Microscale Gas Chemistry, Part 28.

Mini-Ozone generator: 800 nanomole/minute

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Description.

In 2005 we published an article in the ***Journal of Chemical Education*** describing a microscale ozone generator.[2] 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. In our original article, we described the oxidation of food coloring over the course of minutes. Here we greatly expand the list!

In this article we describe an improvement in design using a framework built of elbow drinking straws on a base consisting of a 96-well plate — in the spirit of Professor Steve Thompson's (Colorado State University) microscale architecture. We also describe a wide variety of other oxidations of foods and other materials.

Apparatus.

The apparatus used is shown in Figure 1 and a photograph is provided at our website.

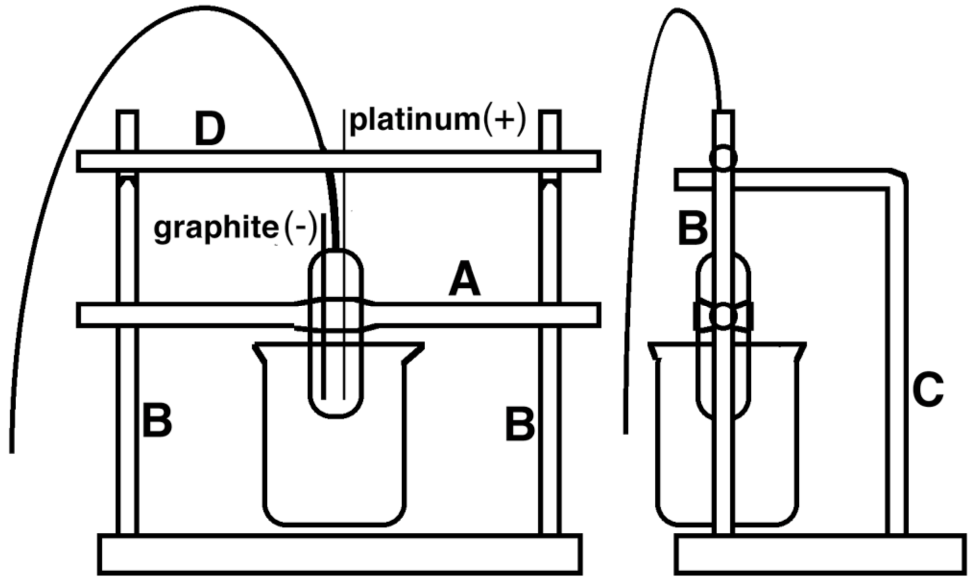

Figure 1. Left: front view; right: side view. A photograph of this device is provided at our ozone website.[3]

Reaction Chamber. The reaction chamber consists of a plastic transfer pipet filled with 3 M H_2SO_4. The stem is stretched into a thin capillary delivery tube prior to filling the bulb with acid. The reaction chamber is constructed from a plastic transfer pipet (thin stem Beral pipet), a piece of mechanical pencil lead, and a length of thin platinum wire at least 5 cm long.

1. Stretch the pipet stem into a delivery tube 30 cm long. Grip 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 (wrap the open end of the pipet around a finger for a better grip), and then pull outward with a firm, steady pull. As the pipet stem is being drawn, it goes from its original diameter to capillary diameter at certain points along the length; that is, the stem is either thin or thick, but never in between. Continue pulling until all of the thick parts are gone. Capillary lengths of 30 cm or more are possible, so that the ozone generated can be delivered some distance away. Cut off the end of the pipet end that was being gripped and did not stretch. It is usually necessary to practice on a few empty pipets as this is somewhat of learned skill. At our ozone website we provide a picture of the pipet being stretched.[3]

2. Next the two electrodes are installed. Both must form an airtight fit through the pipet's bulb. A thumb tack makes a suitable pilot hole for the graphite pencil lead and a stick pin makes a suitable hole for the thinner diameter Pt wire.

3. The reaction chamber is completed by filling it 3/4 full with 3 M sulfuric acid. This is done via a 10 mL syringe equipped with a hypodermic needle. Remove the graphite electrode which has a diameter similar to that of the hypodermic needle and inject the acid. Reinstall the graphite electrode and the reaction chamber is complete.

The reaction chamber will deliver approximately 10 mL gas ($H_2 + O_2 + O_3$) per minute. At this rate, 0.5 mL of water is consumer per hour of use. After just a few hours of use, the level of solution is noticeably lower. Sulfuric acid is not consumed during the electrolysis of water, therefore only distilled water need be added to the pipet reaction chamber to replenish the liquid level. To do this, remove the graphite electrode and inject more distilled water via the syringe, but never exceed 3/4 full. Remove the needle and reinsert the graphite electrode.

Apparatus framework. The apparatus framework that holds the reaction chamber is constructed from six elbow-style soda straws, a 96-well plate, and a beaker as follows.

Straw A. The straw that forms the lower horizontal cross-member (Straw A in Figure 1) has two holes punched through using a paper punch where two vertical straws 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 Figure 2. First cut the slit with a razor, then work the pipet bulb through the slit and ***then*** punch the two holes near 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.)

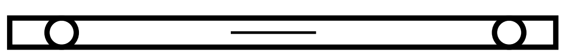

Figure 2. Lower horizontal cross-member.

Straws B, C and D. 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 Figure 1. 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.

Ice bath

The beaker shown in Figure 1 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 will 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

The power supply is connected as shown in Figure 3. The 6-volt setting is optimal and a 6-volt battery can be used as the power supply, although the latter has a short lifetime. Power supplies come with a variety of connectors. The one shown in Figure 3 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. The positive (+) wire is connected to the platinum electrode (anode) and the negative (-) wire is connected to the graphite electrode (cathode.) Two wires with alligator clips on both ends are used to connect the power supply to the electrodes.

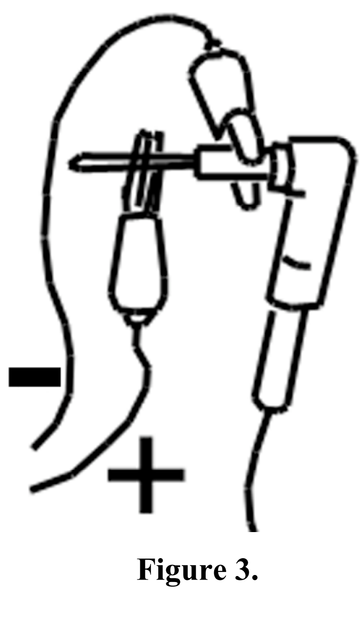

Figure 3.

Electrolysis of Water.

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

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

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

The cathode (graphite) reaction is:

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

The overall major reaction is:

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

and the overall minor reaction is:

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

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.

Note: If the electrodes are connected backwards, the electrolysis reaction does not work and the sulfuric acid solution becomes black from suspended graphite as the graphite electrode slowly disintegrates.

Results.

Food products.

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 (more on this below) and the other was treated with a stream of $H_2/O_2/O_3$ 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.[3]

Table 1. Familiar items exposed to ozone.

Item*	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
Black olive juice	diluted 4 mL juice to 4 mL water	Blackish to yellow in 10 min
Cranberry juice	diluted 2 mL juice to 10 mL water	Red to pink in 34 min
Diet Mtn Dew Code Red	diluted 2 mL juice to 6 mL water	Red to colorless 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 are given at our ozone website.[3]

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 our previous ozone article.[2] 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.

Controls. Using untreated solutions as "controls" contains a design flaw because our assumption was that the ozone was causing the color changes we were observing. In fact, it could well have been the H_2 or O_2 being delivered in much greater quantities. To test this, we built reaction chambers using a palladium wire or a silver wire in place of the platinum wire. When Pd or Ag wires are used, quantities of H_2 and O_2 similar to that obtained from Pt wire are generated but no O_3 is detected by smell after a minute or so of use in the case of Pd and not at all with Ag. This allowed us to expose our control samples to a stream of H_2/O_2 but not O_3. Although we only tried this on a few of the food items listed above (blue food coloring, beet juice, Gatorade, for example), no change in color was detected. Treatment was continued for at least 10 minutes even though the solutions in question would have changed color within much shorter time periods if ozone were present.

Moldy Cheese.

Ozone is able to kill bacteria, algae, spores, fungus, and mold on contact. This was tested with moldy cheese. A blue-gray mold colony approximately 1 cm in diameter and growing on a piece of yellow cheese 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 from 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. Ozone treatment was stopped after one hour, but the results lasted for days: After two days, the untreated mold remained blue and the ozone-treated mold remained cream-white. A photograph of the two chesses samples, side-by-side, is available at our ozone website.[3]

Office paper.

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. We moistened the paper samples before placing them into the test tubes. Exposure times and results are summarized in Table 2. A photograph of a variety of paper samples, side-by-side, is available at our ozone website.[3]

Table 2. Office paper exposed to ozone.

Office paper	Results
Bright pink	Pink turns mostly white within 30 minutes
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
Purple from Chem 13 News cover page	Significantly lighter purple after 35 minutes
Red from Chem 13 News cover page	No significant change after 1 hour
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

Rubber Bands.

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, rubber becomes brittle 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 available at our ozone website.[3]

Starch paper.

Starch paper can be purchased or prepared. To make your own starch paper, prepare a slurry of 1.0 g potato starch in 20 mL distilled water. Heat the slurry over a low flame with continuous stirring until the white slurry becomes suddenly clear (about 1 min). Allow the dissolved starch solution to cool and then add 0.5 g KI dissolved in 3 mL water and stir to mix. Dip strips of office paper in the starch/KI(aq) solution and either allow the papers to dry or use while still wet. Store dried test papers in an airtight sealed bag. In order to use the dry version, first moisten the paper. To test for ozone, hold the moist strip of starch/KI paper in the stream of the ozone coming from the capillary. Ozone will oxidize iodide to iodine, which combines with excess iodide to form the triiodide ion, I_3^-, and forms a blue-black complex with starch (that fades to red-brown with time.)

Wood.

In Youman's 1876 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 effect on wood. At first we tried wooden splints due to their availability in the lab, but no noticeable effect was visible after 1 hour. We surmised this was because of the amount of wood present in splint and the relatively rough surface area. Our second attempt was successful, using paper-thin wood shavings from an ordinary softwood piece of lumber. 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 the wood is available at our ozone website.[3]

Silver.

Youman's 1876 textbook also contains the following passage: *"The most remarkable property of ozone is its powerful oxidizing action. In fact, it is oxygen greatly intensified in activity. It corrodes metals upon which ordinary oxygen could not react, for example, silver…"* To test the reactivity of ozone upon silver, we placed a small sheet of silver in a small beaker covered with Parafilm. One half of the silver was protected from ozone exposure with desk tape. The $H_2/O_2/O_3$ delivery tube was positioned near the silver. Within a few minutes the shiny metallic surface was discolored with a dull gray film, most prominent closest to the delivery tube. After continued exposure, the corner closest to the delivery tube developed a black spot. At this point, half of the tape was removed and the silver was placed in a clean beaker and exposed to just a stream of H_2/O_2 (using the Pd/C generator). The silver was not affected over the same length of exposure time. A photograph of the silver experimental results is available at our ozone website.[3]

Suitability and time required

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.

Equipment required to build an ozone mini-generator: [5]

- five 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 (for example 0.25 mm diameter wire from Aldrich; Part number 26,717-1; Flinn sells platinum wire for $2.70 per inch and 2 – 3 inches would be suitable)
- 100 mL beaker
- scissors
- paper hole punch
- razor blade
- paper clips
- matches
- two connector wires, 20 cm long with alligator clips on both ends
- 6 volt DC power supply from Radio Shack or equivalent (an AC to DC converter can be used)
- 10 mL syringe equipped with a hypodermic needle

Chemicals:

- 3 M H_2SO_4, 3 mL

Hazards

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.

General Safety Precautions

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

Suggested activities.

1. 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.

2. 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.

3. Prepare iodine-starch test paper and test the air in the room and near the ozone generator.

4. 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.

5. 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.

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

Teaching tips.

1. 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.

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

3. Although the amount of ozone being generated is so small and one cannot even detect its 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 (except when we let it run con continuously for 16 hours to determine how far the solution level drops) and we believe that one should not avoid these ozone experiments if a hood is not available.

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. Is it possible to identify the colored component(s) that are 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.

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

4. Ozone is 12 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.

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

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

7. 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?

8. Visit our ozone website to see how ozone reacts with various substances. In all cases ozone is an oxidant and is one of the constituents of photochemical smog.

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

10. 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.

11. Silver has one common oxidation state, Ag^+. Write the reaction that takes place between silver metal and ozone.

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

Endnotes and References:

1. Author to whom correspondence should be addressed. E-mail: xenon@creighton.edu
2. "Laboratory Experiments on the Electrochemical Remediation of the Environment, Part 7. Microscale Production of Ozone"; Ibanez, J. G.; Alatorre-Ordaz, A.; Mayen-Mondragon, R.; Moran-Moran, M. T.; Bruce Mattson, Scot Eskestrand; ***Journal of Chemical Education*** 2005, **82**, 1546-1548.
3. Ozone webpage: http://mattson.creighton.edu/Ozone/Ozone7.html. Our main Microscale Gas website is http://mattson.creighton.edu/Microscale_Gas_Chemistry.html. From there one can click "All Gases" and then "Ozone."
4. ***A Class-book of Chemistry on the Basis of the New System***, Edward Youman, M. D., D. Appleton and Company, New York, 1876, page 220.
5. This equipment and our book can be ordered from a variety of vendors including Educational Innovations (worldwide), Flinn Scientific (US sales only), Fisher Scientific, S17 Science Supplies and Services and Micromole. Part numbers and links to their websites are provided at our microscale gas website, Reference 3 above, and click on "Ordering Gas Stuff."