CHAPTER 25 OZONE

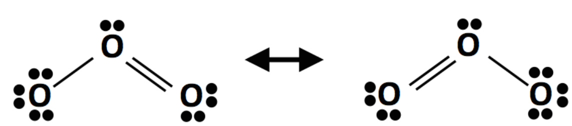
OZONE WAS DISCOVERED by the German-Swiss chemist Christian Freidrich Schonbein in 1840. He generated low levels of ozone by high voltage electrical discharge. Ozone is still generated in this way and the familiar smell of a photocopy machine or even some laser printers or a Tesla coil is due to trace levels of ozone. The fresh smell of the air during and after a thunderstorm is also due, in part, to ozone generated by the lightening. In the 19th Century, the this smell was called "the odor of electricity."

Ozone is the second allotrope of oxygen. It is a light blue gas with a characteristic odor that is associated with the smell of the air after thunderstorms. Pure ozone is obtained as a liquid by cooling an O_2/O_3 mixture to –180 ^oC. Liquid ozone is deep blue-black in color with a boiling point of -111.9 ^oC. Solid ozone is violet-black in color and melts at –193 ^oC.

Pure ozone is exceedingly dangerous due to its tendency to explode to produce oxygen:

$$2\ O_3 \rightarrow 3\ O_2 \qquad \Delta H = -284\ kJ$$

The structure of ozone is bent and is isostructural with SO_2 and NO_2. Two resonance forms contribute to the bonding scheme:



The O-O-O angle is 117^o and the oxygen-oxygen distance is 128 pm which is midway between the normal oxygen-oxygen single bond (149 pm) and double bond (121 pm) lengths. In both resonance forms the central oxygen has a formal charge of +1 while the single-bonded oxygen has a formal charge of -1. Resonance forms with adjacent opposite charges are inherently associated with unstable structures. If all the resonance structures of a molecule have charge separation problems, the molecule is frequently thermodynamically unstable. Such is the case for ozone, which is so reactive that it must be generated as needed.

Ozone has an intense absorption band starting at 290 nm and shorter wavelengths.

Ozone is the second strongest common oxidizing agent, exceeded only by F_2. In Europe and Canada ozone is generated and used to disinfect water much like chlorine is used in the USA. As more is learned about the deleterious effects of chlorine in the environment, particularly the atmosphere, the USA may someday switch to ozone for water treatment.

The ozone layer is a critical part of our atmosphere and occurs at an altitude of 15 - 25 km. The concentration of ozone never exceeds 10 ppm throughout the layer. If the entire ozone layer were brought to sea level, it would produce a layer of ozone gas only 3 mm thick at 1 atm and 25 ^{o}C. Ozone is continuously being produced in this layer from a reaction between oxygen, O_2, and ultraviolet radiation from the sun. Only high-energy ultraviolet radiation with a wavelength less than 240 nm will cause the photodissociation of O_2:

$$O_2(g) \xrightarrow{sunlight(<240nm)} 2\ O(g)$$

The oxygen atoms form ozone by reacting with a oxygen molecules:

$$O(g) + O_2(g) \rightarrow O_3(g)$$

Ozone absorbs ultraviolet radiation of wavelength 310 nm or less by the following reaction.

$$O_3(g) \xrightarrow{sunlight(<310nm)} O(g) + O_2(g)$$

The oxygen atoms, in turn, are chemically very reactive and usually react with an oxygen molecule to exothermically regenerate ozone:

$$O(g) + O_2(g) \rightarrow O_3(g) \qquad \Delta H = -142\ kJ$$

This last pair of reactions allows life on earth to exist! In the first reaction, ozone absorbs dangerous ultraviolet radiation, preventing it from reaching the earth's surface. In the second reaction, ozone is regenerated and heat is released. In essence, the ozone layer converts dangerous UV radiation into harmless heat. This accounts for the fact that the ozone layer is about 50 degrees warmer (about 0 ^{o}C) than the atmospheric layers above or below it. The recombination of O(g) and O_2(g) occurs in a one-step mechanism. The rate expression for the reaction is first order in O(g) and O_2:

$$rate = k[O]^1[O_2]^1$$

The concentration of O_2 in air (including the ozone layer) is about 21% (210,000 ppm) which far exceeds that of ozone. 0.05 ppm at sea level. The oxygen atoms very quickly collide with an oxygen molecule. Because the concentration of O_2(g) remains constant and greatly exceeds that of O(g) the rate expression will appear to be zero order in O_2(g) and first order overall. In this situation the reaction is called ***pseudo-first order***.

The photolysis of ozone to produce O_2(g) and O(g) followed by the exothermic recombination of these species to form ozone constitutes an equilibrium which serves to convert dangerous ultraviolet radiation to harmless heat.

In the last several decades evidence has mounted that suggests that certain man-made air pollutants could potentially jeopardize the ozone/oxygen equilibrium. Chlorofluoro-carbons, called freons, such as CF_2Cl_2 and $CFCl_3$ have been used for decades as aerosol propellants in canned spray products such as hair spray, spray paint, and bug spray. The freons become airborne and eventually migrate to the upper atmosphere where they eventually photodecompose to produce chlorine atoms:

$$CF_2Cl_2(g) \xrightarrow{sunlight(uv)} CF_2Cl(g) + Cl(g)$$

The chlorine atoms catalyze a free radical reaction in which ozone is destroyed:

Step 1: $O_3(g) + Cl(g) \rightarrow O_2(g) + ClO(g)$

Step 2: $ClO(g) + O(g) \rightarrow O_2(g) + Cl(g)$

Overall: $O(g) + O_3(g) \rightarrow 2\ O_2(g)$

A similar sequence of reactions occurs for nitrogen oxides, NO(g) and NO_2(g), which are introduced into the ozone layer by high-altitude aircraft such as the super-sonic transport (SST).

Dilute quantities of ozone can be prepared by either ultraviolet radiation of air or electrical discharge of several thousand volts. Sterilizing lamps use the former method, but generally, the electrical discharge method is more common.

Ozone is used as a disinfectant for air and water, for bleaching a variety of things, including textiles and oils, and in organic synthesis.

Ozone is an oxidant and is one of the constituents of photochemical smog. At low concentrations it is not harmful, but at higher concentrations, it irritates the respiratory tract and can lead to chronic respiratory disease.

Suitability

For use by high school and university-level chemistry students. Experiments and/or classroom demonstrations featuring the ozone generator can be conducted at about the time that the class is discussing ozone, the atmosphere, water purification, and/or oxidation. A typical experiment takes 15 minutes to perform. As a classroom demonstration, the teacher can begin the experiment and then describe ozone's properties while the experiment progresses. Students may wish to bring substances from home for testing. With only one generator, this activity could be done as a before or after school enrichment activity.

Experiment 1. Traditional tests for ozone
Experiment 2. Quantitative determination of ozone
Experiment 3. Reaction between food coloring and ozone
Experiment 4. Ozone reacts with natural and artificial colors
Experiment 5. Ozone reacts with rubber
Experiment 6. Ozone kills mold on cheese
Experiment 7. Ozone discolors colored office paper
Experiment 8. Ozone reacts with wood fibres
Experiment 9. Ozone kills bacteria in water

Experiment 1 demonstrates a common test for ozone – the oxidation of iodide to form a blue starch I_x^--complex. Because ozone is formed in situ and in combination with oxygen, Experiment 2 provides a method for quantifying the amount of ozone being produced per minute. The rest of the experiments explore the oxidative properties of ozone, starting with food colors, and then natural and artificial colors. In Experiment 5, the affect of ozone on rubber is demonstrated – pertinent as ozone destroys automobile tires as well as any rubber product. The oxidative properties of ozone can be harnessed for good uses as well, as demonstrated in Experiment 6 where mold on cheese is killed by exposure to the gas.

Background skills required

If students are conducting any of these experiments, they should be able to:

- ❖ connect a power supply and work with electrical connections in the presence of water
- ❖ follow instructions that utilize vocabulary words used in electrolysis, such as cathode, anode and so on.
- ❖ understand fundamental concepts of high school chemistry, specifically oxidation and reduction, so that observations can be interpreted.

Time required

The initial construction of the device, assuming that the materials are already available, might take an hour or more. Once assembled, the devise lasts indefinitely.

Experiments 1 and 3 are very quick experiments. Experiment 2 involves a titration and takes at least an hour to perform, not including calculations and graphing. The rest of the experiments require time for the ozone to interact with the substances being tested – usually at least 15 minutes and sometimes over an hour. These experiments do not need to be attended while they are proceeding.

Before students arrive: Assemble the equipment required

This entire set of experiments could be done as a combination of classroom demonstrations along with small group activities in which one generator is being shared by multiple groups. The ozone generator(s) should be assembled and tested prior to use by students.

Website

This chapter is available on the web at website:

http://mattson.creighton.edu/Microscale_Gas_Chemistry.html

Instructions for your students

GENERATING OZONE

General Safety Precautions

Always wear safety glasses. Follow the instructions and only use the quantities suggested.

Toxicity

Ozone has a high toxicity. Although ozone is quite dilute under these experimental conditions, ozone is explosive when concentrated. Its high oxidizing power promotes strong interaction frequently leading to degradation with surrounding materials. Its oxidizing action is non-selective.

Chemical caution

Sulfuric acid (3 M) is corrosive and should be handled with care. Eye protection must be used. Unwanted acid solutions may be neutralized and discarded down the drain. Other solutions can be discarded according to local regulations.

How ozone is produced

In 2005 we published an article in the *Journal of Chemical Education* describing a microscale ozone generator.[1] The generator is capable of producing 800 nanomole of ozone per minute. At this rate, it would take 18 days of continuous operation to generate one gram of ozone! Nevertheless, enough ozone is generated to detect the odor at a level similar to that produced by a photocopy machine or a Tesla coil. Despite the small amount of ozone generated, there is enough to cause a variety of interesting oxidations.

Oxygen and ozone are generated at the anode (platinum electrode) and the reactions are:

$$3\ H_2O \rightarrow O_3 + 6\ H^+ + 6\ e^- \qquad E^o_{ox} = -1.51\ \text{V (minor product)}$$

$$2\ H_2O \rightarrow O_2 + 4\ H^+ + 4\ e^- \qquad E^o_{ox} = -1.23\ \text{V (major product)}$$

The cathode (graphite) reaction is:

$$2\ H^+ + 2\ e^- \rightarrow H_2 \qquad E^o_{red} = 0.00\ \text{V}$$

The overall major reaction is:

$$2\ H_2O \rightarrow O_2 + 2\ H_2 \qquad E_{tot} = -1.23\ \text{V}$$

and the overall minor reaction is:

$$3\ H_2O \rightarrow O_3 + 3\ H_2 \qquad E_{tot} = -1.51\ \text{V}$$

Thus, the gas mixture collected is about $^2/_3$ hydrogen and $^1/_3$ oxygen. We have found that ozone represents 0.25 - 0.38% of the total gas produced.[2] Typically, 10 mL of gas are generated per minute.

The Ozone Generating Apparatus

[1] Content for this chapter first appeared in "Laboratory Experiments on the Electrochemical Remediation of the Environment, Part 7. Microscale Production of Ozone"; Ibanez, J. G.; Alatorre-Ordaz, A.; Mayen-

Equipment

The following equipment is required to build a ozone mini-generator:

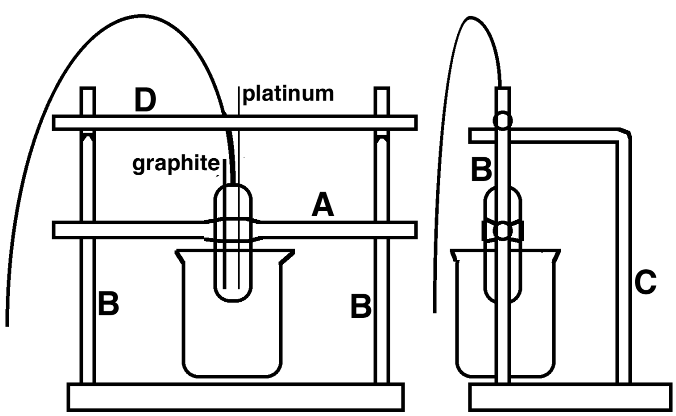
- six elbow-style soda straws
- 96-well plate
- plastic transfer pipet (thin stem Beral pipet)
- a piece of 0.7 mm mechanical pencil lead
- 10 – 15 cm length of thin platinum wire
- 100 mL beaker or 9 oz clear plastic beverage cup
- scissors
- paper hole punch
- razor blade
- paper clips
- matches
- two wires, 20 cm long with alligator clips on both ends
- 6 volt DC power supply from Radio Shack or equivalent

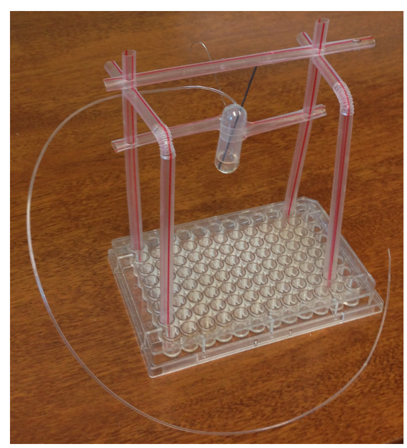
Chemicals:

3 M H_2SO_4, 3 mL

Construction of the apparatus

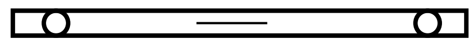
The apparatus used for the generation of ozone is shown in the figure below. The actual device is shown at right. The graphite electrode is the cathode where hydrogen is produced and the platinum electrode is the anode where oxygen and ozone are produced.





The apparatus is constructed from six elbow-style soda straws, a 96-well plate, a plastic transfer pipet (thin stem Beral pipet), a piece of mechanical pencil lead, a length of thin platinum wire at least 5 cm long and a beaker. The reaction chamber consists of a plastic transfer pipet which is first $^3/_4$ filled with 3 M H_2SO_4. The stem is stretched into a thin capillary tube by gripping the pipet stem with one hand just at the point where it joins the bulb, and at the open end of the tube with the other hand, and then pulling outward with a firm, steady pull. We suggest that individuals practice on a few empty pipets. Capillary lengths of 30 cm or more are possible, so that the ozone generated can be delivered some distance away.

With prolonged use, the level of solution goes down inside the pipet reaction chamber. The acid can be replenished (instead of making a new chamber) with a syringe and needle: Remove the graphite electrode which has a diameter similar to that of the needle. Inject more acid, but never exceed $^3/_4$ full. Remove the needle and reinsert the graphite electrode.



The straw that forms the lower horizontal cross-member (A) has two holes punched through (with a paper punch) where the vertical pieces will intersect as well as a slit about 2 cm in length, midway between the holes and in line with the holes as shown in the figure below. First cut the slit with a razor, then work the pipet bulb through the slit and *then* punch the two holes hear the end so that the distance between the holes will match the distance between the vertical straws (10 cm if the wells along the edge of the 96-well plate are used.)

Cut two straws (B) to a length of 15 cm and without elbows. Work Straws B through the punched holes and position them in wells of the 96-well plate. Next add the two front straws (C) that add support to the device. Note that the elbows of the C straws form the corners as best shown in the side view (right) in the figure. Punch holes through the two rear vertical members about 2 cm below the top of the vertical so that the C straws can intersect with the B straws. Trim excess straw length from the ends of the C straws. The sixth straw (D) is the top horizontal straw and has suitable end holes punched so that they can slip over the vertical rear members. The sixth straw also has one or two smaller holes near the middle created by poking a hot paperclip through the straw. Through one of these holes, the Pt wire is threaded (if it is long enough.) The capillary delivery tube of the pipet is threaded through the other hole.

The two electrodes must form airtight fits through the pipet's bulb. Using a hot paperclip usually results in a hole that is too large. A stick pin makes a suitable hole for the thinner diameter Pt wire and a thumb tack makes a suitable hole for the graphite pencil lead.

Ice bath

The beaker shown in the previous line drawing is for an ice bath necessary to keep the system cool. Without the ice bath, the electrodes will heat up and may enlarge the holes through the pipet. If this occurs, the gases will no longer be delivered through the capillary tube but rather they would leak out the enlarged hole(s) around the electrode(s). The ice bath should contain more water than ice so that every surface of the pipet bulb is in contact with ice water. The ice bath also improves the yield.

Power Supply

Next, the power supply is connected as shown in the figure at right. The 6-volt setting is optimal and a 6-volt battery can be used as the power supply. Power supplies come with a variety of connectors. The one shown here is a push-pin style. We fashioned a U-shaped wire from part of a paperclip to slip inside the connector where the pin would go. A nail of suitable diameter would work as well. Two wires with alligator clips on both ends are used to connect the power supply to the electrodes.

IN SITU PREPARATION OF OZONE

Ozone is generated and used *in situ* — that is, it is used as it is made and not collected in a syringe. Ozone reacts quickly with rubber and many other organic substances.

Chemicals required for each preparation

3 mL 3 M sulfuric acid

This quantity of reagents will produce approximately 10 mL of 0.25% $O_3(g)$ per minute for several hours. The reactions were discussed earlier.

1. Wear your safety glasses!

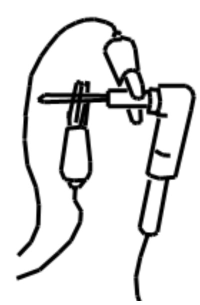
2. Add acid to the pipet bulb acid reservoir of the ozone generator if necessary.

The pipet reservoir should be $^2/_3$ – $^3/_4$ full. Add more acid through via a syringe equipped with a needle through the hole for the graphite electrode if necessary.

3. Position ice bath.

The ice bath should cover as much of the pipet bulb acid reservoir as possible. The ice bath should contain water and ice rather than just ice. This produces a far more effective heat sink.

4. Connect the power supply



The graphite electrode is the cathode where hydrogen is produced and the platinum electrode is the anode where oxygen and ozone are produced. The alligator clip attached to the paperclip inserted into the connector is connected to the platinum wire. The larger, outer part of the plug is connected to the graphite electrode. Not all power supplies are the same and you may have to experiment with the connections by arbitrarily trying it one way or the other. If it is *improperly* connected, the solution will turn black due to suspended graphite from the disintegrated electrode. If this happens, make note of the correct way to connect the wires, then start over, replacing the solution and the graphite electrode.

5. Commence generation of ozone

Insert the stretched pipet stem into a test tube of water to detect the flow of gases. Waft some of the gas past your nose (you will need to be fairly close to the mouth of the test tube) in order to detect the characteristic odor of ozone.

6. Unplug the power to stop generation of gases

Simply unplug the power supply to stop the generation of gases.

7. Disposal

The ozone generator can be stored with the sulfuric acid in place indefinitely. If the ozone generator is being dismantled, the acid solution in the generator may be neutralized and discarded down the drain.

Teaching tips

1. If the electrodes are connected backwards, the electrolysis reaction does not work and the sulfuric acid solution with become black from suspended graphite as the graphite electrode slowly disintegrates. Write the correct wire connection scheme on some part of the apparatus (such as on a label folded around the electrical wires with the alligator clips: "Connect paperclip to platinum," for example.

2. Although the amount of ozone being generated is so small and one cannot even detect it's smell even a few inches away from the generator, as a practice of laboratory safety, use a fume hood if one is available. This precaution is advisory only; we did not use a fume hood in any of our studies and we believe that one should not avoid these ozone experiments if a hood is not available.

3. Using a 10-mL graduated cylinder filled with water and inverted in a beaker of water, determine the flow rate for gas production using water displacement.

Questions

1. Place the delivery tube into a small test tube of water. Describe the smell of ozone. You will need to position your nose near the mouth of the test tube. Where else have you smelled this ozone smell?

2. Ozone has a structure that is bent, like that of SO_2. Sketch the Lewis dot structure for SO_2 and O_3.

3. Ozone is over 10 times more soluble in water than O_2. Use Lewis dot structures to determine the polarity of O_2 and O_3 and to account for this phenomenon.

4. Use the Internet or your chemistry book to find one good use of ozone and one bad thing about ozone.

5. Ozone is an oxidant. It is capable of oxidizing metals that ordinary oxygen cannot. Write and balance the reaction that takes place when ozone reacts with silver to produce silver(I) oxide and oxygen.

6. Look up the definition of the word allotrope, if you do not know it already. Give an example pertinent to ozone.

7. Write the half reaction that takes place at the cathode.

8. Write the two half reaction that takes place at the anode.

9. Add the two combinations of half reactions together. Make sure that the electrons transferred is properly balanced.

10. Gather information about ozone from your chemistry book, the library and the internet. Try to evaluate the soundness of the articles found on the Internet (watch for misspelled words, "bad science," outrageous claims, "facts" that do not appear on several websites, websites that are offering to sell ozone products for health reasons, and so on.) From the information gathered, make a list of positive things ozone can do and a list of problems ozone causes.

11. Gather information about stratospheric ozone. What role does that play in maintaining life on earth?

EXPERIMENTS WITH OZONE[2]

EXPERIMENT 1. TRADITIONAL TESTS FOR OZONE.

Equipment

Ozone generator
Test tubes, 150 mm x 18 mm, several

Chemicals

1.7 g KI
1 g potato starch

Suitability

advanced high school chemistry lab, university lab, and classroom demonstration

Applications, Topics, Purpose

chemical formulas, chemical properties of gases, types of chemical reactions, oxidation-reduction reactions, characterization of gases

Instructions

Prepare starch-iodide solution.

Make a slurry of 1 g potato starch in 20 mL distilled water in a small beaker. Heat the slurry with stirring until the color goes from the opaque white to a translucent gel. Remove from heat. Prepare 1.0 M KI solution: dissolve 1.7 g potassium iodide, KI, in 10 mL water. For each demonstration, mix 3 mL KI(aq) with 1 mL starch.

[2] Some of these experiments were first published with our original article (Footnote 1) and the rest were published as "Microscale Gas Chemistry, Part 28. Mini-Ozone generator: 800 nanomole/minute," Bruce Mattson, Janel Michels, Stephanie Gallegos, Jorge G. Ibanez, Alejandro Alatorre-Ordaz, Rodrigo Mayen-Mondragon, M. T. Moran-Moran, ***Chem13 News*** **2007**, **344**, 6 – 11.

Prepare starch-iodide papers.

Cut filter paper into strips about 1 cm wide. Dip the filter paper into the starch-iodide solution and remove.

Starch paper test for ozone.

While the filter paper is still wet, hold it in the stream of ozone issuing from the stretched pipet stem. The filter paper should darken almost immediately.

Starch-KI test for ozone.

Add 2 – 3 mL distilled water to a test tube. Add about ten drops of the KI-starch solution. Place the pipet stem from the ozone generator into the solution. The solution will darken blue rather quickly. The solution should turn blue indicating the presence of $I_3^-(aq)$ produced by the reaction between KI(aq) and $O_3(g)$:

$$I^-(aq) + O_3(aq) + H^+(aq) \rightarrow HOI(aq) + O_2(g)$$

$$HOI(aq) + 2\ I^-(aq) + H^+(aq) \rightarrow I_3^-(aq) + H_2O(l)$$

$$2\ I_3^-(aq) + \text{starch} \rightarrow \text{starch-}I_5^- + I^-(aq)$$

Teaching tips

1. Although the amount of ozone being generated is so small that one cannot detect it's smell even a few inches away from the generator, as a practice of laboratory safety, use a fume hood if one is available.
2. If the iodine-starch paper is dry, moisten it with distilled water before use.
3. With iodine-starch test paper, test the air in the room and near the ozone generator.
4. The starch solution (without the KI) can be stored in a refrigerator. It will need to be heated up until it is clear before use.

Questions

1. Describe the color changes noted with the iodine-starch paper when exposed to ozone. How long did it take to react?
2. Was iodide oxidized or reduced?
3. Suppose an entire sheet of paper were treated with the iodine-starch solution and taped to a wall. Then suppose that the ozone generator were placed near the bottom edge of the iodine-starch paper. What would you expect to happen?

EXPERIMENT 2. QUANTITATIVE DETERMINATION OF OZONE

Equipment

Ozone generator

Test tubes, 150 mm x 18 mm, several

Volumetric flask, 100 mL
Magnetic stirrer and magnetic stirring bar
Buret

Chemicals

$Na_2S_2O_3$ solution, approximately 5 x 10^{-3} M; the exact concentration should be known
Starch-KI solution from Experiment 1
3 M H_2SO_4(aq)

Suitability

advanced high school chemistry lab, university lab

Applications, Topics, Purpose

quantification of ozone, rate of gas generation, analytical chemistry

Instructions

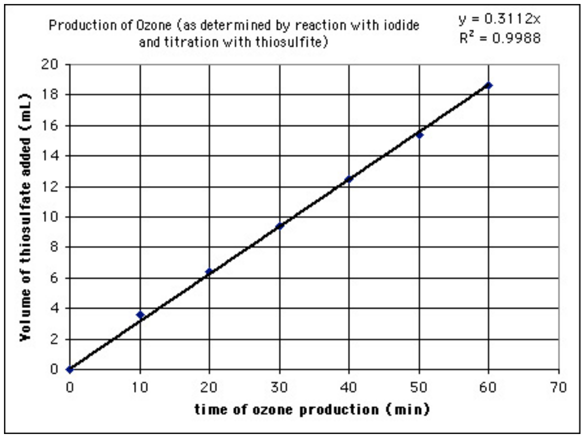
The rate of ozone produced is determined by bubbling the gases produced (H_2, O_2 and O_3) through a solution containing dilute starch-iodide solution. Add 30 mL distilled water to a 100-mL volumetric flask. Next add 1 mL 3 M H_2SO_4(aq) and approximately 1 mL of the starch-KI solution. The exact amount of the starch-iodide solution is not critical, however we used a solution that was 0.001 M KI in the experiments with results described here.

Position a buret containing $Na_2S_2O_3$ solution of known concentration above the mouth of the flask. As the ozone is generated, it bubbles through the KI(aq) to produce KI_3(aq), which is blue in the presence of starch. This produces I_3^-, which then reacts with starch to form the distinctive blue starch-triiodide complex. Upon adding standardized $S_2O_3^{2-}$ to the blue solution, the blue color disappears signaling the endpoint. The reactions are:

$$O_3(aq) + 3\ I^-\ (aq) + H_2O \rightarrow O_2 + I_3^- + 2\ OH^-$$

$$2\ S_2O_3^{2-} + I_3^- \rightarrow S_4O_6^{2-} + 3\ I^-$$

In a typical experiment, the titration with $Na_2S_2O_3$ solution can be conducted as the ozone is being generated with a new endpoint established as a function of time. Thus, the volumes of $Na_2S_2O_3$ solution required to attain the endpoints as a function of time for a typical ozone generator are given in the chart below. The slope gives the rate of $Na_2S_2O_3$ solution added to be 0.311 mL/minute. Given the concentration of $Na_2S_2O_3$ solution (5.06 x 10^{-3} M), the rate of $Na_2S_2O_3$ added in terms of moles is 1.57 x 10^{-6} mol $Na_2S_2O_3$/min. Thus, the rate of KI_3 production is determined to be 7.85 x 10^{-7} mol KI_3/min. Given the reaction between ozone and KI to produce KI_3 (above), the rate of ozone production is determined to be 7.85×10^{-7} mol O_3/min (785 nanomole/min). The rate of all gases produced was determined to be 7.6 mL/min that corresponds to 3.1×10^{-4} mol/min at 300 K and 1 atm. Thus, ozone constitutes approximately 0.25% (or 2500 ppm) of the gases produced.



Teaching tips

1. Although the amount of ozone being generated is so small that one cannot detect it's smell even a few inches away from the generator, as a practice of laboratory safety, use a fume hood if one is available.

2. This titration is conducted in real time with a continuously changing endpoint. A careful explanation may be necessary in order for students understand this rather unusual experiment.

Questions

1. The ozone is delivered at a concentration of about 800 nanomoles per minute. Convert this to grams ozone per hour.

2. For gases, concentrations are frequently expressed in parts per million, which is defined as:

$$\text{Concentration (ppm)} = n_a \times 10^6/n_{total},$$

where n_a = moles of substance A and n_{total} = total number of moles. The ozone in this experiment is being produced at a rate of no more than 0.40 % by volume ($V_{O3} \times 100/V_{total}$). Volume and moles are directly proportional from the ideal gas law, PV = nRT, so percent by volume and percent by moles are equivalent. Percent by volume (or moles) can be defined in a way that is analogous to ppm:

$$\text{Concentration (\%)} = V_a \times 10^2/V_{total} = n_a \times 10^2/n_{total}.$$

Thus, percent and ppm differ by a factor of 10^4. What is the concentration of ozone being delivered in units of ppm?

3. If the flow rate of ozone is 800 nanomoles per minute, how long would it take to deliver 1.0 g ozone, expressed in days?

EXPERIMENT 3. REACTION BETWEEN FOOD COLORING AND OZONE

Equipment

Ozone generator
Test tubes, 150 mm x 18 mm, several
Visible spectrophotometer (optional)

Materials

Food coloring, blue, green, red, yellow

Suitability

high school chemistry lab, university lab, classroom demonstration

Applications, Topics, Purpose

Oxidation power of ozone, bleaching ability of ozone, rates of chemical reactions, kinetic rate law, solutions of two components, chemical properties of gases

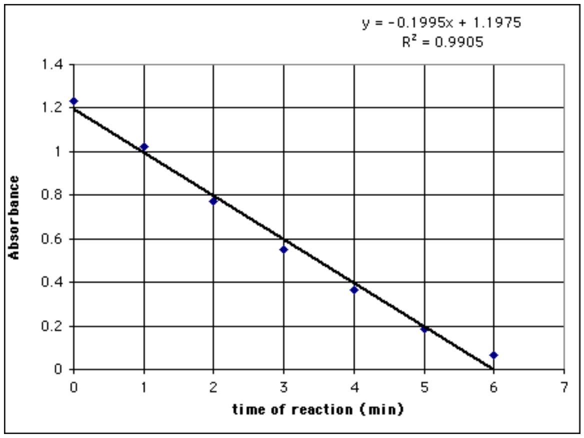
Instructions

Classroom Demo Option without Spectrophotometer

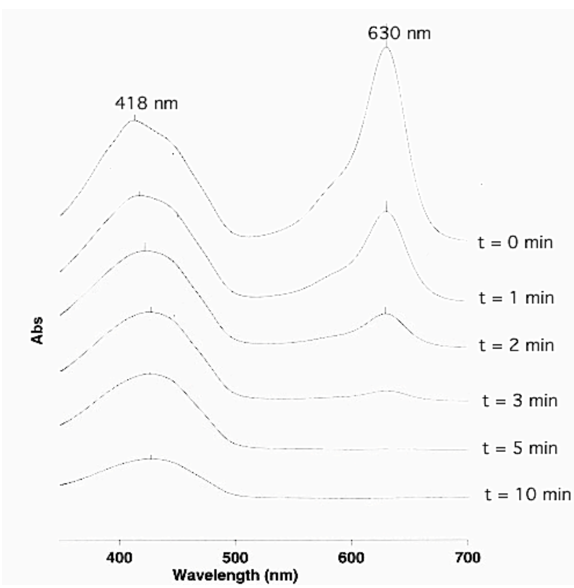
Because the colors disappear in these reactions, it is possible to demonstrate the reactive power of ozone without the quantitative aspects provided by the spectrophotometer. Divide the food color sample into two parts so that one can serve as a control. Expose the other to the stream of ozone. Within minutes, the samples exposed to ozone will fade, eventually to colorless.

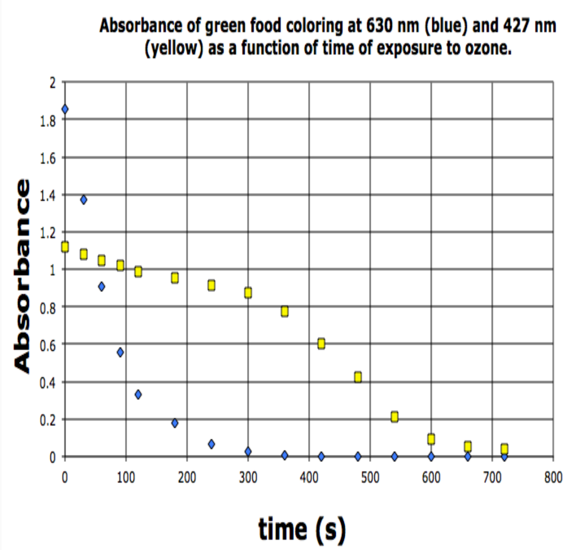
Blue Food Coloring and Ozone.

To observe the effect of ozone on some dyes, a solution of blue food coloring can be reacted with ozone. The absorbance is measured at λ_{max} = 630 nm with a UV-VIS spectrophotometer. The sample is then returned to the flask for continued reaction. Typical results are shown here.



Green Food Coloring and Ozone. Green food coloring is a mixture of blue and yellow. The yellow color is far less reactive towards ozone than blue, so that solutions of green food coloring turn yellow then colorless. In an experiment analogous to the one described above for blue food coloring, one can monitor the absorbance of green food coloring at its two absorption maxima wavelengths, 630 nm and 427 nm. Typical results are given here.





Teaching tips

1. Although the amount of ozone being generated is so small that one cannot detect it's smell even a few inches away from the generator, as a practice of laboratory safety, use a fume hood if one is available.
2. Red (and yellow) food coloring also works.
3. Using an Excel scatter graph, one can add the equation to the line by going to the "Chart" menu and picking "Add trend line." Click "Options," and select "Display equation on chart." You can also make the y-intercept zero.

Questions

1. Using the graph you made of Absorbance (y-axis) vs. time (x-axis) for the Blue experiment, determine what fraction of the original amount of Blue remains after 1.0 minute, 2.0 minutes, and 3.0 minutes. You may use the equation for the line if you have chosen that option.

2. If you have studied kinetics, what is the reaction order? Write the rate law? What else is needed in order to determine the rate constant.

3. In the Green experiment, which color component faded fastest? From the graph of Absorbance vs time at λ = 427 nm and 630 nm, when is the Blue color "gone"?

4. Which dye is more reactive towards ozone, Blue or Yellow?

5. Suppose Red dye had a reaction rate with ozone that is similar to that of Blue's. What would one observe if one were to make Orange dye from Red and Yellow dyes and watch its reaction with ozone?

EXPERIMENT 4. OZONE REACTS WITH NATURAL AND ARTIFICIAL COLORS

Equipment

Ozone generator
Test tubes, 150 mm x 18 mm, many

Materials

Samples of colored substances from home

Suitability

classroom demonstration, laboratory activity

Applications, Topics, Purpose

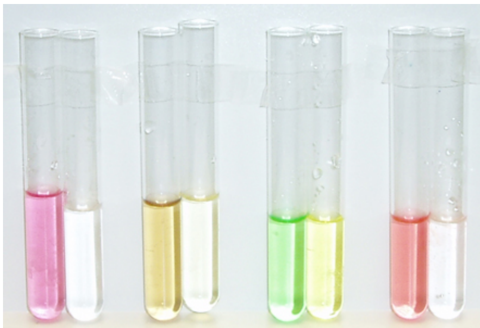
Oxidation power of ozone, bleaching ability of ozone, chemical properties of gases, household chemicals

Instructions

A variety of food products and household materials were tested and yielded positive results in terms of a noticeable color change within 10 – 30 minutes as summarized in Table 1. In each experiment, a sample of a food juice or liquid was diluted with water as indicated in Table 1. The diluted solution was divided into two equal samples and placed in two small test tubes. One test tube served as a control and the other was treated with a stream of ozone by placing the capillary from the generator all the way to the bottom of the test tube so that the bubble stream traveled the entire distance through the solution. Before and after photographs of all of the substances tested in Table 1 are available at our ozone website.

Substance*	Preparation	Results
Beet juice	juice from boiled beats, 1 drop in 5 mL water	Pink color disappears within 5 minutes
Cherry Coke	1 mL Cherry Coke + 2 mL water	Brown color fades to faint yellow within 30 min
Green Koolaid	"normal" Kool Aid mixed 50-50 with water	Turns from green to yellow within 15 min
Red Koolaid	"normal" Kool Aid mixed 1:3 with water	Turns colorless within 15 minutes
Maraschino cherry juice	diluted 2 mL juice to 8 mL water	Red turns to light pink in 16 minutes
Dill pickle juice	not diluted	Green-yellow to colorless within 23 min
Pure cherry juice	diluted 2 mL juice to 6 mL water	Brown-red to yellow in 20 min
Tomato juice	diluted 2 mL juice to 8 mL water	Reddish suspension becomes pinkish in 15 min
Orange soda	diluted 2 mL juice to 10 mL water	Orange to colorless in 20 min
Red cabbage juice	diluted 2 mL juice to 6 mL water	Purple to tan in 10 min
Canned carrot juice	not diluted	Orange suspension becomes white in 30 min
Grape concentrate	diluted 1 mL juice to 10 mL water	Purple to colorless in 15 min

* Product names for all substances tested is given at our ozone website.



The first four substances listed above are shown at right. A large variety of other substances could be tried and added to the list and we leave this to the reader to attempt. A few other substances that will yield color changes include: Fruit Punch, Powerade (blue), Grape Jelly dissolved in water, Hot Sauce, red wine, orange juice and coffee. Excellent results are obtained with red, blue and yellow food coloring as described in the previous experiment. Many substances do not show appreciable color change in reasonable lengths of time. In designing new experiments, it is important to prepare solutions that are dilute enough so that the feeble stream of ozone (800 nmol/min) can oxidize the color within a reasonable amount of time, yet concentrated enough so that a color and color change are easily noticed.

Teaching tips

1. Although the amount of ozone being generated is so small that one cannot detect it's smell even a few inches away from the generator, as a practice of laboratory safety, use a fume hood if one is available.

2. For liquids, be sure to dilute the substance as much as possible while maintaining the definite color of the substance. See ozone website for examples.

3. For solids, moisten the surface with water for faster results.

4. Test liquids with bright colors, especially red, pink, blue and purple. Liquids should be clear. Most of our work was with beverages and the colored liquids with foods and most of these solutions lost part or all of their colors.

5. Read the list of substances from the labels of materials that change color. Try to identify the substance that causes the color. For artificially colored foods, the list of approved dyes is rather short and it should be easy to find two or more foods that have the same food coloring in them. Determine if the two substances behave in a similar way upon exposure to ozone.

Questions

1. Why must one dilute the colored substances prior to exposure to ozone? What would happen if one did not do this?

2. What substance discolored the fastest?

3. What exactly is occurring when a colored compound becomes colorless?

4. Is it possible to identify the colored component(s) that are most affected by ozone? Sometimes artificial colors are listed on the package label. With the help of your teacher, if necessary, determine which component gives the substance its color.

EXPERIMENT 5. OZONE REACTS WITH RUBBER

Equipment

Ozone generator
Test tubes, 150 mm x 18 mm, several

Materials

Rubber bands

Suitability

high school lab, university lab, and classroom demonstration

Applications, Topics, Purpose

Oxidation power of ozone, bleaching ability of ozone, chemical properties of gases, household products

Instructions

As an air pollutant, ozone epoxidizes carbon-carbon double bonds in organic compounds. The epoxides are not stable and degrade to two parts. Rubber is an example of an organic polymer that has double bonds throughout. Upon exposure to ozone, the double bonds form epoxides; an oxygen atom adds across the double bond, replacing it with a three-member ring that has two carbon members and an oxygen:

$$\sim(C_2H_4)_nCHCH(C_2H_4)_n\sim + O_3(g) \rightarrow \sim(C_2H_4)_nCH(O)CH(C_2H_4)_n\sim + 3\ O_2$$

Epoxides are notoriously unstable and break between at the epoxide:

$$\sim(C_2H_4)_nCH(O)CH(C_2H_4)_n\sim \rightarrow \sim(C_2H_4)_nCHO + CH_2CH(C_2H_4)_{n-1}\sim$$

In this experiment, rubber becomes brittle after brief exposure to ozone and easily breaks upon stretching. In order to demonstrate this, two identical rubber bands were stretched to make sure they were in similar condition. Both stretched the length of a 12-inch ruler without difficulty. Each was placed in a dry test tube and one was exposed to a stream of ozone for fifteen minutes. The other one was stoppered to prevent inadvertent exposure to ozone. Within 15 minutes, the rubber band exposed to ozone was broken in three places on its own and without any disruption or contact. A photograph of the two rubber bands, side-by-side, is given at right.

Teaching tips

1. Although the amount of ozone being generated is so small that one cannot detect it's smell even a few inches away from the generator, as a practice of laboratory safety, use a fume hood if one is available.

2. Experiment takes 15 minutes for results

Questions

1. Sketch 2-butene, $CH_3CH{=}CHCH_3$, as a simple model for rubber. Sketch the epoxide that is expected upon exposure to ozone.

2. Look up the chemical reason why rubber stretches. What sort of bonds are involved when rubber stretches?

3. What products are made of rubber and may be affected by ozone degradation?

EXPERIMENT 6. OZONE KILLS MOLD ON CHEESE

Equipment

Ozone generator
Test tubes, 150 mm x 18 mm, several

Materials

Cheese with mold

Suitability

high school lab, university lab, and classroom demonstration

Applications, Topics, Purpose

Oxidation power of ozone, bleaching ability of ozone, chemical properties of gases, food

Instructions

Ozone is able to kill bacteria, algae, spores, fungus, and mold on contact. This was tested with moldy cheese. A blue-gray mold colony on a piece of yellow cheese approximately 1 cm in diameter was cut in half with a razor blade. One half was lowered into a medium size test tube with the aid of a glass pipet poked into the cheese (away form the mold colony.) Ozone was delivered to the test tube for one hour at which time the cheese mold was bleached to a pale cream color. After two days, the untreated mold remained blue and the ozone-treated mold remained cream-white, as shown in the photograph.

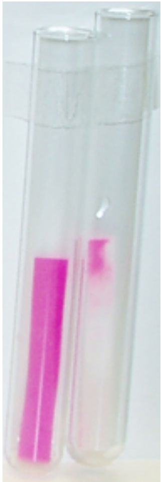
Teaching tips

1. Although the amount of ozone being generated is so small that one cannot detect it's smell even a few inches away from the generator, as a practice of laboratory safety, use a fume hood if one is available.
2. Do not eat the cheese. Discard all samples in the trash.

Questions

1. Describe your experimental observations for this reaction.
2. What other materials mold? Do you think the ozone generator would mitigate the mold on these products?
3. Do you think the cheese would be safe to eat after treatment with ozone (assuming it was done commercially and not in a chemistry lab)?
4. Milk spoils by a bacterial process. Ozone readily kills bacteria. Do you think spoiled milk could be made fresh again with an ozone treatment?

EXPERIMENT 7. OZONE DISCOLORS COLORED OFFICE PAPER



Equipment

Ozone generator
Test tubes, 150 mm x 18 mm, several

Materials

Colored office paper

Suitability

high school lab, university lab, and classroom demonstration

Applications, Topics, Purpose

Oxidation power of ozone, bleaching ability of ozone, chemical properties of gases, food

Instructions

One of the major industrial uses of ozone is in water purification. Ozone dissolves twelve times more readily in water compared to pure oxygen.[2] We tested a variety of office papers and found that brightly colored papers were fairly likely to change colors upon exposure to ozone while light colors were generally less affected. In each case, two strips, about 5 mm wide and 5 cm long were cut from the sample. Because ozone dissolves twelve times more readily in water compared to pure oxygen, we moistened the paper samples before placing them into the test tubes. Exposure times and results are summarized in the following table. A photograph of a variety of paper samples, side-by-side, is available at our ozone website.

Office paper exposed to ozone.

Office paper:	Results:
Bright pink	Pink turns mostly white within 30 minutes (shown in figure)
Bright orange	Orange turns to yellow within 25 minutes
Bright green	Some areas of green turned to white within 45 minutes
Bright yellow	Almost no change after 40 minutes
Bright red	Some areas of red turned to white within 45 minutes
Bright violet	Violet mostly converted to white within 40 minutes
Light blue	No significant change after 30 minutes
Light green	No significant change after 30 minutes
Pink post-it note	Pink turns to yellow within 30 minutes

Teaching tips

1. Although the amount of ozone being generated is so small that one cannot detect it's smell even a few inches away from the generator, as a practice of laboratory safety, use a fume hood if one is available.

2. Discard all samples in the trash.

Questions

1. If a sample changes from one color to another, does that necessarily mean there is more than one substance in the original sample? Explain.

2. If a substance takes a long time to change color (or does not change at all), what does that say about the activation energy for the rate of reaction with ozone?

3. Which colors would you predict would fade the fastest if left in direct sunlight for prolonged periods of time?

EXPERIMENT 8. OZONE REACTS WITH WOOD FIBRES

Equipment

Ozone generator
Test tubes, 150 mm x 18 mm, several

Suitability

high school lab, university lab, and classroom demonstration

Applications, Topics, Purpose

Oxidation power of ozone, bleaching ability of ozone, chemical properties of gases, food

Instructions

In Youman's 1876 chemistry textbook, there is the following passage: *"[Ozone] deodorizes tainted flesh, destroying its effluvium instantly, and carries woody fibre in a short time through a course of decomposition, which, with oxygen, would require years."* We elected against testing the former assertion, but did test ozone's affect on wood. Use paper-thin wood shavings from an ordinary softwood piece of lumber. Cut the shavings were also cut into strips about 2 mm wide and 3 – 4 cm long. After a 30 minute exposure, the wood was a deep brown over much of its surface. A photograph of wood shavings before and after is available at the website.

Teaching tips

1. Although the amount of ozone being generated is so small that one cannot detect it's smell even a few inches away from the generator, as a practice of laboratory safety, use a fume hood if one is available.

2. Discard all samples without handling in the trash.

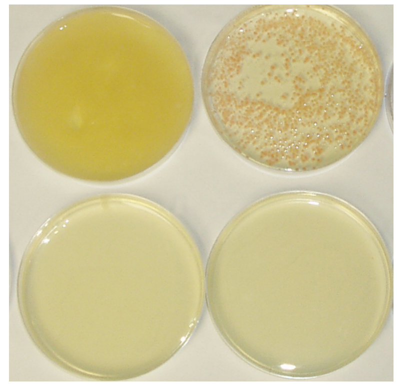
Questions

1. Wood is a mixture of cellulose in a matrix of lignin. Find out which of these two materials gives wood its strength.

2. Predict if the ozone damage was only on the surface.

3. In the previous experiments, ozone usually discolored substances. Here it is seen as causing an increase in color. What do you think is the reason?

EXPERIMENT 9. OZONE KILLS BACTERIA IN WATER[3]



Equipment

Ozone generator
Test tubes, 150 mm x 18 mm, several
Petri dishes with nutrient-rich agar
Natural water sample

Suitability

high school lab, university lab, and classroom demonstration

Applications, Topics, Purpose

Oxidation power of ozone, bleaching ability of ozone, chemical properties of gases, drinking water

Instructions

Agar. We prepared our own nutrient-rich agar media (2.5 g tryptone, 1.25 g yeast, 2.5 g NaCl, 3.75 g agar, and 7.5 mL 0.1 M NaOH in water to make 250 mL.) The solution is poured into Petri dishes and then autoclaved for 1.25 hour. Rich agar media are stored in a refrigerator until needed.

Collect water from a natural source such as a stream, lake, river, or swamp. Transfer about 15 mL of water to a clean 30-mL test tube (15 x 150 mm.) Transfer about 3 mL water sample to a nutrient agar plate. Gently swirl in order to coat the entire surface with the water sample. Place the ozone delivery tube all the way to the bottom of the test tube containing the water sample. Ozone generation commences immediately when the power supply is plugged in. Remove 3 mL samples of water with a disposable pipet after 5, 15 and 30 minutes. As before, the samples were added to fresh agar dishes, covered, and swirled. Samples are incubated at room temperature. Three days later, the results should be bacteria and coliform colonies developed in the non-ozone treated samples, but not in the sample treated with ozone for 30 minutes. In the figure above, water-on-agar samples are shown after 3-days culturing time for: upper left: no $O_3(g)$; upper-right: 15 min of $O_3(g)$ exposure, lower left: 30 minutes $O_3(g)$ exposure and lower right: 45 min $O_3(g)$ exposure. Ozone was delivered at a flow rate of 800 nanomole per minute.

[3] "Microscale Gas Chemistry, Part 29. The Mini-Ozone Generator and Bacteria in Natural Aquatic Samples," Bruce Mattson, Stephanie Gallegos, Laleh Mehrrafiee, Jiro Fujita, ***Chem13 News* 2007,** 351, 8 – 10.

Teaching tips

1. Although the amount of ozone being generated is so small that one cannot detect it’s smell even a few inches away from the generator, as a practice of laboratory safety, use a fume hood if one is available.
2. Discard all samples without handling in the trash.
3. Watch YouTube video of this reaction in time-lapse (1 s = 6 hr): https://www.youtube.com/watch?v=Zd8xuvtq0_w&sns=em

Questions

1. At a flow rate of 800 nmol/min, how many moles of O_3 are delivered in 30 minutes?
2. Where do coliform bacteria come from in natural waters? *E. Coli*?
3. How does ozone kill bacteria?
4. What other chemicals are commonly used to kill bacteria? What are the pros and cons to ozone and these other chemicals?
5. Using the microscale ozone generator, it takes more than five minutes to completely kill all of the bacteria in the water samples that we tested. Why does it take so long? Are some bacteria simply harder to kill? Or is the ozone the limiting reagent?
6. Use the Internet or your chemistry book to read more about the use of ozone to disinfect water samples.

Clean-up and Storage

Unplug the power supply and disconnect it from the platinum and graphite electrodes. The pipet bulb can be left full of the acid solution. Leave the water bath cup under the pipet bulb to catch any drips, should they occur. Store the generator in a safe location where it will not be tipped over or otherwise damaged.

Summary of Materials and Chemicals Needed for Chapter 25. Experiments with Ozone

Construction of the ozone generator for long-term use

Item (recommend combo of demos and small group sharing of one generator)	Demo:	5 pairs:	10 pairs:
elbow-style soda straws	1	5	10
96-well plate	10	50	100
plastic transfer pipet (thin stem Beral pipet)	1	5	10
0.7 mm mechanical pencil lead*	1	5	10
length of thin platinum wire	2 in	10 in	20 in
100 mL beaker or 9 oz clear plastic beverage cup	1	5	10
20 cm long with two alligator clips	2	10	20
6 volt DC power supply from Radio Shack or equivalent	1	5	10
Miscellaneous items for construction**			

* 0.25 mm diameter wire; Flinn sells platinum wire for $2.70 per inch

** scissors, paper hole punch, razor blade, paper clips, matches

Additional equipment required

Item	Demo:	5 pairs:	10 pairs:
small test tubes	10	50	100
volumetric flask, 100 mL (Expt 2)	1	5	10
buret, 50 mL (Expt 2)	1	5	10
visible spectrometer	1	1 - 5	1 - 10
magnetic stirrer and stir bar	1	5	10

Materials required

Item	Demo:	5 pairs:	10 pairs:
food coloring, red, green, blue yellow	1	1	1
rubber band	1	5	10
cheese with mold	1	5	10
colored office paper	1	5	10
wood shavings	1	5	10

Chemicals required

Item	Demo:	5 pairs:	10 pairs:
sulfuric acid, 3 M	10 mL	50 mL	100 mL
potassium iodide, KI	2 g	10 g	20 g
potato starch	1 g	5 g	10 g
sodium thiosulfate, $Na_2S_2O_3$, 5.0×10^{-3} M	60 mL	300 mL	600 mL