Teaching unit - Learning about ozone

In collaboration with:

European Geosciences Union — Consello Social Universidade de Vigo — Universidade Vigo

Authors: Juan Antonio Añel Cabanelas and Antonio Cid Samamed.

Basic skills to acquire
- Understand the environment of our planet. - Reflect on the human impact on the environment. - Understand the techniques for monitoring the atmosphere. - Measure, collect data and process it. - Use of new technologies, applications and computer systems.

Objectives
In this teaching unit we will reflect on the following concepts: - understanding of the evolution of air pollution on our planet. - Daily variations of pollution and its anthropogenic sources. - Chemistry of ozone. - Possibilities to measure ozone.

Contents
1. History of the discovery of ozone. 2. Precursors and sources of ozone in the troposphere. 3. Chapman cycle. 4. Temporal cycles of ozone. 5. Ozone measurement. 5.1. Schönbein technique. 5.1.1. Advanced level. 5.1.2. Basic level. 5.2. Current techniques.

Timing
4 classroom hours

Method
Among others, the following strategies may be used for effective learning: - Reading about ozone. - Visit to an air quality measurement station. - Use of small handled ozonometers. - Split the students into working groups to measure ozone and check results with nearby

measurement stations.

Resources
- Video on the traditional Schönbein ozone measurement technique. https://tv.uvigo.es/series/607ff5a3ca40eb00d41e93a3 - Application and software for mobile devices (phones, tablets) and computers: https://github.com/EPhysLab-UVigo/O3METER https://play.google.com/store/apps/details?id=com.apercloud.o3meter&hl=en - Ramírez-González et al. (2020) https://doi.org/10.5194/gc-3-99-2020. - Fabian y Dameris (2014) Ozone in the Atmosphere, Ed. Springer, 137 pp. ISBN: 978-3-642-54098-1.

Evaluation
- Learn about the history of the discovery and measurement of ozone. - Know the structure of the ozone molecule. - Know the reactions that give rise to the formation and destruction of ozone. - Distinguish between tropospheric and stratospheric ozone and the ozone layer. - Identifies different devices and principles of ozone measurement. - It is capable of representing data and time series of ozone concentration. - Identifies the time cycles of ozone concentration. - Knows the safety procedures of the reagents used and the techniques necessary to manufacture ozone paper. - It is able to use the additional software available to measure the concentration of ozone in the strips. - Independently obtains ozone data series using external sources (available at Internet) and is able to compare them with their own measured values.

Contents

1. History of the discovery of ozone

The discovery of ozone (O_3) is attributed traditionally to Christian Schönbein, a Swiss-German chemist, who in 1839 was the first to isolate said gas and name it (ozone is the Greek for “smell”). Previously, in 1785 the Dutch chemist Martinus van Marum had already detected it, but without realizing that it was a previously unnamed gas. However, the ozone (O_3) formula was not determined until 1865.

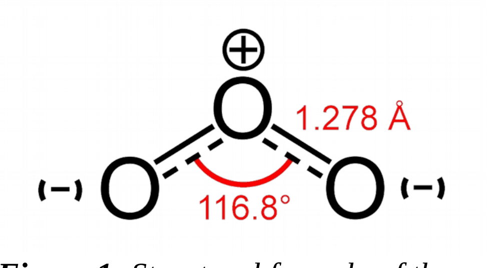

Figure 1: *Structural formula of the ozone molecule. Source: Wikipedia. License: Public Domain.*

For much of the 19th century, ozone was considered a gas with beneficial properties, given that its smell somehow evoked pure environments with clean air. That is why many observatories measuring ozone during this time are related to medical schools and not to meteorological observatories.
Ozone can cause severe damage to health due to its exposure for long periods and in sufficiently high concentrations. Most of the ozone in our atmosphere is found in the stratosphere, and only 10% of the total is located in the lower part of the atmosphere, where we live. Ozone also interacts with ultraviolet radiation. Thanks to this property, in 1920, it was possible to determine the thickness of the so-called "ozone layer" found in the stratosphere.

2. Precursors and sources of ozone in the troposphere

The origin of ozone is biogenic, in the same way as oxygen. However, anthropogenic processes give rise to the formation of ozone precursors.
These processes are emissions from car combustion engines, burning for domestic use (for example, heating that can be coal-fired in some world areas), and emissions from industries. The ozone precursors they give rise to are mainly nitrogen oxides (NOx), carbon monoxide (CO) and volatile organic compounds (VOCs).

The emission of nitrogen oxides can cause the formation of ozone following this mechanism:

$$NO_2 + h\nu\ (\lambda < 420\ nm) \longrightarrow NO + O$$

hv: Planck's constant multiplied by the frequency of the radiation

$$O + O_2 + M \longrightarrow O_3 + M$$

M: air

However, NO and O_3 react with each other very quickly:

$$NO + O_3 \longrightarrow NO_2 + O_2$$

This reaction removes the ozone again. However, CO and VOCs, which are also found among the mixture of precursors, through a set of reactions give rise to the NO that becomes NO_2 without eliminating O_3. Therefore, the initial reaction is the one that dominates the process, resulting in a net increase in ozone concentrations.

3. Chapman Cycle

The Chapman cycle, named after British mathematician and geophysicist Sydney Chapman, who proposed it in 1930, is the process that explains the generation of ozone in the stratosphere of our planet. It is summarized as follows:

$$O_2 + h\nu\ (\lambda < 242\ nm) \longrightarrow O + O$$

hv: Planck's constant multiplied by the frequency of the radiation

$$O + O_2 + M \longrightarrow O_3 + M$$

M: air

$$O_3 + h\nu\ (\lambda < 1.200\ nm) \longrightarrow O + O_2$$

$$O + O_3 \longrightarrow 2O_2$$

4. Temporal cycles of ozone.

As shown by the reactions, the existence of ultraviolet radiation is necessary for the chain of reactions of ozone production to start. That is why tropospheric ozone will have a clear daily cycle, with maximum concentration peaks during the day and minimum concentrations at night. Likewise, it will have a seasonal cycle in the extratropical regions of the planet, with higher values during the summer months and minimum values during the winter months.

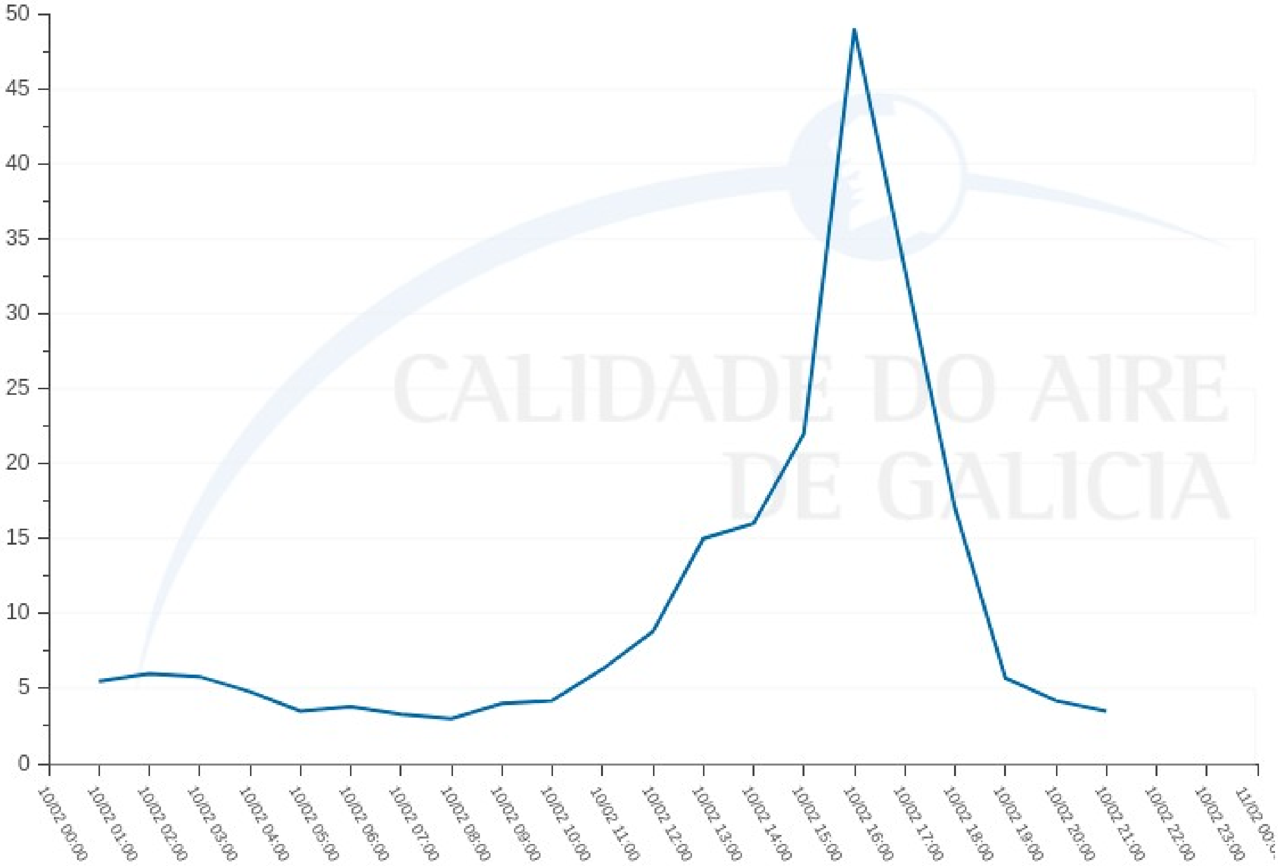

Figure 2: *Daily ozone cycle (µg/m^3). Data: Station Gómez Franqueira (Ourense, Spain) (10/02/2022). Source: MeteoGalicia.*

5. Ozone measurement.

5.1. Schönbein technique.

This technique is named after Christian Friedrich Schönbein (1799-1868), who developed it and discovered O_3. It is a rudimentary method based on strips of paper impregnated with a solution of potassium iodide (KI) and starch ($(C_6H_{10}O_5)n–(H_2O)$) and submerged in distilled water. Several versions of the technique vary in the concentrations of starch, KI, and used paper. As a result of these different concentrations, during the 19th century, they were produced various types of paper strips to measure O3, which had different levels of accuracy. The strips made by Jame de Sedan was traditionally the most widely used because they allowed the greatest accuracy.

Figure 3: *Ozone strip measurement color scale. Values from 1 to 10 (top row) correspond to the Schönbein scale. Values of 1 to 21 (lower row) correspond to the Berigny scale.*

The practice can be done at two levels, one advanced and one basic. The advanced implies, in addition to carrying out the measurements, the manufacture of the paper to carry them out.

5.1.1. Advanced level

Materials
Potasium iodide (KI)
Starch ($C_6H_{10}O_5$)
Drying paper
Distilled water
Self-closing bags

Instruments
Beakers
Scale
Rods
Stove

To make the paper, we follow the instructions of Jame de Sedan, who made one of the most widely used types of measuring paper in the 19th century. For it, we will follow the following six steps (there is a video on the procedure available in the list of resources of this teaching unit):

1. 100 mL of distilled water is poured into a beaker, which is heated up to a temperature of around 80 ºC (it should be checked with a thermometer submerged).
2. 10 g of starch is added to the beaker with stirring until a gelatinous mixture is obtained (taking care not to boil because the resulting chains of polysaccharides could be broken).
3. 1 g of KI is added with stirring until homogeneous.
4. The resulting mixture (see Fig. 5) is allowed to cool in a location shaded from sunlight. When it is cool, the drying paper or filter strips are impregnated with it (for example using a brush or dipping them) for about 6 h and then removed.

Figure 4: *Materials necessary to make the mixture for the measurement paper.*

5. After this, the strips are removed from the solution and allowed to dry horizontally for 2 h (also protected from sunlight and in an environment without O_3 as they are already reactive).
6. When the strips are dry, they are stored in self-closing bags.

Figure 5: *Mixture resulting from the solution of KI and starch in hot distilled water.*

Figure 6: *Strip collected, from which to take the measurement, after being exposed for 24 hours outdoors and immersed in distilled water.*

Once the strips are prepared, the measurements are made. As the strips must be allowed to dry, which cannot happen in a few hours with the traditional technique, it is recommended that the laboratory practice is carried out over two days. The procedure of measurement and data collection is simple. It consists of exposing the strips outdoors, protected from sunlight, for 12 or 24 hours (in this case, 24 hours may be preferable to adapt to the daily teaching schedule). The strip is then collected and moistened with distilled water. After reacting, it changes from white to bluish-purple. The degree of colouration is compared to the given scale (see Fig. 3). Then the students can measure the value and enter it on a blank sheet, which we also provide (see Table 1).

Table 1. Annotation list

Exposure		Collection		Values		
Date	Time	Date	Time	Visual	O3Meter	Observations

5.1.2. Basic level

This level differs from advanced in the manufacture of strips because it avoids the difficulty of access to all materials and part of the necessary laboratory work. There is the option to buy the strips from a supplier (for example, Sigma-Aldrich “Potassium Iodide Starch Paper ref.37215”) and take measurements with them. In this way, even the first-year high-school students could perform the experiments. Fig. 7 compares strips made by us with strips commercially available for highlighting the differences. The remainder of the practice is the same as the advanced level.

Figure 7: *Comparison between the measurement paper strip manufactured following the procedure exposed here (left) with a commercially supplied one (right).*

Figure 8: *(Above) Estefanía Sakharyk Lysyk, a student at the IES Alcántara (Alcantarilla, Murcia, Spain), making the measurement strips in the laboratory. (Bottom) one of the resulting strips exposed to air.*

5.2. Current techniques

Current ozone meters, widely used in air quality monitoring, generally use the ultraviolet absorption method at a wavelength of 254 nm.

The technique consists of passing a pulse of light through an air sample that the device has taken from outside. On the other side of the instrument, a photodiode measures the radiation that arrives after passing through the sample, giving an ozone value based on what has been absorbed.

There are simpler and more affordable meters that can be used for applications in a teaching laboratory whose measurement principle is Gas Sensitive Semiconductor (GSS).

The measurement values are usually given in parts per billion (ppb) or $\mu g/m^3$, thus referring to the amount of ozone in an air sample.

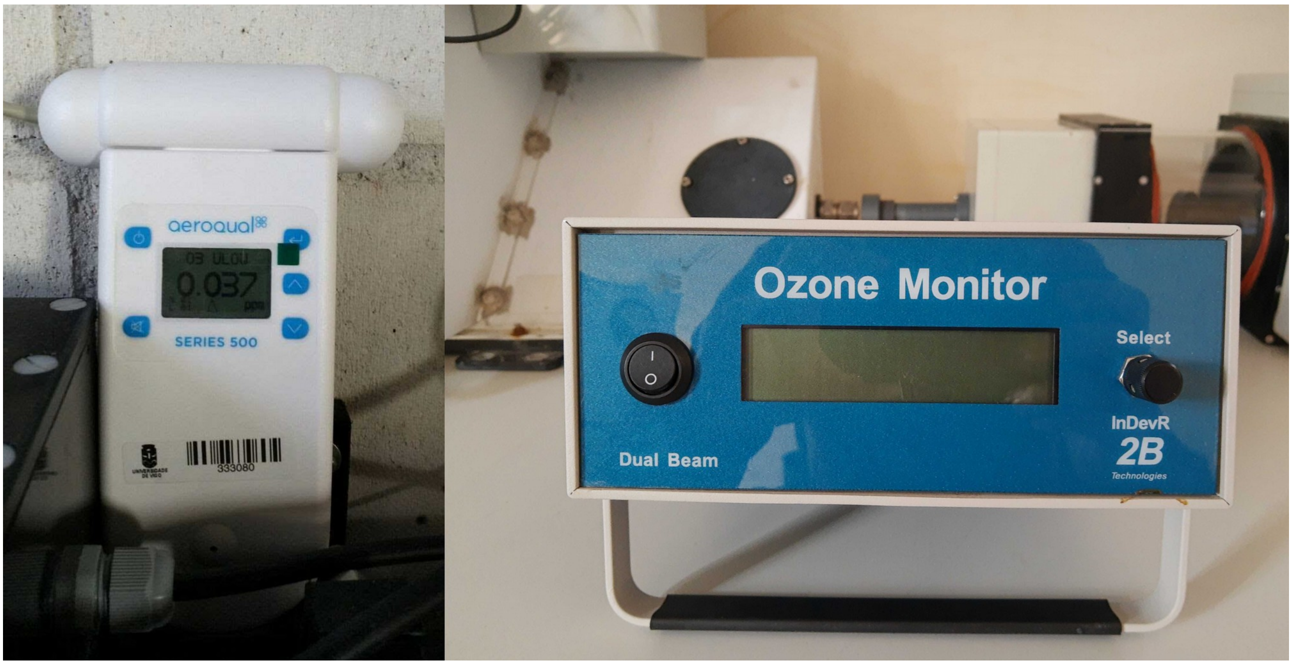

Figure 9: *(Left) gas-sensitive semiconductor measurement ozonometer; (Right) ultraviolet absorption measurement ozonometer.*