \times [I_3^-] \frac{\text{mol}}{\text{L}}}{\left(\frac{P_{air} V_{air}}{RT}\right) \text{ mol}} \\ &= \frac{0.0100 \text{ L} \times [I_3^-] RT}{P_{air} V_{air}} \times 10^9 \text{ ppb} \end{aligned}$$

where n is the amount of substance (moles), V_{soln} is the volume of the reaction solution, P_{air} is the barometric pressure, V_{air} is the total volume of air sampled, R is the gas constant, and T is the air temperature. Note that the ozone concentration is normally reported as the mole fraction multiplied by 10^9 ; this results in a quantity with units of parts-per-billion by volume.

Hazards

Most of the operations involve dilute solutions and are not particularly hazardous. However, all of the chemical re-

agents used for this experiment are considered irritants so eye protection should be worn at all times. In addition, the production of triiodide for calibration curve generation involves the use of 0.1 M sulfuric acid (a corrosive agent) and potassium iodate (a strong oxidant). Thus, students should be advised to wear protective clothing, such as gloves and a lab coat, during the preparation of standard solutions.

Results

Undergraduate chemistry students have used this technique to make atmospheric ozone measurements from the top of the Science and Engineering Building at Oakland University in Rochester, MI. Their results agree well with values reported by four ozone monitoring stations surrounding Oakland University (New Haven, Lansing, Flint, and Oak Park stations). In Michigan, ozone is monitored by the Michigan Department of Environmental Quality at 25 locations dispersed throughout the state. The hourly average ozone concentrations measured at these sites are posted on the Web (16).

Example results obtained for days with low, moderate, and high levels of ozone are displayed in Figure 4. Air samples were collected between 11:00 a.m. and 4:00 p.m. The minimum and maximum results reported by the four surrounding ozone stations are shown in Figure 4 as dotted lines. The ozone concentrations determined with the iodometric technique (shown as solid markers connected with solid lines in Figure 4) fall within the range of values reported by the ozone stations approximately 75% of the time. The dynamic nature of ozone production makes it difficult to determine whether results outside the range are due to experimental error or just an observation of the variable nature of ozone concentrations. By comparing numerous iodometric measurements with the results from the surrounding monitoring stations, we estimate that the iodometric assay has a relative error of $\pm 20\%$. There are many potential sources of error including interfering chemical reactions and improper calibration of the photometer. Fortunately, the assay is sufficiently accurate to observe many of the interesting features of atmospheric ozone including seasonal, daily, and hourly concentration variations.

Conclusions

The simple assay presented here can be used to measure ozone under a wide range of atmospheric conditions. Laboratories that have access to vacuum pumps and visible spectrophotometers can employ this method using their existing equipment. Laboratories that do not have access to such items can achieve comparable results using simple sampling and analytical instruments fabricated from readily obtained materials. We have found that most high school and undergraduate students can execute the measurement protocol in approximately one hour. However, two additional hours are needed for the generation of a series of standard I_3^- solutions and the construction of a calibration curve.

We use this assay as an activity associated with our high school outreach program. Teachers and students from local high schools participate in a workshop at Oakland University where the importance of atmospheric ozone is discussed.

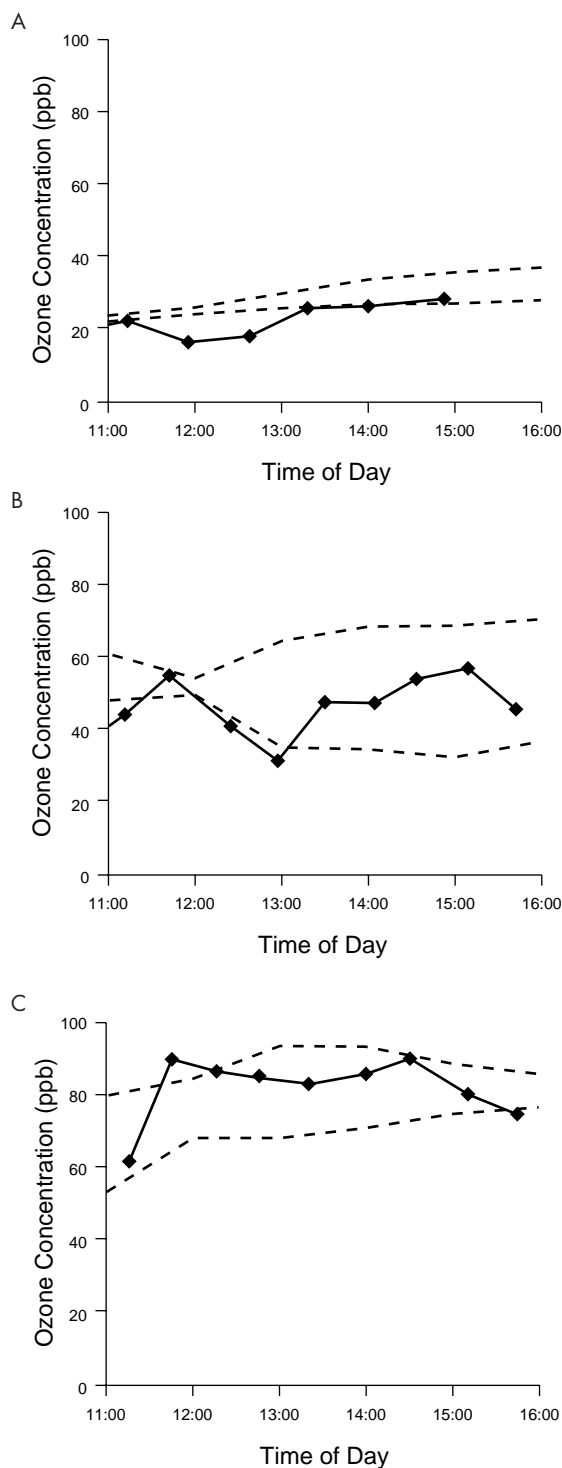


Figure 4. Ozone concentrations measured for three different days. The dashed lines represent the minimum and maximum values of ozone concentration observed at four surrounding ozone monitoring stations maintained by the Michigan Department of Environmental Quality:

(A) August 7, 2002, low ozone concentrations were observed throughout southeast Michigan

(B) July 22, 2002, moderate but highly variable ozone levels were observed in southeast Michigan

(C) August 1, 2002, high ozone levels were observed throughout southeast Michigan.

The measurement protocol is taught to each group. The teachers and students then take a sampling system and photometer back to their schools and make measurements on predetermined dates. The groups look for trends associated with sampling time and local weather conditions. The students are also encouraged to develop their own experiments such as comparing indoor and outdoor levels, measuring the concentration near photocopiers, and measuring the levels near electrical power generation and transmission facilities.

Supplemental Material

Detailed documentation for the experiment is available in this issue of *JCE Online*. The documentation is divided into three sections. The first section describes the materials and apparatus used to measure ground-level ozone. These items can be prepared by either the instructor or students. The next section provides step-by-step instructions for making an ozone measurement. The steps are normally executed by students. The final section describes an adaptation of the measurement protocol that is suitable for use in a high school setting.

Acknowledgments

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