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Ozone measurement practice in the laboratory using Schönbein's method

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Abstract. We present a laboratory technique that can be used to measure tropospheric ozone, following a traditional method developed by Christian Friedrich Schönbein in the 19^{th} century. The practice is described with two levels of complexity (the advanced level includes the production in the lab of paper strips as they were produced in the 19^{th} century while the basic level does not), and is suitable for use by both high-school and first-year undergraduate students. The overall aim is to familiarise students with both the scientific methods involved and the related concepts of pollution and ozone. This technique was developed and presented in high schools during a communication campaign to celebrate the annual Galician Scientist Day and based on the detected need for a better understanding of the problems of climate change and pollution. Moreover, we discuss the teaching approach used and the results obtained from surveys and feedback obtained from the students and teachers.

1 Introduction

Usually, the study of the atmosphere at this educational levels and from the practical point of view is focused at best on the use of cheap and small weather stations that measure physical variables (e.g. temperature, pressure, humidity). However the study of the atmosphere and the environment needs of knowledge on its chemical composition. For example, global warming and ozone depletion are issues broadly taught but mostly from a theoretical approach (documentaries, lectures...). That said, this laboratory practice introduces a hands-on approach to the study of the chemical composition of the atmosphere, letting the students be much more familiar with it.

This laboratory practice is intended as an additional tool to assist in the teaching of atmosphere and environment science. Thus it is presented as project-based learning with proven competence, as defended in previous works (Blumenfeld et al., 1991; Bell, 2010). Using this learning method, students developed their skills through "learning-by-doing".

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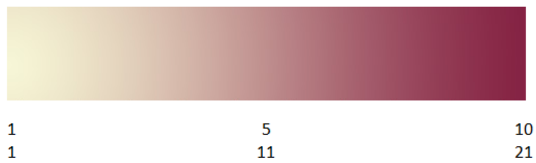

Figure 1. Typical scale used to compare colours using two scales: Schönbein (top line) and Berigny (botton line).

O_3 occurs in gaseous form in the Earth's atmosphere (Fabian and Dameris, 2014; Añel, 2016). An allotropic form of oxygen (O_2) formed by three oxygen atoms, it has a blueish colour, which is only observed when it is found in large concentrations. It is well known for its existence in the famous "ozone layer" of the stratosphere, which protects us from ultraviolet radiation, thanks to the fact that its absorption band is in the ultraviolet spectrum (Hartley Band 200 - 300 nm). However, our work focuses on O_3 in the troposphere, the atmospheric layer closest to the Earth's surface in which all living organisms are found.

This O_3 that surrounds us, and which we breathe, does not offer protection in the same way that the stratosphere does. The difference lies in its ability to act as a powerful oxidant, and in large concentrations it can affect the respiratory systems of living organisms, and alter the coverage and healthiness of vegetation. The proliferation of heavy industry has been liked with increased concentrations of O_3, from average values of 10-15 ppbv in the pre-industrial era to 30-40 ppbv today (Marenco, 1995).

Measurements are possible using Schönbein's method, named after Christian Schönbein, who developed the method and also discovered O_3; his is a rudimentary method based on paper strips impregnated with potassium iodide solution (KI) and starch (($C_6H_{10}O_5$) $_n$- (H_2O)) in distilled water. There are several versions of the method, which vary in the concentrations of starch (($C_6H_{10}O_5$) $_n$- (H_2O)), potassium iodide (KI), and paper used. The precision of the measurements varies considerably as a result of the different concentrations used. Among the different types of paper available, that produced by Jame de Sedan is the most widely used and is recognised as that which allows the greatest precision (Bojkov,1986).

Exposed to the open air but protected from sunlight, the KI of the strip reacts with the O_3 and the humidity in the environment. The strips are exposed for a given time, 12 or 24 hours, after which they must be collected, taken to a laboratory, and dipped in distilled water, which causes them to turn a shade of purple related to the concentration of O_3 present (Bojkov, 1986). By comparison against a given scale (similar to that shown in Figure 1) a numerical value can be obtained. These values were generally recorded as O_3 in the logbooks of observatories as discussed previously (Añel et al., 2012; Linvill et al., 1980).

It is clear that the choice of numerical value from Fig.1 involves a great deal of subjectivity, because it depends on the observer and each one has different physiological features (Solomon and Lennie, 2007). Different people have different abilities to distinguish colours, and the ambient light can also have an effect. Only with experience can an observer reduce the error associated with this subjectivity.

Ozone (O_3) and air quality are generally unfamiliar among students over the age of 11; nevertheless it is a topic that can arouse their interest due to the potential issues involved (Shepardson et al., 2009; Punter et al., 2011). Their knowledge of climate change tends to vary and is often contradictory, and they tend to confuse it with the problem of the ozone layer. One of the reasons for advancing this technique is to expose them to these topics by supplementing their knowledge of scientific methods (Boyes et al., 1995).

We herein present a technique based on Schönbein's method of measuring tropospheric ozone. To make it more accessible to students, we propose two different levels of test. The first could be used by high school students, in which the measurement and its subsequent validation are developed using Schönbein's method. The second is more advanced, and includes the entire process including manufacture and use of the strip. The didactic objectives are to measure O_3, to teach the measurement of environmental pollution to students, and to highlight the difference between subjective and objective measurement. We propose the use of this scientific method to identify these differences. This practice can be used as experience and demonstration of the development work that underpins all scientific activity, allowing the assessment of the work of any scientist to be assessed. The authors are well aware of the existence of an old technical report (Fukushima, 1993) on this topic. We nevertheless propose to take the work a step further by incorporating photos and graphics, performing a survey, developing specific software and a communication campaign, with the clear aim of achieving objective measurements.

We presented the technique to students in ten Galician high schools and at the same time we conducted surveys (243 students) to ask students about their knowledge of general environmental issues such as climate change, pollution, and ozone, and the steps taken to raise awareness of these issues. The age range of the students who responded to the survey was 14-19, with the same gender balance and education system (of the Regional Government) in all the high schools. The survey (which could be completed in person or online) consisted of 19 questions, of which we discuss the five most relevant in terms of the knowledge to be acquired through the use of the technique.

By analysing the responses, we obtained the following results (see Figure 2). Taking each question in turn, "Do you know what climate change is?" received an almost universally positive answer (98,7%); "Do you know how to differentiate between the problem of climate change and the problem of the ozone layer?" resulted in one-third negative answers (31,9%); "Have you ever worried about the problems of air quality in your neighbourhood?" produced the same proportion of responses as the previous question (35,3%); "Are there activities in your area to raise awareness of this issue?" produced three-quarters negative response (75,4%); "Would you like more information about it?" received almost universally positive answers (90,5%).

These results reinforce the idea that students have gaps in their knowledge of these subjects and that they know they have them. It is also clear that they require activities to raise their awareness of them because they know they do not have all the information they need. Hence there is a need to establish this kind of practice in order to meet the needs expressed by students.

In the following sections we discuss the ethical considerations relevants for the work here performed, expose the teaching approach used and the results obtained with it. Finally we extract some conclusions on this experience and the result of the laboratory practice.

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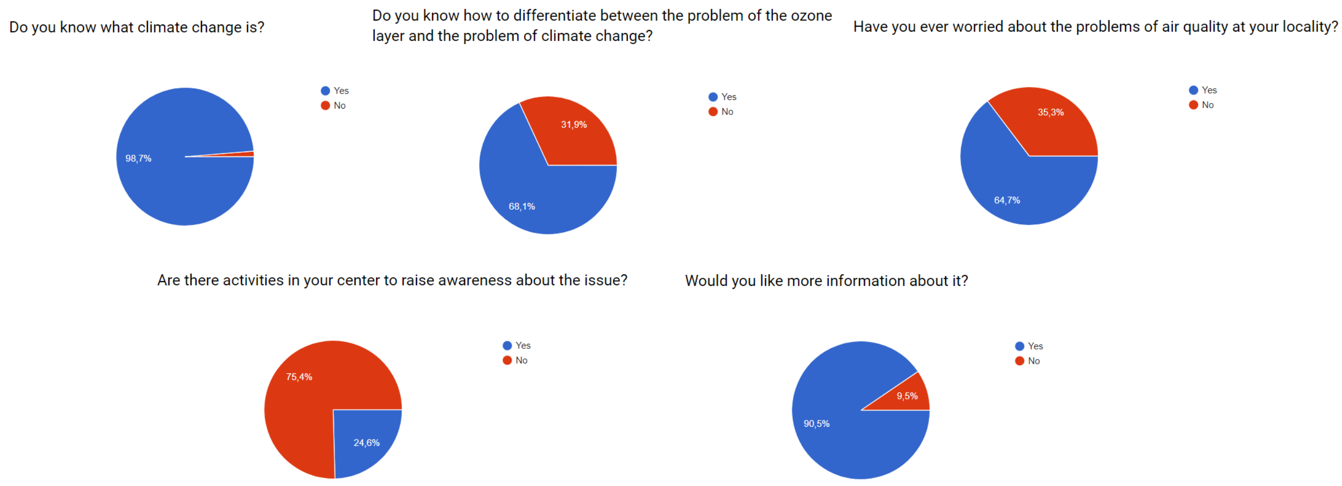

Figure 2. The five most relevant questions related to knowledge acquired through practice: "Do you know what climate change is?" received almost universally positive responses; "Do you know how to differentiate between the problem of climate change and the problem of the ozone layer?" resulted in around one-third negative answers; "Have you ever worried about the problems of air quality in your neighbourhood?" received the proportion of responses as the previous question; "Are there activities in your area to raise awareness of this issue?" produced three-quarters negative response; "Would you like more information about it?" received almost universally positive answers.

2 Ethical considerations

The anonymity of the persons involved in the surveys for this research, both during the development of the project and regarding the preservation and publication of the results were guaranteed. The surveys were collected and processed anonymously. Because of the nature of the experiment, we did not need previous clearance from the commission of ethics of our research centre. It was enough to follow the rules exposed approved by our university. They are available in the document 'Ethical Recommendations in Research by the Universidade de Vigo' (https://www.uvigo.gal/sites/uvigo.gal/files/contents/paragraph-file/2019-06/Ethical_Recommendations_1.pdf).

3 Method

Based on the idea of "learning by doing", project-based learning (PBL) is a student-centered pedagogy that involves a dynamic classroom approach. That means students manage all the activities by ownselfs, gathering information and responding to a complex question, challenge, or problem. In this case, the topic is air quality, focus in ozone.

As an introduction to the activity, a theoretical class is proposed to the students, this is what all the information related to the laboratory practice is presented to them and the distribution of the work.

In the next section, it is explained the laboraty practice itself.

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4 Teaching method

As previously explained, we have created two levels of test, one basic and one more advanced. We will now explain the more advanced one, which also includes the essential elements of the basic version.

4.1 Advanced level

This level of test is designed for high school and first year college students. The following materials are required to conduct the test (Figure 3 shows some of these):
Materials:

– potassium iodide (KI)

– starch (($C_6H_{10}O_5$))

– drying paper

– distilled water

– self-closing bags

Instrumentation

– beakers

– balance

– rods

– stove

To dry the strips, we propose using boxes of any appropriate material, for example cardboard, in which the strips are allowed to dry for twelve hours. They are then stored in airtight bags shaded from sunlight until they are used for the measurements. The strips should be protected from inclement weather and sunlight, therefore the drying box can also be used to display the strips (with the proper protection).

The next stage consists of two parts: making the strips and using then for the measurements. To make the strips, we follow the instructions of Jame de Sedan (these strips were the most widely used throughout the nineteenth century) in different studies.

We use a solution of KI and starch in distilled water, via the following steps:

1. 100 mL of distilled water is poured into a beaker, which is heated up to a temperature of around 80 ºC;

2. 10 grams of starch are 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);

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Figure 3. Instrumentation and materials (potassium iodide (KI), starch (($C_6H_{10}O_5$), rods, beakers, balance and stove)

Annotation List						
Exposure date	Exposure time	Collection date	Collection time	Visual value	App value	Observations

Table 1. Annotation list

3. 1 gram of KI is added with stirring until homogeneous;
4. the mixture is allowed to cool in a location shaded from sunlight. Once it is cool, the drying paper or filter strips are added for about six hours and then removed;
5. , after the strips are removed from the solution and allowed to dry horizontally for two hours (also protected from sunlight and in an environment free from O_3 (it is reactive);
6. once dry these are stored in self-closing bags.

After the manufacturing the strips, the measurements can then take place. Because the strips must be allowed to dry, which cannot happen in just a few hours, it is recommended that the experiments are run over a period of two days.

The procedure for measurement and data collection is very simple. It consists of exposing the strip outdoors, protected from sunlight, for 12 or 24 hours (in this case 24 hours may be preferable due to the timing of the school day). After 24 hours, the strip is wetted with distilled water, which turns it from white to blueish purple. The degree of coloration will be as indicated by the colour of the strip. By comparing the colour of the strip with a given scale (see Figure 1) the students can measure the value and enter it on a blank sheet, which we also provide (see Table 1).

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Figure 4. Example of strips (left: made by ourselves, right: comercial strips)

If time, part of the experiment could involve the students making a series of measurements over a period of time (e.g., two weeks) to allow the strips to be exposed to different atmospheric conditions, which would then highlight the changes in O_3 concentration.

In order to gain a better understanding of the procedure and of ozone measurement in general, it would be desirable to compare the values of O_3 obtained with data from the nearest state-of-the-art ozonometer. This would enable students to understand that although O_3 mixes locally in a very homogeneous manner, there can be considerable differences between different places in the same neighbourhood due to the different factors that affect O_3. It would also allow assessment of the reliability and validity of the method. It is furthermore possible to buy a hand-held ozonometer, which is much cheaper than a fixed ozonometer, to take measurements in situ. For example, the S200, S300, S500 models from Aeroqual (https://www.aeroqual.com/) have been shown to be useful (Lin et al., 2015).

4.2 Basic level

This level differs from the more advanced level in the use of the strips. This part is not used at this level because of the potential difficulty accessing all the materials and the necessary laboratory work behind this. There is an option to buy the strips from a supplier (for example Sigma Aldrich «Potassium Iodide Starch Paper ref.37215») and to perform the measurements using these strips. In this way, even students in the first year of secondary school could carry out the experiments (Figure 4 compares strips made by ourselves with commercially available strips to highlight the differences). The remainder of the technique is the same as it is for the advanced level.

Our own experience suggests that it takes some time to acquire the necessary degree of consistency and accuracy in the measurements. The availability of photographic and computational tools means that it is possible to eliminate all human error in terms of colour choice, and a method free from human subjectivity is thus possible.

To this end, our setup consists of a camera assembly, under controlled light and focal length conditions, and a software package developed to ensure the precision of the result according to the correct shade of colour. The software uses a graduated scale of the whole spectrum that is possible when the strip is used; from this, a pixel-by-pixel scaled comparison algorithm provides an output with a numerical value within that scale (Ramírez-González et al., 2018).

This application (see Figure 5) facilitates the use of the technique by students – in essence all they need is a mobile phone with a camera, a shoebox and a light from a mobile phone, or possibly a torch or some other device with a light bulb (e.g., a second mobile phone with a light). Everything is assembled by placing the strip inside the box, and photographs can be taken through an opening in the box (a second hole is required to allow illumination of the strip by the light source). It is understood that errors of measurement are possible, and there could be some variability in the controlled lighting conditions, but for educational purposes it is also useful and entirely acceptable to discuss these errors. The image obtained is then processed using the software, and objective ozone results can be obtained.

4.3 Discussing the results

After obtaining the results, the students must debate the subjectivity of the measure. As mentioned above, the measure depends very much on the capacity of the observer. Two different observers could see two different shades in the colouration of the strips, and for this reason we propose the following activity after the first 24 hours of the experiment.

Different students would evaluate the colour of the strips and write down the results without discussing them with anyone. These results would then be shared and the difference between the different measures would be debated. To expand on the possibility of different measurements, the observation conditions could be altered (more or less lighting, less observation time, differences when comparing using the given scale). All this information would be noted, and form part of the debate allowing different points of view to be discussed.

It is in this ensuing debate that we would wish students to become familiar with the scientific method (Añel, 2019), where all experiments to be compared must be carried out under the same conditions with some understanding of the attenuation (errors) that accompany each measurement.

5 Results

As previously discussed, we presented the technique in 10 Galician high schools (to more than 350 students) and it was well received.

Figure 6 shows the response to other two important questions. Taking each question in turn, "Are there other activities in your highschool that let you learn about this topic?" received almost three-quarters negative answers."Would you like to know more about this topic?" received nine out ten of positive answers. By the same token, we can asume that there is a lack of activities and that students want more events like this.

We gathered information about the activity from teachers. As an example we include next the comments by one of the teachers from the Pontepedriña highschool.

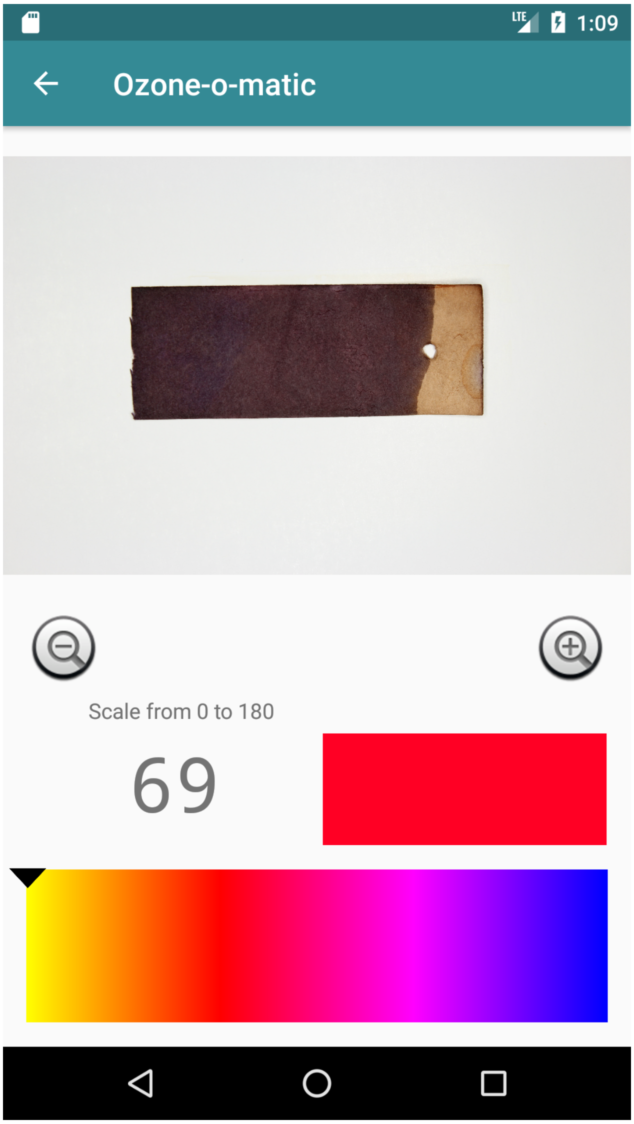

Figure 5. Capture of the output by O3METER

"In general, any activity that is carried out with students and people different from the teaching staff has great value since it reinforces the teacher and the contents that are worked in the classroom.

On the other hand, everything that is experimental or can be seen in some way is better for the students provided it is based on a theoretical basis (normally it is better that it be before the experience, although it can be an incentive to continue researching). If also the experience is simple and playful, then the success of it and the improvement of learning is guaranteed."

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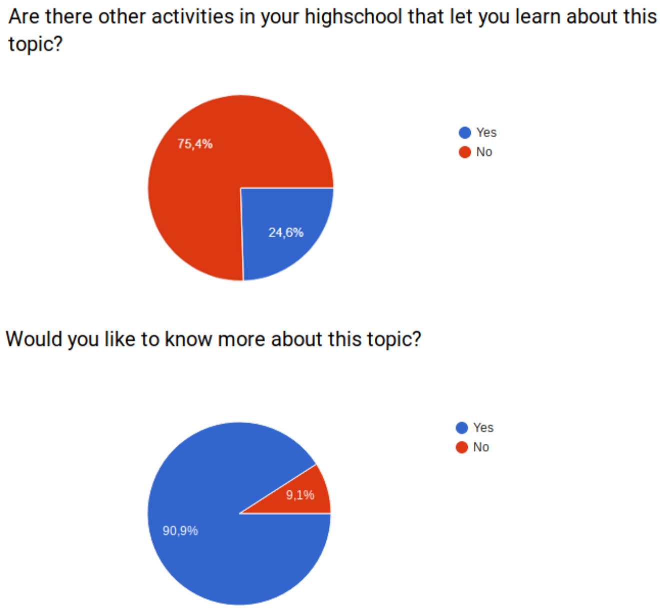

Figure 6. Figure 6. The two most relevant questions related to the interest of students about the laboratory practice and aroused interest.

Figure 7 shows an introductory class in the technique; here it is being presented to high-school students. We witnessed the initial ignorance of the subject that the students had, and the curiosity that was awakened in them when they took part in these exercises. We believe that our success was due to the good disposition of the students, together with the cooperation we enjoyed from the high school staff.

6 Discussion and Conclusions

Our practice has the advantage of being extremely cheap in terms of student / practice ratio. The cost per application ranges between 20 and 30 euros per group of students. The use of low-cost materials and the simplicity of assembly are most attractive when the test is used in the classroom. Most importantly, teachers can follow the instructions and carry out the activity themselves.

This work was presented during the last meeting of the Royal Spanish Society of Physics in the Symposium on Teaching of Physics and some of the attendees approached us, requesting the information necessary to develop this laboratory practice in their highschools. This demonstrates that there are interested in activities like this. A way of seeing close up atmospherics science to students, potential scientists.

This practice allows students to become familiar with the scientific method, with questions of physics and atmospheric chemistry, concepts of atmospheric pollution, and basic meteorology. It also allows them to deepen their knowledge of the

Figure 7. One of the authors presenting the technique to students of Santiago Apostol School in 2017.

history of science, related to the hole in the ozone layer, the development of ways to measure air quality, and the influence of new technologies in measurement, for example.

Having conducted these experiments it is expected that students would have acquired basic knowledge about O_3 (understanding the difference between 'good' and 'bad' ozone, for example), together with an understanding of the scientific method and air quality.

As mentioned above, we have presented the technique to students in 10 Galician high schools (to more than 350 students) and were pleased to see its widespread acceptance. We witnessed the initial ignorance of the subject that students had, and the curiosity that is awakened in them when they develop exercises such as these. We believe its success was due to the good disposition of the students towards new knowledge, together with the cooperation of the high schools themselves.

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