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FINAL DEGREE PROJECT

Degree in Chemical Engineering

ADVANCED CONTRIBUTIONS IN QUALITY CONTROL OF WATER CONSUMPTION

Project report

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Abstract

The present project is composed of two differentiated parts. In the first part, a study is carried out on the validation of the methylene blue method for the detection and quantification of chlorine dioxide present in water. Chlorine dioxide oxidizes leuco-blue methylene reagent, which is colorless, causing it to turn blue. This method is based on the spectrophotometric determination of the direct linear dependence between the absorbance and the chlorine dioxide concentration. When this method is used with real water a precipitate is formed due to the sulfates present in the water that makes impossible the reading in the spectrophotometer. For this reason, two methods are studied and validated to solve this problem: on the one hand, the precipitation of the sulfates is carried out by the addition of barium chloride and, subsequently, a filtration. The second method studied is based on extraction with the solvent 1,2-dichloroethane.

In the second part, a sensory study about geosmin is carried through, where a linear relationship is found between the intensity of the odor as a function of the concentration of geosmin present in the water. This study is carried out by an expert group of panelists in water tasting.

Resumen

El presente trabajo se compone de dos partes diferenciadas. En la primera parte, se ha realizado un estudio sobre la validación del método del azul de metileno para la detección y cuantificación del dióxido de cloro presente en el agua. El dióxido de cloro oxida el reactivo leuco-azul de metileno, que es incoloro, haciendo que se vuelva de color azul. Este método se basa en la determinación espectrofotométrica de la dependencia lineal directa entre la absorbancia y la concentración de dióxido de cloro. Cuando se utiliza con agua real se forma una turbidez debida a la reacción entre el reactivo leuzo-azul de metileno y los sulfatos presentes en el agua, que imposibilita su lectura en el espectrofotómetro. Por este motivo, se han estudiado y validado dos métodos para solucionar este problema: Por un lado se ha realizado la precipitación de los sulfatos mediante la adición de cloruro de bario y, posteriormente, una filtración. El segundo método estudiado se basa en una extracción mediante el disolvente 1,2- dicloroetano.

En la segunda parte, se ha realizado un estudio sensorial de la geosmina, donde se ha encontrado una relación lineal entre la intensidad de olor en función de la concentración de geosmina presente en el agua. Este estudio se ha llevado a cabo mediante un grupo de panelistas expertos en catas de aguas.

Resum

El present treball es compon de dues parts diferenciades. En la primera part, s'ha realitzat un estudi sobre la validació del mètode del blau de metilè per a la detecció i quantificació del diòxid de clor present en l'aigua. El diòxid de clor oxida el reactiu leuco-blau de metilè, que és incolor, fent que es torni de color blau. Aquest mètode es basa en la determinació espectrofotomètrica de la dependència lineal directa entre l'absorbància i la concentració de diòxid de clor. Quan s'utilitza amb aigua real es forma una terbolesa deguda a la reacció entre el reactiu leuco-blau de metilè i els sulfats presents en l'aigua, que impossibilita la seva lectura en el espectrofotòmetre. S'han estudiat i validat dos mètodes per solucionar aquest problema: Per una banda s'ha realitzat la precipitació dels sulfats mitjançant l'addició de clorur de bari i, posteriorment, una filtració. El segon mètode estudiat es basa en una extracció mitjançant el dissolvent 1,2- dicloroetà.

En la segona part s'ha realitzat un estudi sensorial de la geosmina, on s'ha trobat una relació lineal entre la intensitat d'olor en funció de la concentració de geosmina present en l'aigua. Aquest estudi s'ha dut a terme mitjançant un grup de panelistes experts en tastos d'aigües.

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1. Introduction

Water is an essential element for the existence of the life on our planet. Living beings need to consume it continuously to live. In the past, civilizations have located their settlements near geographical areas where there was fresh water, such as lakes and rivers. In this way, they could irrigate their crops, use it for human consumption and as a means of communication.

The humanity has stored and distributed water practically since its origins. When these civilizations evolved and grew extensively, they had to look for different sources of water. They developed systems that allowed them to take advantage of the underground water resources, which led to the first construction of wells.

It is in ancient Greece when the first water collection, purification and distribution systems were developed, which have a certain similarities with those of the present. In addition, they were the first society to have a clear interest in the quality of the water they consumed. For this reason, the water used was removed by means of wastewater systems, as well as rainwater, and aeration reservoirs were used for its purification.

Nowadays, in addition to the processes of disinfection and treatment, it is necessary to make a quality control of the drinking water that is distributed in the network to ensure that it is safe for human consumption. The two characteristics that it have to comply are:

- The absence of substances and microorganisms that are dangerous for consumers.
- The absence of substances that transmit unpleasant sensory sensations, such as color, turbidity, smell and taste.

1.1. Objectives

<u>CHEMICAL ANALYSIS</u>

- Carry out a validation study of the methylene blue method for the determination of chlorine dioxide in water.
- Propose two methods to eliminate the turbidity that is generated when using the methylene blue method with real water.
- Carry out a validation study of the two proposed methods.

SENSORY ANALYSIS

- Determine a linear relationship that relates the odor intensity as a function of the geosmin concentration. This study is carried out by a group of expert panelists in water tasting.

FIRST PART: CHEMICAL ANALYSIS

2. Water disinfection

As explained above, water is a vital element for the human being. For this reason, it is important that the water that is supplied in the consumption networks goes through a series of treatments and controls to ensure its quality and cannot harm our health.

The water, until it becomes potable, passes through a series of stages. Disinfection is one of them. Chlorine and chlorine dioxide are two of the most commonly used compounds in this stage.

2.1. Chlorine

Chlorine is one of the most common elements for water disinfection. It is soluble in water and is one of the most reactive elements, forming unions with other elements very easily.

The chlorine molecule is produced by the union of two chlorine atoms by chemical or electrolytic oxidation. This is usually achieved by electrolysis of seawater or salt rocks. The salt pans, which are formed by the salts that are dissolved in the sea water, are sent to electrolytic cells of great electrical power. Chlorine ions are transformed into chlorine atoms thanks to electricity. At the cathode is sodium hydroxide and hydrogen gas and, at the anode, hydrogen gas. The cathode and the anode have to be separated because the hydrogen gas reacts aggressively with the chlorine gas.

Chlorine is a very reactive element, so that it forms compounds with other elements quickly. It also has the particularity of forming unions with substances that normally do not react between them.

The present study focuses on the application of chlorine for water disinfection. Chlorine is a very practical and effective compound for the disinfection of pathogenic microorganisms in water. It can be easily used, measured and controlled.

Chlorine kills pathogens, such as bacteria and viruses, breaking the molecular chemical bonds. For example, in the case of enzymes, when it comes in contact with chlorine, it replaces one or several hydrogen atoms its molecule with one of chlorine, causing the transformation or breakage of the molecule and, subsequently, its death. Below it can see the disinfection mechanism:

$$Cl_2 + H_2O \leftrightarrow HClO + Cl^- + H^+ \qquad \textbf{(Eq. 2.1)}$$

$$HClO + H_2O \leftrightarrow H_3O^+ + ClO^- \qquad \textbf{(Eq. 2.2)}$$

$$ClO^- \leftrightarrow Cl^- + O \qquad \textbf{(Eq. 2.3)}$$

When chlorine is added to water, hypochlorous acid is formed, which is electrically neutral. Hypochlorous acid decomposes into electrically negative hypochlorite ions, which in turn decompose into chlorine and oxygen atoms. The disinfection properties of chlorine in water are based on the oxidation power of free oxygen atoms and on the substitution reactions of chlorine.

As the cell wall of pathogenic microorganisms is negatively charged, hypochlorous acid, being a neutral compound, can enter in the cell. Once inside the cell, the hypochlorous acid reacts to the hypochlorite ion and, this, to the chlorine ion. Once the chlorine ion is obtained, it can substitute the hydrogens of the enzymes for chlorine ions, achieving death or inhibition the cellular activity.

The water have to be at a certain pH as, at basic pH, the hypochlorite ion is formed directly and it cannot enter in the interior of the cell as effectively as the hypochlorous acid does. The optimum pH is from 5,5 to 7,5.

The amount of chlorine that have to be supplied in the water for its disinfection is conditioned by the amount of organic matter present in the water, the temperature, the PH and the contact time. For the elimination of bacteria, a low amount of chlorine is required, around 0,2-0,4 mg / L. It should be noted that the concentration of chlorine added is usually higher, due to the great solubility of chlorine in water.

2.2. Chlorine dioxide

Chlorine dioxide is an effective disinfectant at low concentrations. It is a synthetic gas that is not generated naturally in the environment. It has a yellowish-green color and an irritating smell similar to chlorine. It is a small and volatile molecule. Chlorine dioxide is an unstable gas that dissociates into chlorine and oxygen molecular. In addition, sunlight oxidizes it to form chloride, hypochlorite ion and chlorate.

Chlorine dioxide has a high solubility in water, especially at low temperatures, approximately 10 times more than chlorine. When it comes into contact with water it remains like a gas dissolved in solution. Chlorine dioxide can be removed by aeration or by using carbon dioxide. It is an explosive and unstable compound.

Chlorine dioxide has a large number of uses although, currently, it is more commonly used as a bleaching. Chlorine dioxide has the advantage that it generates less harmful byproducts than chlorine. It is also used for the sterilization of medical and laboratory equipment, surfaces, rooms and utensils. It is a very strong oxidant that efficiently kills fungi, bacteria and viruses. It is also used as a disinfectant and pesticide.

As an oxidant it is very selective, allowing it to attack the electron-rich center of the organic molecules. In this way, an electron is transferred and the chlorine dioxide is reduced to chlorite ion, (ClO_2^-). Compared to chlorine and ozone, a smaller amount of chlorine dioxide is required to produce an effective disinfectant concentration.

The treatment of drinking water is the main application of chlorine dioxide as a disinfectant. The disinfection process is based on oxidation, reacting with substances that produce electrons. Unlike chlorine, which is based on the replacement of hydrogen with chlorine, chlorine dioxide reacts with the amino acids and the RNA of the cell, attacking the cell structure or the acids present inside the cell and preventing the formation of proteins. Chlorine dioxide is more effective in viruses than ozone or chlorine and, in addition, organisms cannot become resistant to it.

Some of the disadvantages of using chlorine dioxide as a disinfectant instead of chlorine are:

- It is an explosive and unstable compound.
- In contact with solar radiation, it decomposes.
- Less effective in the disinfection of rotaviruses and E.Coli bacteria.
- The byproducts generated, such as chlorides and chlorates, can be a problem for patients with dialysis problems.
- Production is more expensive, 5 to 10 times more than chlorine.

3. Analytical methods for the determination of chlorine dioxide

3.1. Iodometric method

The iodometric method is probably the most method used to measure oxidizing species in aqueous solutions. In this method, the iodide ion is oxidized to iodine, which in turn is titrated with a solution of sodium thiosulfate ($Na_2S_2O_3$). In addition, the reactivity of the iodide ion depends on the pH at which the sample is adjusted at the time of titration. The reactions are described in the following equations:

$$Cl_2 + 2I^- \leftrightarrow I_2 + 2Cl^- \quad \text{pH 7} \qquad \text{(Eq. 3.1)}$$

$$2ClO_2 + 2I^- \leftrightarrow I_2 + 2ClO_2{}^- \quad \text{pH 7} \qquad \text{(Eq. 3.2)}$$

$$2ClO_2 + 10I^- + 8H^+ \leftrightarrow 5I_2 + 2Cl^- + 4H_2O \quad \text{pH 2} \qquad \text{(Eq. 3.3)}$$

$$ClO_2^- + 4I^- + 4H^+ \leftrightarrow 2I_2 + Cl^- + 2H_2O \quad \text{pH 2} \qquad \text{(Eq. 3.4)}$$

$$ClO_3^- + 6I^- + 6H^+ \leftrightarrow 3I_2 + Cl^- + 3H_2O \quad \text{pH2} \qquad \text{(Eq. 3.5)}$$

At a neutral pH, chlorine and chlorine dioxide react with the iodide ion, while the chlorite ion and the chlorate ion do not react. At an acid pH, all species (chlorine dioxide, chlorine, chlorite ion and chlorate ion) react with the iodide ion. Finally, at a basic pH, only chlorine dioxide reacts.

3.2. Colorimetric methods

Colorimetric methods for the detection of chlorine dioxide are based on the reaction between chlorine dioxide and a dye. There are two types of colorimetries: the direct colorimetry, when the sample dyes of a color, and the inverse colorimetry, when the color disappears of the sample.

To carry out this type of methods, the following considerations have to be taken into account:

- Due to the lack of knowledge of the reaction kinetics, absorbance measurements should be carried out at different time periods to determine the estimated time at which the reaction stabilizes.

- Absorbance readings have to be performed at the wavelengths corresponding to the maximum absorbance of the spectrum of a certain substance.

The main colorimetric methods studied so far are described below.

3.2.1. N, N’-diethyl-p-phenylenediamine (DPD) method

DPD is a chemical compound that oxidizes with the presence of chlorine, acquiring a violet color. It is a direct colorimetry since, as the concentration of chlorine increases, so does the absorbance.

This method was developed for the determination of free chlorine and, subsequently, it was adapted for the measurement of chlorine dioxide. Therefore, chlorine can be an interference in the measurement of chlorine dioxide. To avoid this, glycine is added, which masks free chlorine. Aspects to take into account for the use of this method:

- The optimum pH of the DPD reagent is between 6,2 to 6,5.
- The maximum absorbance of the resulting solution is obtained at 515 nm or at 555 nm.
- The interferences of this method include oxidized manganese, monochloramine, chlorite, and chromate ions. Manganese and chromate ion can be masked by using ethyelenediamine tetraacetic acid (EDTA).
- It is important that the spectrophotometric measurements are taken after the same period of time after mixing since the color varies with time.

In addition to the above, it have to be taken into account that the reagent in solution is not stable.

Finally, it should be noted that the DPD method is a very popular method and is widely used despite these deficiencies. This method works well to measure free chlorine, but the measured concentrations of chlorine dioxide are inaccurate. For this reason, the use of the DPD method is not recommended for the measurement of chlorine dioxide.

3.2.2. Lissamine Green B (LGB) method

This reagent was studied due to its high reduction potential, + 1,0 V, which is high enough to eliminate most of the interferences. These measurements were made at pH 9,0. The results obtained indicated that the reduction potential of chlorine dioxide was similar to the reduction potential of the LGB reagent, while the potential of the possible interferences was less. To eliminate possible interferences, an ammonia/ammonium chloride buffer was added, which reacts with the chlorine to form the chloramines, with no interference expected from them. Manganese dioxide and oxidized iron species were not shown as an interference in the measurement of chlorine dioxide.

Some of the advantages of this method are:

- The color that is produced is stable. This allows mixing the sample with LGB at the sampling point and measuring the absorbance in the laboratory.
- The method is relatively simple and pretreatment of the sample is not necessary.

Finally, it was found that there was interference when the ammonia / ammonium chloride buffer was added in a certain range of concentrations.

3.2.3. Amaranth method

This method corresponds to a reverse colorimetry, based on the discoloration of the amaranth. The absorbance is measured at 522 nm, obtaining a linear response in the concentration range of 0,1 to 1,0 mg/L.

The minimum interferences observed correspond to the presence of chlorite, monochloramine, chlorate ions and iron (III). Significant interference with oxidized manganese was also observed. It was found that the use of ammonia/ammonium buffers eliminated the interference of free chlorine.

3.2.4. Acid chrome violet potassium salt method

This method is also about an inverse colorimetry. In this case, no interferences were observed due to the presence of free or combined chlorine. On the other hand, ozone does react with the reagent in question. However, this is not a significant problem because chlorine dioxide and ozone react with each other.

The main problem of this method is based on the complex preparation of the reagent and its possible instability.

3.2.5. Clorophenol red method

In this method, the determination of chlorine dioxide is based on a reverse colorimetry. The reaction is immediate and stable over time, but free chlorine can be a considerable interference. By the addition of glycine, forming chloramine, the presence of free chlorine is masked.

3.2.6. Methylene blue method

Methylene blue is a blue dye, in its oxidized form, or colorless, in its reduced form. This method is based on a direct colorimetry, therefore, the concentration and absorbance are directly proportional. The reagent used is leuco-methylene blue, which is colorless. This reagent is produced by adding stannous chloride to methylene blue, which is reduced. When the leuco-blue of methylene comes into contact with the chlorine dioxide, it is oxidized again to methylene blue, recovering the characteristic blue color of this one.

This method is the one that will be studied in the analytical part of this project.

3.3. Spectrophotometry fundamentals

Spectrophotometry is one of the most commonly used methods of chemical analysis in the actuality. It is based on the relationship between the absorption of light by a compound and its concentration. If a beam of monochromatic light is incised on a homogeneous medium, a part of this light is absorbed by the medium and another part is emitted. The amount of radiant energy absorbed is the absorbance of the substance.

3.3.1. Lambert-Beer law

The Lambert-beer law is the combination of the Lambert law and the Beer law. These laws establish the following:

- Lambert law: Dstablishes that when a monochromatic light passes through a homogeneous medium, the decrease in intensity of the incident light beam is proportional to the thickness of the medium.

$$\frac{P}{P_0} = e^{-kb} \qquad \textbf{(Eq. 3.6)}$$

Where:

  - P_0 = intensity of the incident light.
  - P = intensity of the light emitted.
  - b = length or thickness of the medium.
  - k = constant depending on the nature of the solute, the wavelength of the incident light, the thickness of the absorbent medium and the nature of the medium.

- Beer law: The intensity of a monochromatic light beam decreases exponentially as the concentration of the absorbing substance increases, when this beam passes through a homogeneous medium

$$\frac{P}{P_0} = e^{-kc} \qquad \textbf{(Eq. 3.7)}$$

Where:

- P_0 = intensity of the incident light.
- P = intensity of the light emitted.
- c = solution concentration.
- k = constant depending on the nature of the solute, the wavelength of the incident light, the thickness of the absorbent medium and the nature of the medium.

The combination of these two laws gives rise to the following equation:

$$A = log\left(\frac{P_0}{P}\right) = a \cdot b \cdot c = -log(T) \qquad \textbf{(Eq. 3.8)}$$

Where:

- a = absorptivity.
- b = length or thickness of the medium.
- c = solution concentration.
- T = transmittance.
- A = absorbance.

4. Methodology

4.1. Material and reagents

Material:

- 25 mL, 50 mL, 100 mL, 250 mL and 1 L Flasks.
- Pipettes.
- Spatula.
- Dropper.
- Magnetic stirrer.
- Beakers.
- Balance.
- Spectrophotometer UV/VIS diode array 8453. Hewlett Packard.
- 5 cm^2 cuvette.
- Erlenmeyer flasks.
- Separating funnels.
- Funnels.
- 10 mL graduated cylinder.
- Automatic stirrer.
- Filter paper.
- Filter for chromatography, 0,45 µm of pores, filter material: PET.
- Wash bottle.

Reagents:

- Methylene blue dissolution of 20 mg/L concentration. To prepare 250 mL of this dissolution, add 25 mg of methylene blue in a 250 mL flask and dilute to the mark with distilled water.
- Stannous chloride dyhidrate dissolution of 0,5 mol/L concentration. To prepare 50 mL of this dissolution, add 5,64 g of stannous chloride dyhidrate in a 50 mL flask. When it have been added 25 mL of distilled water, add 5 mL of hydrochloric acid to acidy the dissolution and help to dissolve the stannous chloride dyhidrate. Finally, dilute to the mark with distilled water.
- Hydrochloric acid.
- Chlorine dioxide sample, received weekly due to the instability of this compound in the water, with a concentration that varies from 0,5 g/L to 1,5 g/L.
- Bleach.
- Chloroform.

- 1, 2-dichloroethane.
- Hexane.
- Diethyl ether.
- Barium chloride dihydrate. To prepare 1 L of this dissolution, add 25,5 g of barium chloride dihydrate in a 1L flask and dilute to the mark with distilled water.

4.2. Preliminary tests

The only source of information on the methylene blue method is an article, which is detailed in the bibliography, in addition to the previous work by Xavier Aldazabal in his final degree project ''Aportacions avançades en el control de qualitat de l'aigua potable. Vessant d'anàlisi química i sensorial'' (UPC, 2017). For this reason, a series of preliminary tests are carried out to define the analytical procedure of the methods, which are the following:

- Stability of the patterns.
- Determination of the compound that causes turbidity in the patterns with tap water.
- Use of different filters for the precipitation method.
- Interference from barium chloride.
- Use of different solvents for the extraction method.

First, the leuco-methylene blue reagent is prepared. Steps to follow:

1. Add 20 mL of methylene blue dissolution in a 100 mL flask.
2. Add 3 mL of stannous chloride dyhidrate.
3. Dilute to the mark with distilled water.
4. Shake for 60 minutes, approximately, until the blue color just disappears.

4.2.1. Stability of the patterns

When a pattern is prepared it is observed that it has a blue color characteristic of the reaction between chlorine dioxide and methylene blue. In the following study, it is verified whether the absorbance of a pattern is stable over time, by reading the absorbance of a pattern at different times.

Steps to prepare the pattern:

1. Add 6 mL of leuco-methylene blue in a 50 mL flask.
2. Add the necessary mL of chlorine dioxide.
3. Dilute to the mark with distilled water.
4. Shake.
5. Read the absorbance in the spectrophotometer.

Table 1. Absorbance variation over time. Preliminary test.

Time (min)	Absorbance
1	0,0607
2	0,0603
3	0,0492
4	0,0427
5	0,0422
6	0,0354

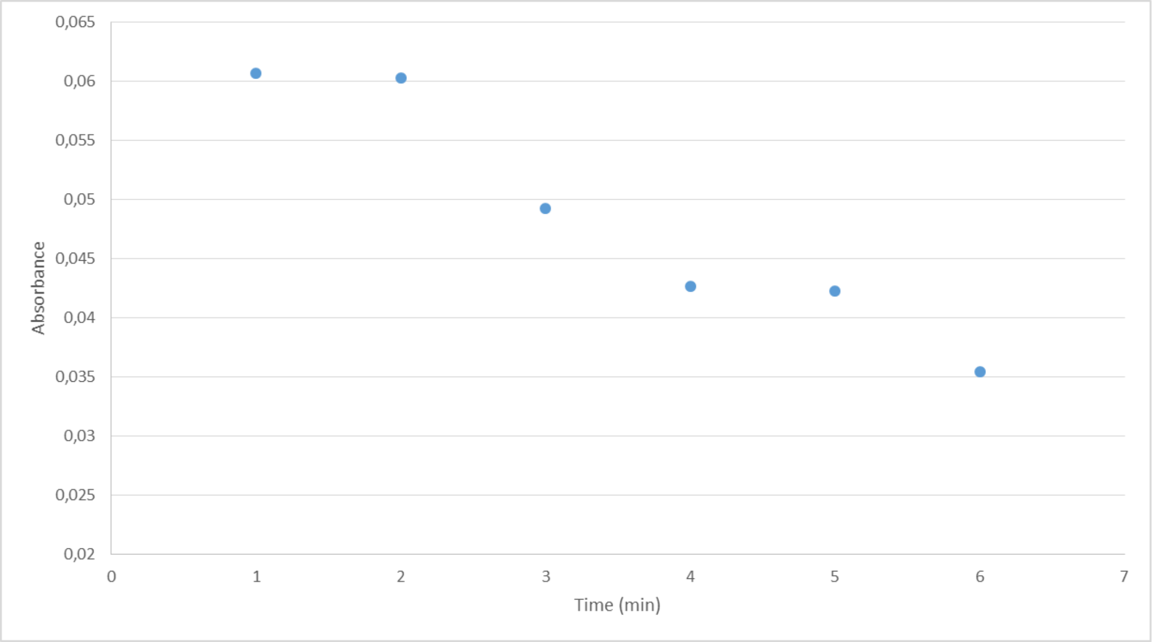

Figure 1. Absorbance variation over time. Preliminary test.

From the previous graph, it can be verified that the absorbance of a pattern decreases as time passes. Therefore, it is necessary to determine a time to read the absorbance of each pattern and, in this way, ensure that all absorbance readings are in the same conditions. The time that is defined is 3 minutes.

4.2.2. Determination of the compound that causes turbidity in the patterns with tap water

Xavier Aldazabal, in his TFG ''Aportacions avançades en el control de qualitat de l'aigua potable. Vessant d'anàlisi química i sensorial'' (UPC, 2017), he could verify that when a pattern of chlorine dioxide is prepared with tap water, a certain turbidity appears. This turbidity is due to the reaction of the leuco-methylene blue reagent with some substance present in the tap water. Xavier found that this turbidity was due to potassium sulfate. To prove it, he prepare some patterns with different substances presents in the tap water, which are the following: Potassium hydrogen carbonate, potassium chloride, potassium nitrate and potassium sulfate. He also prepared two more patterns, one with tap water and the second with distilled water. All the patterns were prepared with the leuco-methylene blue reagent and a certain amount of chlorine dioxide.

He read the turbidity of each pattern to find the compound responsible for the turbidity present in the patterns prepared with tap water. The following table summarizes the results obtained.

Table 2. Turbidity. Source: TFG Xavier Aldazabal.

Compound	Turbidity
Distilled water	2,97
Tap water	28,1
Potassium hydrogen carbonate	3,10
Potassium chloride	3,15
Potassium nitrate	3,20
Potassium sulfate	16,4

As can be appreciated from the above table, all the solutions showed a certain turbidity, due to the reaction of the leuco-methylene blue reagent with the chlorine dioxide. But it should be noted that, the turbidity that most resembles that of tap water is that of potassium sulfate. The others are more similar to the pattern prepared with distilled water. Therefore, the compound to be eliminated from the patterns that are prepared with tap water is the potassium sulfate.

4.2.3. Use of different filters for the precipitation method

Filters to study:

- Glass-fiber filter paper (diameter: 70 mm) between 1 and 2 microns of pore.
- Syringe with a filter for chromatography of 0,45 µm of pores.

Two patterns of 0,364 mg/L and 0,728 mg/L are prepared. All experiments are prepared in 50 mL flasks.

First, prepare a blank by adding 6 mL of leuco- methylene blue reagent in a 50 mL flask and dilute to the mark with distilled water. The experiments carried out with the different filters are:

1. Pattern with distilled water, with a chlorine dioxide concentration of 0,364 mg/L. Add 6 mL of leuco- methylene blue reagent and dilute to the mark with distilled water.
2. Pattern with distilled water, with a chlorine dioxide concentration of 0,728 mg/L. Add 6 mL of leuco- methylene blue reagent and dilute to the mark with distilled water.
3. Pattern with tap water, with a chlorine dioxide concentration of 0,364 mg/L and filtering with a glass-fiber filter paper.
4. Pattern with tap water, with a chlorine dioxide concentration of 0,364 mg/L and filtering with a syringe with a filter for chromatography of 0,45 µm of pores.
5. Pattern with tap water, with a chlorine dioxide concentration of 0,728 mg/L and filtering with a glass-fiber filter paper.
6. Pattern with tap water, with a chlorine dioxide concentration of 0,728 mg/L and filtering with a syringe with a filter for chromatography of 0,45 µm of pores.

Steps to prepare the patterns with distilled water:

1. Add 6 mL of leuco-methylene blue in a 50 mL flask.
2. Add the necessary mL of chlorine dioxide.
3. Dilute to the mark with distilled water.
4. Shake.
5. Wait 3 minutes.
6. Read the absorbance in the spectrophotometer.

Steps to prepare the patterns with tap water:

1. Take a sample of tap water.
2. Add the necessary ml of barium chloride to form the precipitate of sulfates.
3. Decant for 15 minutes.
4. Add 6 mL of leuco-methylene blue in a 50 mL flask.

5. Add the necessary mL of chlorine dioxide.
6. Dilute to the mark with the previous tap water, filtering it previously with the corresponding filter.
7. Wait 3 minutes.
8. Read the absorbance in the spectrophotometer.

Table 3. Use of different filters for the precipitation method.

Experiment number	Type of filter	$[ClO_2]_{expected}$(mg/L)	$[ClO_2]_{obtained}$ (mg/L)	Relative error (%)
1	-	0,364	0,378	3,98
2	-	0,728	0,886	21,75
3	Glass-fiber filter paper	0,364	0,533	46,65
4	Syringe with a filter for chromatography of 0,45 µm of pores.	0,364	0,398	9,48
5	Glass-fiber filter paper	0,728	0,812	11,58
6	Syringe with a filter for chromatography of 0,45 µm of pores.	0,728	0,894	22,9

In Table 3, it is observed that the best results are obtained with the syringe with filter for chromatography of 0.45 µm of pores. Therefore, it is the filter that is chosen to be used in the precipitation method.

4.2.4. Interference from barium chloride

It wants to study if the addition of barium chloride interferes in the determination of the chlorine dioxide concentration of a pattern.

First, three patterns with a known concentration of chlorine dioxide are prepared. The procedure is:

1. Add 6 ml of leuco-methylene blue reagent in a 50 ml flask.
2. Add the necessary ml of chlorine dioxide.
3. Dilute to the mark with distilled water.
4. Wait 3 minutes.
5. Read the absorbance.

Then, six other patterns are prepared by combining the chlorine dioxide concentrations of the three previous patterns. The procedure is:

1. Add 6 mL of leuco- methylene blue reagent in a 50 mL flask.
2. Add the necessary mL of chlorine dioxide.
3. Dilute to the mark with tap water.
4. Add different amounts of barium chloride: 0,5, 0,6, 1 or 2 mL.
5. Wait 3 minutes and filter with a syringe with filter for chromatography of 0,45 µm of pores.
6. Read the absorbance.

Table 4. Interference from barium chloride.

Pattern	$[ClO_2]_{expected}$ (mg/L)	$[ClO_2]_{obtained}$ (mg/L)	Relative error (%)
With distilled water	0,182	0,185	1,65
With distilled water	0,364	0,433	18,96
With distilled water	0,728	0,859	17,99
With tap water + 0,6 mL of barium chloride	0,182	0,216	18,68
With tap water + 0,6 mL of barium chloride	0,364	0,448	23,07
With tap water + 0,6 mL of barium chloride	0,728	0,878	20,60
With tap water + 0,5 mL of barium chloride	0,364	0,466	28,02
With tap water + 1 mL of barium chloride	0,364	0,427	17,30
With tap water + 2mL of barium chloride	0,364	0,477	31,23

From the previous table, it is observed that the relative error is approximately 20%, except in the addition of an excess of barium chloride (2 ml) which increases the relative error. Therefore:

- For tap water with a conductivity lower than 500 µS/cm: Add 0,5 mL of barium chloride.
- For tap water with a conductivity greater than 500 µS/cm: Add 1 mL of barium chloride.

4.2.5. Use of different solvents for the extraction method

A series of extractions with different solvents are carried out to find the one that transfers the methylene blue to the organic phase. The solvents to be studied are: Chloroform, Hexane, diethyl ether and 1,2-dichloroethane.

The procedure to follow is:

1. Add 6 mL of leuco-methylene blue in a 50 mL flask.
2. Add the necessary mL of chlorine dioxide.
3. Dilute to the mark with distilled water.
4. Shake.
5. Wait 3 minutes.
6. Pour the previous solution into a separating funnel.
7. Add 10 mL of the solvent to study.
8. Start the automatic agitator.
9. This section is done differently for extractions in which the organic phase is present in the top of the separating funnel or is presented under.

9.1. Extractions in which the organic phase is presented in the top of the separating funnel:
    - Deposit the inorganic phase in a 50 mL flask.
    - Deposit the organic phase in a 25 mL flask, using a funnel and a filter paper.

9.2. Extractions in which the organic phase is presented under of the separating funnel:
    - Deposit the organic phase in a 25 mL flask, using a funnel and a filter paper.

10. Repeat steps 7, 8 and 9 in order to transfer all the methylene blue from the aqueous phase to the organic phase.
11. Dilute to the mark with the solvent.
12. Read the absorbance in the spectrophotometer.

RESULTS OBTAINED

Extraction with chloroform

Chloroform has not transferred the methylene blue to the organic phase. Figure 2 shows that the organic phase does not have the blue color characteristic of methylene blue.

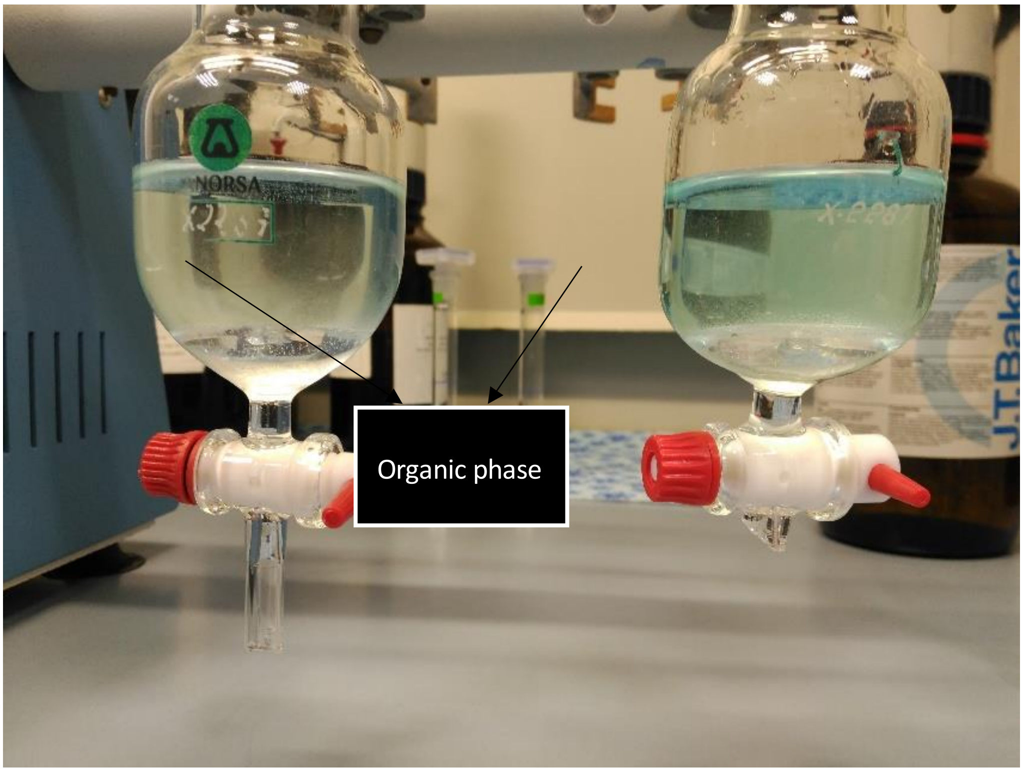

Figure 2. Extraction with chloroform.

Extraction with hexane

Hexane has not transferred the methylene blue to the organic phase. Figure 3 shows that the organic phase does not have the blue color characteristic of methylene blue.

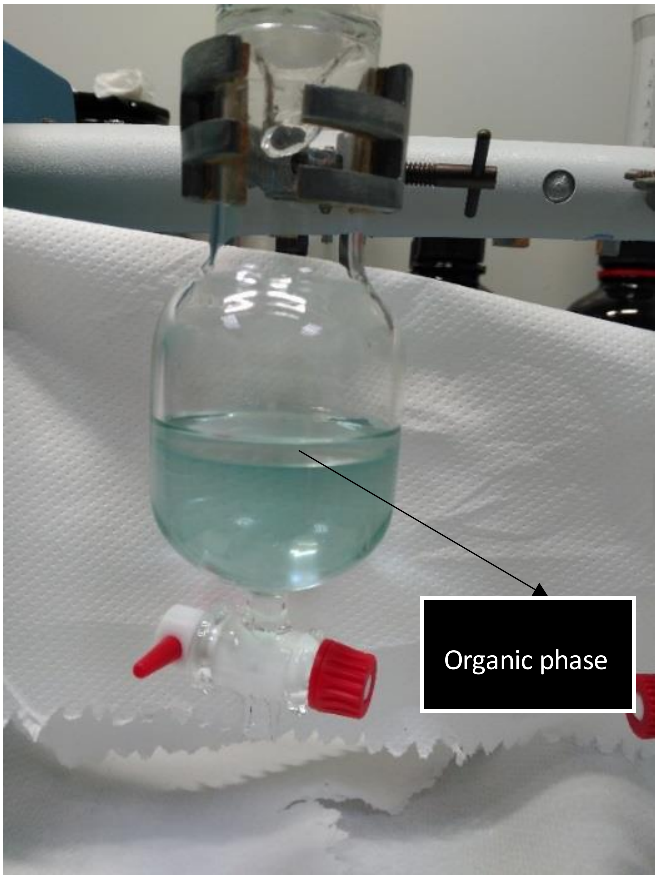

Figure 3. Extraction with hexane.

Extraction with diethyl ether

Diethyl ether has not transferred the methylene blue to the organic phase. Figure 4 shows that the organic phase does not have the blue color characteristic of methylene blue.

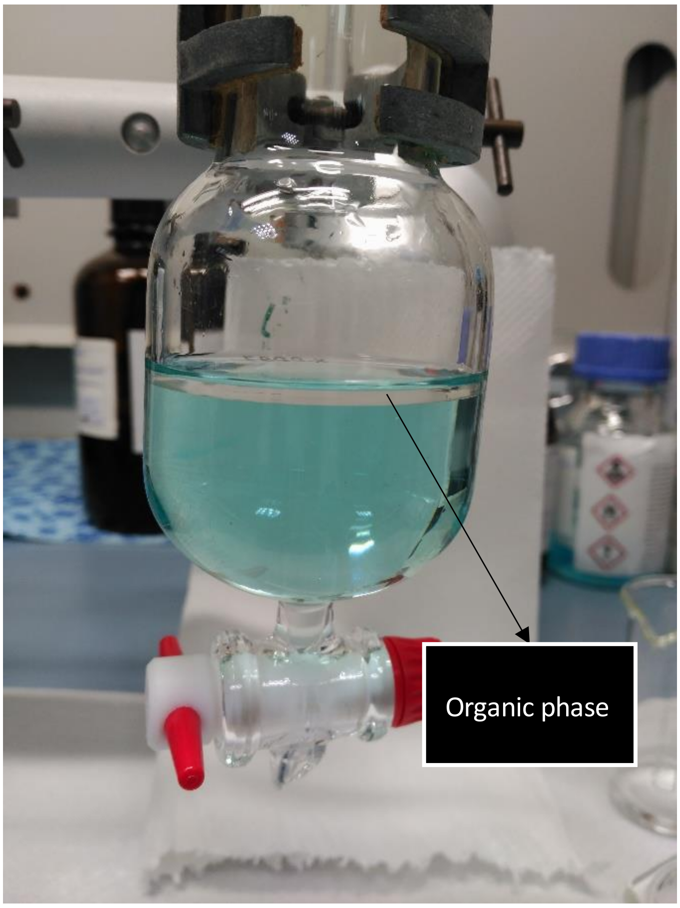

Figure 4. Extraction with diethyl ether.

Extraction with 1,2- dichloroethane

Finally, the solvent 1,2-dichloroethane has transferred the methylene blue to the organic phase. Below it can see a series of figures showing that the organic phase has the blue color characteristic of methylene blue.

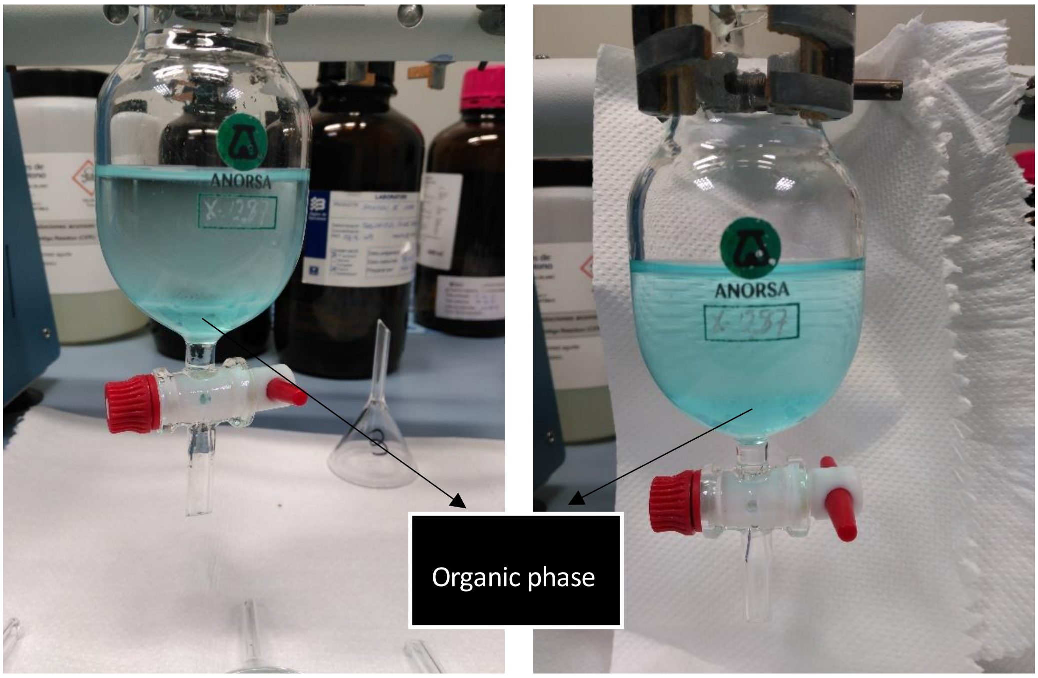

Figure 5. Extraction with 1,2- dichloroethane.

After the tests carried out with the different types of solvents, the 1,2-dichloroethane is chosen to make the extraction because it is the only solvent that transfers the methylene blue to the organic phase.

4.3. Analytical procedure

In previous studies, it has been found that the methylene blue method works with the exception of the patterns prepared with tap water because a turbidity is formed due to potassium sulfates, which makes it impossible to read the absorbance in the spectrophotometer. To solve this problem, two methods are proposed. The first method to be proposed is to precipitate said sulfates, with barium chloride, and then filter the sample with a syringe with a filter for chromatography of 0,45 µm of pores. The second method proposed is an extraction by 1,2-dichloroethane. For each method, the calibration line have to be made with the method used and, therefore, there cannot be a single calibration line that is valid for both methods.

Method 1: Precipitation of sulfates

The precipitation of the sulfates is achieved by the addition of barium chloride. The method used is the one carried out in Aigües de Barcelona, which indicates that 1 mL of the barium chloride solution precipitates 100 mL of sulfates per liter (SO42-) in 100 mL of sample. The amount of barium chloride added depends on the conductivity of the tap water:

- For tap water with a conductivity below than 500 µS/cm: Add 0,5 mL of barium chloride.
- For tap water with a conductivity greater than 500 µS/cm: Add 1 mL of barium chloride.

First the calibration line is made, in which the patterns with tap water are read. A series of patterns are prepared, with a known chlorine dioxide concentration, ranging from 0 mg/L to 1,5 mg/L. The procedure that is carried out is:

1. Add 6 mL of leuco-methylene blue in a 50 mL flask.
2. Add the necessary mL of chlorine dioxide.
3. Dilute to the mark with distilled water.
4. Shake.
5. Wait 3 minutes.
6. Pour the previous solution into a beaker.
7. Filter.
8. Read the absorbance in the spectrophotometer.

The first spectrophotometer reading is the blank (0 mg/L of chlorine dioxide), which is prepared exactly as the patterns except the second point. In addition, the absorbance readings in the spectrophotometer are carried out in order of increasing chlorine dioxide concentration to reduce the reading error.

Four calibration lines are made in order to verify if the lines that are obtained are similar from each other and, thus, it does not have to perform a calibration line every time that it wants to read a pattern. The procedure to follow in the preparation of a pattern with real water is:

1. Add 6 mL of leuco-methylene blue in a 50 mL flask.
2. Add the necessary mL of chlorine dioxide.
3. Add tap water.
4. Add 0,5 mL of BaCl2 or 1 mL, depending on the conductivity.
5. Dilute to the mark with tap water.
6. Shake.
7. Wait 3 minutes.
8. Pour the previous solution into a beaker.

9. Filter.
10. Read the absorbance in the spectrophotometer.

Method 2: Extraction with 1,2-dichloroethane

First the calibration line is made, in which the patterns with tap water are read. A series of patterns are prepared, with a known chlorine dioxide concentration, ranging from 0 mg/L to 1,5 mg/L. The procedure that is carried out is:

1. Add 6 mL of leuco-methylene blue in a 50 mL flask.
2. Add the necessary mL of chlorine dioxide.
3. Dilute to the mark with distilled water.
4. Shake.
5. Wait 3 minutes.
6. Pour the previous solution into a separating funnel.
7. Add 10 mL of 1,2-dichloroethane.
8. Start the automatic agitator.
9. Deposit the organic phase in a 25 mL flask, using a funnel and a filter paper.
10. Repeat steps 7, 8 and 9 in order to transfer all the methylene blue from the aqueous phase to the organic phase.
11. Dilute the volumetric flask with 1,2-dichloroethane.
12. Read the absorbance in the spectrophotometer.

The first spectrophotometer reading is the blank (0 mg/L of chlorine dioxide), which is prepared exactly as the patterns except the second point. In addition, the absorbance readings in the spectrophotometer are in increasing order of chlorine dioxide concentration, in order to reduce the reading error.

Four calibration lines are made in order to verify if the lines that are obtained are similar from each other and, thus, it does not have to perform a calibration line every time that it wants to read a pattern. The procedure to prepare a pattern with real water is the same as that explained above.

5. Results

5.1. Absorbance variation

In a previous studies, it has commented that the blue color of the patterns disappears with the time. For this reason, it has studied the variation of absorbance over time for the two methods.

5.1.1. Precipitation of sulfates

A pattern is prepared, with a chlorine dioxide concentration of 0,45 mg/L, and the absorbance is read for one hour. The results obtained are reflected in the following table and graph.

Table 5. Absorbance variation. (Method: Precipitation of potassium sulfates).

Time (min)	Absorbance
1	0,4560
2	0,4517
3	0,4484
4	0,4454
5	0,4414
6	0,4361
7	0,4243
8	0,4162
9	0,3963
10	0,3897
11	0,3823
12	0,3777

13	0,3706
14	0,3693
15	0,3525
20	0,3131
25	0,3033
30	0,2733
35	0,2523
40	0,2294
45	0,2113
50	0,1920
55	0,1771
60	0,1583

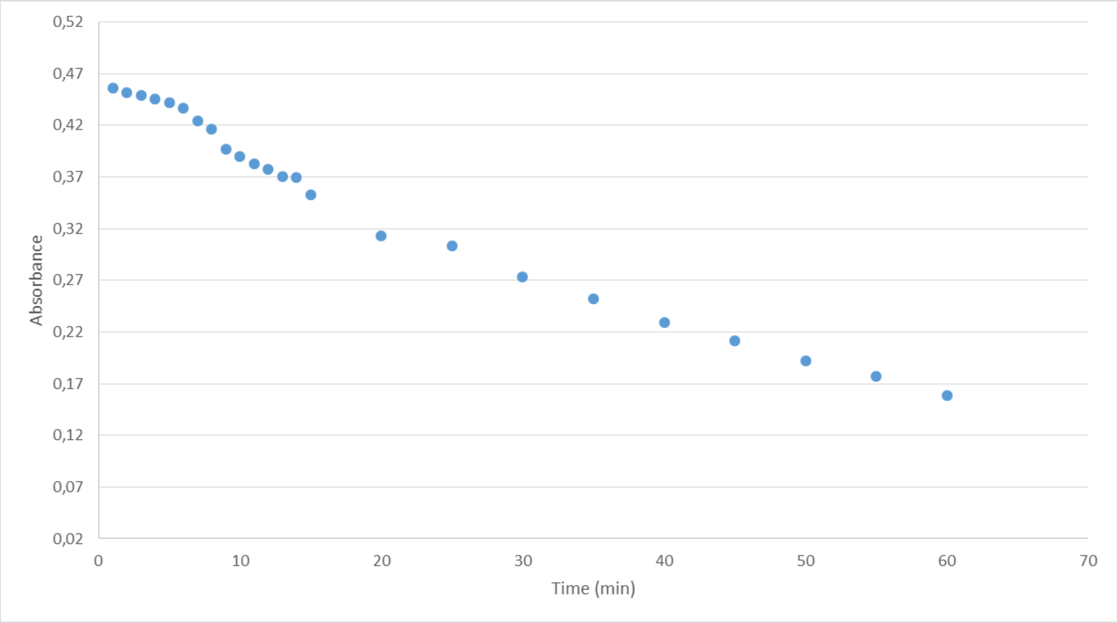

Figure 6. Absorbance variation. (Method: Precipitation of sulfates).

The absorbance decreases as time passes, for this reason it has to choose a time in which, once the pattern is prepared, proceed to read its absorbance since, otherwise, the absorbance readings would not be equivalent.

The time chosen to read the absorbance of each pattern is 3 minutes.

5.1.2. Extraction with 1,2-dichloroethane

A pattern is prepared, with a chlorine dioxide concentration of 0,6 mg/L, and the absorbance is read for an hour and a half. The results obtained are reflected in the following table and graph.

Table 6. Absorbance variation. (Method: Extraction with 1,2-dichloroethane).

Time (min)	Absorbance
10	0,7111
15	0,7173
20	0,7241
30	0,7255
40	0,7376
50	0,7440
60	0,7469
75	0,7619
90	0,7637

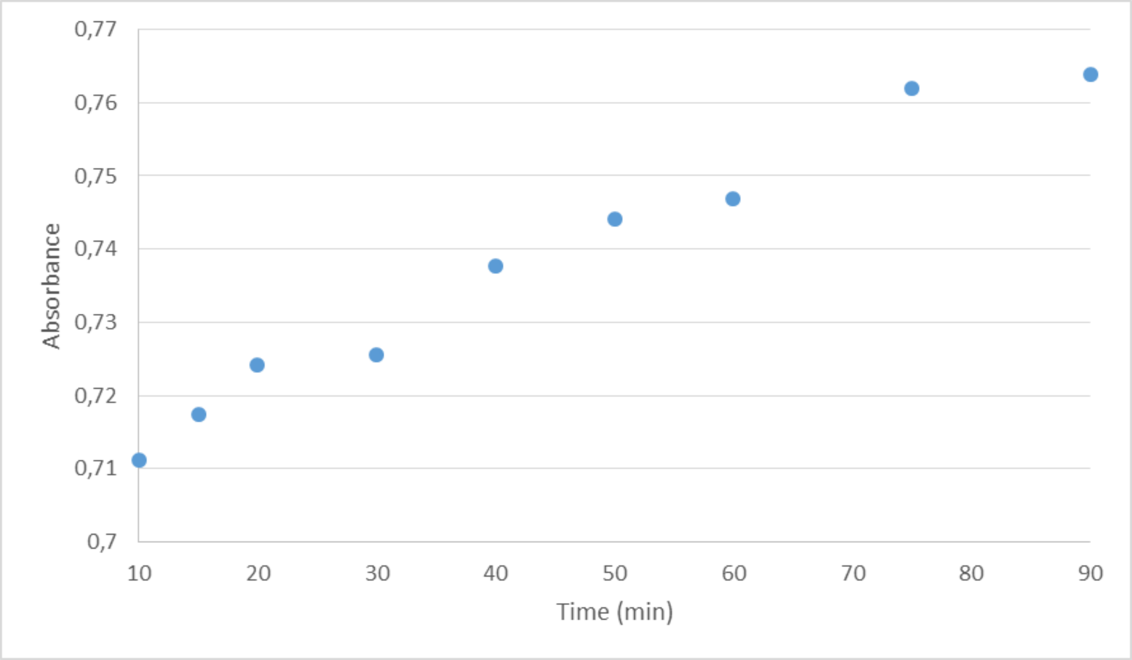

Figure 7. Absorbance variation. (Method: Extraction with 1,2-dichloroethane).

In the graph, it can see how the absorbance increases, in a non-significant way, over time, since it does not even increase one tenth after an hour and a half. Therefore, it is considered that for the extraction method with 1,2-dichloroethane, the absorbance remains constant as time passes.

5.2. Reproducibility tests

5.2.1. Precipitation of sulfates

Four calibration lines are made, with different patterns, in order to verify if it resembles each other.

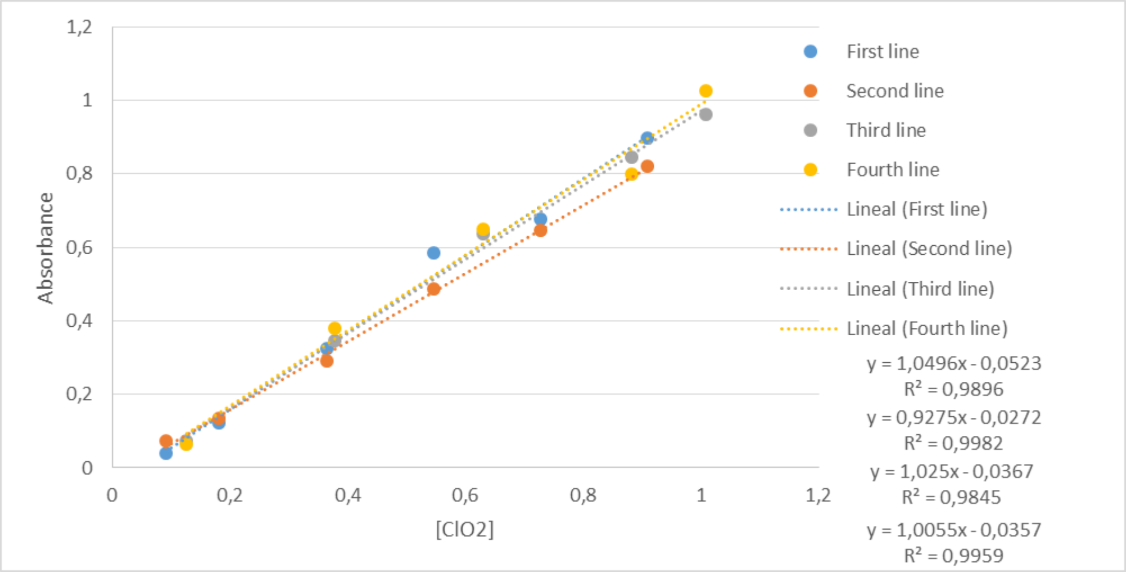

Figure 8. Calibrated lines. (Method: Precipitation of potassium sulfates).

In the Figure 8 it can see the four calibration lines, the linear regression for each of them and its corresponding equation of the line. It can be observed how the lines resemble each other since the slope and the ordinate at the origin are similar in the four cases. Therefore, it is not necessary to make a calibration line every time it wants to read a pattern with real water and, in addition, it is valid to use the average equation to calculate the chlorine dioxide concentration. The equation is:

$$[ClO_2] = \frac{Absorbance+0,0379}{1,0019} \qquad \textbf{(Eq. 5.1)}$$

To confirm that the calibrated lines are reproducible, is calculated the error that would be made in the case of calculating the chlorine dioxide concentration for an absorbance of 0,64 between the lines that differ most from each other, which are the second and fourth lines.

Table 7. Reproducibility test error. (Method: Precipitation of sulfates).

Line	Slope	Ordinate	$[ClO_2]$ (mg/L)	Absolute error	Relative error (%)
2	0,9275	-0,0272	0,719	0,0473	6,58
4	1,0055	-0,0357	0,672	0,0473	7,05

Since the error is very small, approximately 7%, the use of equation 5.1 is valid for the determination of chlorine dioxide from the absorbance of a pattern.

5.2.2. Extraction with 1,2-dichloroethane

Four calibration lines are made, with different patterns, in order to verify if it resembles each other.

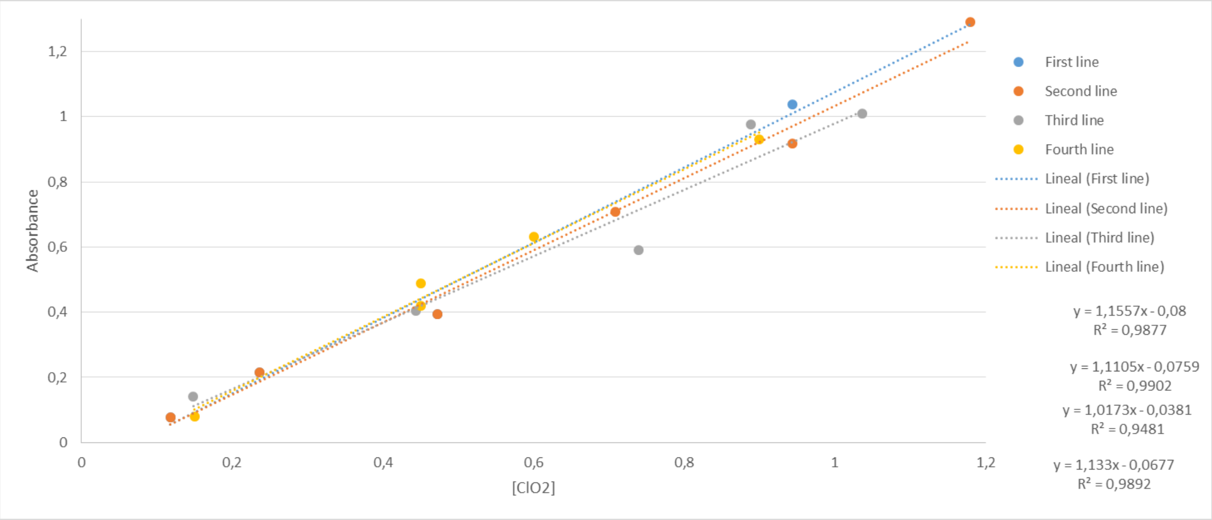

Figure 9. Calibrated lines. (Method: Extraction with 1,2-dichloroethane).

In the Figure 9 it can see the four calibration lines, the linear regression for each of them and its corresponding equation of the line. It can be observed how the lines resemble each other since the slope and the ordinate at the origin are similar in the four cases. Therefore, it is not necessary to make a calibration line every time it wants to read a pattern with real water and, in addition, it is valid to use the average equation to calculate the chlorine dioxide concentration. The equation is:

$$[ClO_2] = \frac{Absorbance + 0,065425}{1,104125} \qquad \textbf{(Eq. 5.2)}$$

To confirm that the calibrated lines are reproducible, is calculated the error that would be made in the case of calculating the chlorine dioxide concentration for an absorbance of 0,64 between the lines that differ most from each other, which are the second and fourth lines.

Table 8. Reproducibility test error. (Method: Extraction with 1,2-dichloroethane).

Line	Slope	Ordinate	[ClO_2] (mg/L)	Absolute error	Relative error (%)
1	1,1557	-0,08	0,623	0,0436	6,99
3	1,0173	-0,0381	0,667	0,0436	6,54

Since the error is very small, approximately 7%, the use of equation 5.2 is valid for the determination of chlorine dioxide from the absorbance of a pattern.

5.3. Interference study

A series of tests are carried out to check whether the presence of free chlorine in the water interferes in the determination of chlorine dioxide of a pattern.

5.3.1. Precipitation of sulfates

5.3.1.1. With distilled water

Bleach is used, with an approximate concentration of 37 g/L. The concentration of the commercial bleach bottle may vary. The main reason is because the chlorine is unstable and the manufacturer cannot guarantee that the concentration does not decrease after the packaging. For this reason, the concentration of free chlorine present in each dilution is read by means of the colorimetric method with DPD, which is the procedure standardized by the laboratory of Aïgues de Barcelona.

Three solutions are prepared with a lower chlorine concentration than the present in the bleach. Therefore, a first dilution 1:250 is prepared, where an approximate chlorine concentration of 148 mg/L is obtained. From this, three more dilutions are prepared, which are the dilutions that are used for the preparation of the different patterns.

- **Dilution 1:** Add 6 mL of the 148 mg/L dilution in a 1 L flask. Dilute to the mark with distilled water. The concentration of free chlorine that is obtained is 0,54 mg/L.
- **Dilution 2:** Add 12 mL of the 148 mg/L dilution in a 1 L flask. Dilute to the mark with distilled water. The concentration of free chlorine that is obtained is 0,94 mg/L.
- **Dilution 3:** Add 20 mL of the 148 mg/L dilution in a 1 L flask. Dilute to the mark with distilled water. The concentration of free chlorine that is obtained is 1,83 mg/L.

Table 9. Interference study. Method: precipitation of sulfates (with distilled water).

$[ClO_2]_{expected}$ (mg/L)	$[Cl_2$ free$]$ (mg/L)	Absorbance	$[ClO_2]_{obtained}$ (mg/L)	Absolute error	Relative error (%)
0,252	0	0,2472	0,2846	0,0326	12,95
0,504	0	0,4424	0,4794	0,0245	4,87
1,008	0	0,9836	1,0196	0,0116	1,15
0	0,54	0,0105	0,0483	0,0483	-
0	0,94	0,0092	0,0470	0,0470	-
0	1,83	0,0109	0,0487	0,0487	-
0,252	0,54	0,2463	0,2837	0,0317	12,59
0,252	0,94	0,2426	0,2800	0,0280	11,12
0,252	1,83	0,2673	0,3046	0,0526	20,90
0,504	0,54	0,4942	0,5311	0,0271	5,38
0,504	0,94	0,4838	0,5207	0,0167	3,32
0,504	1,83	0,4724	0,5093	0,0053	1,06
1,008	0,54	0,9830	1,0189	0,0109	1,09
1,008	0,94	0,9845	1,020	0,0125	1,24
1,008	1,83	0,9980	1,0340	0,0260	2,58

From Table 9 it can be verified that the presence of free chlorine does not interfere in the chlorine dioxide concentration. In addition, it can see how the relative error is less as the chlorine dioxide concentration increases. Then, it can see a graph showing that, for each case, the concentrations are quite similar, regardless of whether it contains only chlorine, a mixture of chlorine and chlorine dioxide, or only chlorine dioxide. Besides, it is observed that for patterns that only contain free chlorine, the absorbance is practically zero.

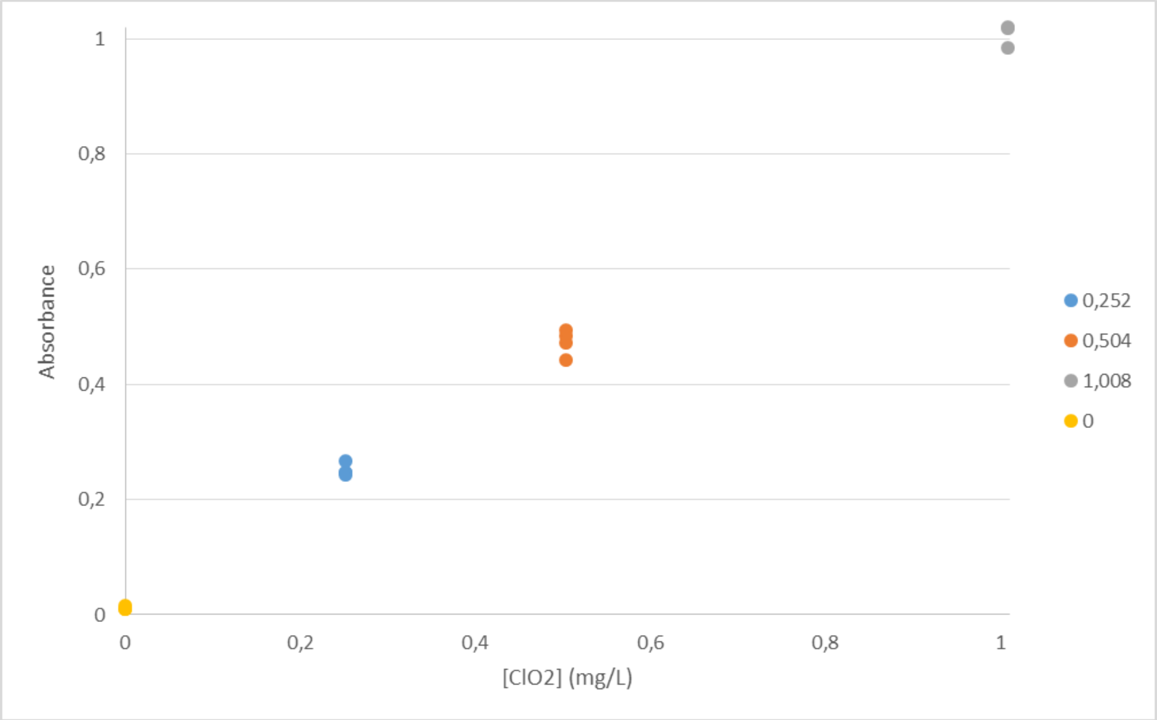

Figure 10. Interference study. Method: precipitation of sulfates (with distilled water).

5.3.1.2. With tap water

Bleach is used, with an approximate concentration of 37 g/L. The concentration of the commercial bleach bottle may vary. The main reason is because the chlorine is unstable and the manufacturer cannot guarantee that the concentration does not decrease after the packaging. For this reason, the concentration of free chlorine present in each dilution is read by means of the colorimetric method with DPD, which is the procedure standardized by the laboratory of Aïgues de Barcelona.

In this case, the dilutions are filled with tap water, which has a conductivity of 997 µS/cm and a free chlorine concentration of 0,46 mg/L. Since the method used is the precipitation of sulfates, it have to add a certain amount of barium chloride. The conductivity is 997 µS/cm, therefore, 1 ml of barium chloride is added.

Three solutions are prepared with a lower chlorine concentration than that present in the bleach. Therefore, a first dilution 1:250 is prepared, where an approximate chlorine concentration of 148 mg/L is obtained. From this, three more dilutions are prepared, which are the dilutions that are used for the preparation of the different patterns.

- **Dilution 1:** Add 6 mL of the 148 mg/L dilution in a 1 L flask. Dilute to the mark with tap water. The concentration of free chlorine that is obtained is 1,25 mg/L.

- **Dilution 2:** Add 12 mL of the 148 mg/L dilution in a 1 L flask. Dilute to the mark with tap water. The concentration of free chlorine that is obtained is 1,59 mg/L.
- **Dilution 3:** Add 20 mL of the 148 mg/L dilution in a 1 L flask. Dilute to the mark with tap water. The concentration of free chlorine that is obtained is 2,36 mg/L.

Table 10. Interference study. Method: precipitation of sulfates (with tap water).

$[ClO_2]_{expected}$, (mg/L)	$[Cl_2$ free], (mg/L)	Absorbance	$[ClO_2]$ $_{obtained}$ (mg/L)	Absolute error	Relative error (%)
0,252	0	0,2528	0,2901	0,0381	15,15
0,504	0	0,4271	0,4641	0,0398	7,91
1,008	0	0,9764	1,0123	0,0043	0,43
0	1,25	-0,0497	-0,0118	0,0118	-
0	1,59	-0,0424	-0,0045	0,0045	-
0	2,36	-0,0210	0,0167	0,0167	-
0,252	1,25	0,1674	0,2049	0,0470	18,68
0,252	1,59	0,1896	0,2271	0,0248	9,86
0,252	2,36	0,2743	0,3116	0,0596	23,67
0,504	1,25	0,4654	0,5024	0,0015	0,31
0,504	1,59	0,4501	0,4870	0,0169	3,35
0,504	2,36	0,4499	0,4868	0,0171	3,39
1,008	1,25	1,0299	1,0657	0,0577	5,73
1,008	1,59	0,9831	1,0191	0,0111	1,10
1,008	2,36	0,9917	1,0276	0,0196	1,95

From Table 10 it can be verified that the presence of free chlorine does not interfere in the chlorine dioxide concentration. In addition, it can see how the relative error is less as the chlorine dioxide concentration increases. Then, it can see a graph showing that, for each case, the concentrations are quite similar, regardless of whether it contains only chlorine, a mixture of chlorine and chlorine dioxide, or only chlorine dioxide. In addition, it is observed that for patterns that only contain free chlorine, the absorbance is practically zero.

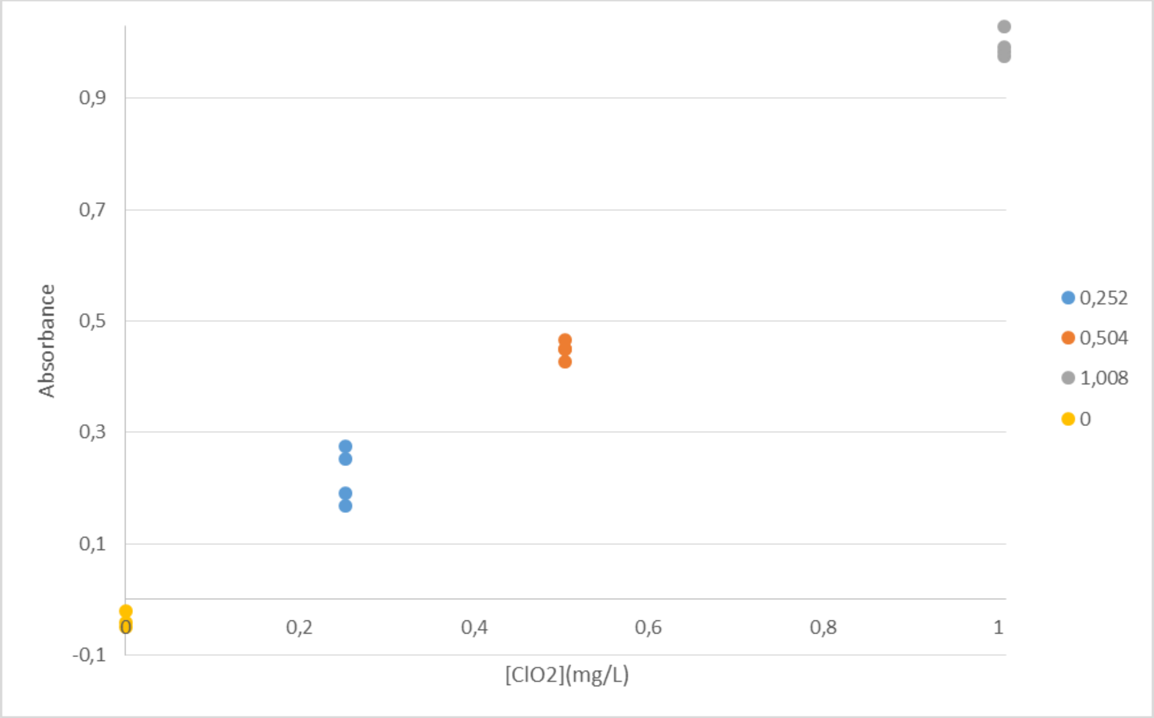

Figure 11. Interference study. Method: precipitation of sulfates (with tap water).

5.3.2. Extraction with 1,2-dichloroethane

5.3.2.1. With distilled water

Bleach is used, with an approximate concentration of 37 g/L. The concentration of the commercial bleach bottle may vary. The main reason is because the chlorine is unstable and the manufacturer cannot guarantee that the concentration does not decrease after the packaging. For this reason, the concentration of free chlorine present in each dilution is read by means of the colorimetric method with DPD, which is the procedure standardized by the laboratory of Aïgues de Barcelona.

Three solutions are prepared with a lower chlorine concentration than that present in the bleach. Therefore, a first dilution 1:250 is prepared, where an approximate chlorine concentration of 148 mg/L is obtained. From this, three more dilutions are prepared, which are the dilutions that are used for the preparation of the different patterns.

- **Dilution 1:** Add 6 mL of the 148 mg/L dilution in a 1 L flask. Dilute to the mark with distilled water. The concentration of free chlorine that is obtained is 0,30 mg/L.
- **Dilution 2:** Add 12 mL of the 148 mg/L dilution in a 1 L flask. Dilute to the mark with distilled water. The concentration of free chlorine that is obtained is 0,87 mg/L.
- **Dilution 3:** Add 20 mL of the 148 mg/L dilution in a 1 L flask. Dilute to the mark with distilled water. The concentration of free chlorine that is obtained is 1,45 mg/L.

Table 11. Interference study. Method: Extraction with 1,2-dichloroethane (with distilled water).

$[ClO_2]_{expected}$, (mg/L)	$[Cl_2$ free], (mg/L)	Absorbance	$[ClO_2]_{obtained}$ (mg/L)	Absolute error	Relative error (%)
0,276	0	0,0732	0,1256	0,15037	54,48
0,69	0	0,6767	0,6721	0,01786	2,59
0,966	0	0,9297	0,9013	0,06467	6,69
0	0,30	0,0507	0,1052	0,10520	-
0	0,87	0,0195	0,0770	0,07696	-
0	1,45	0,0459	0,1009	0,10086	-
0,276	0,30	0,2690	0,3029	0,02690	9,74
0,276	0,87	0,2859	0,3182	0,04221	15,29
0,276	1,45	0,3403	0,3675	0,09147	33,14
0,69	0,30	0,7105	0,7028	0,01283	1,86
0,69	0,87	0,7714	0,7580	0,06799	9,85
0,69	1,45	0,8177	0,7999	0,10990	15,93
0,966	0,30	0,8856	0,8613	0,10466	10,83
0,966	0,87	1,0458	1,0064	0,04043	4,19
0,966	1,45	1,0278	0,9901	0,02413	2,50

From Table 11 it can be verified that the presence of free chlorine does not interfere in the chlorine dioxide concentration. In addition, it can see how the relative error is less as the chlorine dioxide concentration increases. Then, it can see a graph showing that, for each case, the concentrations are quite similar, regardless of whether it contains only chlorine, a mixture of chlorine and chlorine dioxide, or only chlorine dioxide. In addition, it is observed that for patterns that only contain free chlorine, the absorbance is practically zero.

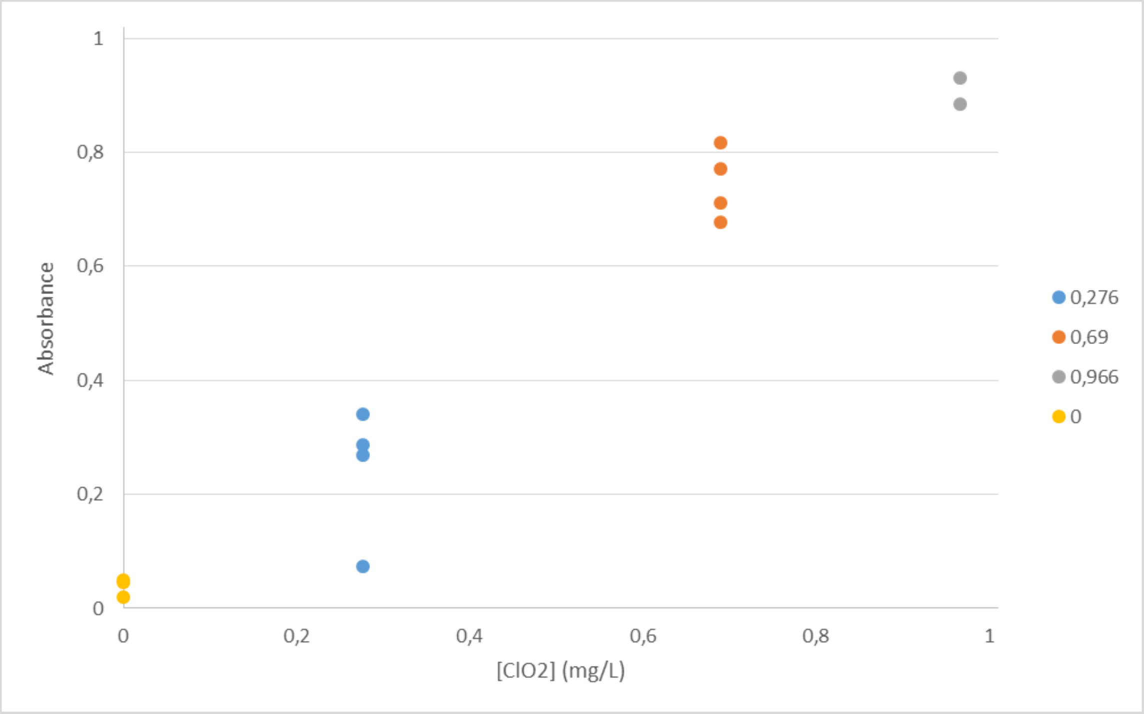

Figure 12. Interference study. Method: Extraction with 1,2-dichloroethane (with distilled water).

5.3.2.2. With tap water

Bleach is used, with an approximate concentration of 37 g/L. The concentration of the commercial bleach bottle may vary. The main reason is because the chlorine is unstable and the manufacturer cannot guarantee that the concentration does not decrease after the packaging. For this reason, the concentration of free chlorine present in each dilution is read by means of the colorimetric method with DPD, which is the procedure standardized by the laboratory of Aïgues de Barcelona.

In this case, the dilutions are filled with tap water, which has a conductivity of 1240 µS/cm and a free chlorine concentration of 0,46 mg/L. Since the method used is the precipitation of sulfates, it have to add a certain amount of barium chloride. The conductivity is 997 µS/cm, therefore, 1 ml of barium chloride is added.

Three solutions are prepared with a lower chlorine concentration than that present in the bleach. Therefore, a first dilution 1:250 is prepared, where an approximate chlorine concentration of 148 mg/L is obtained. From this, three more dilutions are prepared, which are the dilutions that are used for the preparation of the different patterns.

- **Dilution 1:** Add 6 mL of the 148 mg/L dilution in a 1 L flask. Dilute to the mark with tap water. The concentration of free chlorine that is obtained is 1,17 mg/L.

- **Dilution 2:** Add 12 mL of the 148 mg/L dilution in a 1 L flask. Dilute to the mark with tap water. The concentration of free chlorine that is obtained is 1,69 mg/L.
- **Dilution 3:** Add 20 mL of the 148 mg/L dilution in a 1 L flask. Dilute to the mark with tap water. The concentration of free chlorine that is obtained is 1,77 mg/L.

Table 12. Interference study. Method: Extraction with 1,2-dichloroethane (with tap water).

$[ClO_2]_{expected}$, (mg/L)	$[Cl_2$ free], (mg/L)	Absorbance	$[ClO_2]_{obtained}$ (mg/L)	Absolute error	Relative error (%)
0,344	0	0,3133	0,3430	0,0010	0,29
0,688	0	0,4985	0,5108	0,1772	25,75
1,032	0	0,9102	0,8836	0,1484	14,38
0	1,17	0,0986	0,1485	0,1486	-
0	1,69	0,0648	0,1179	0,1179	-
0	1,77	0,3583	0,3837	0,3838	-
0,344	1,17	0,5309	0,5401	0,1961	57,02
0,344	1,69	1,1784	1,1265	0,7825	227,48
0,344	1,77	0,5423	0,5504	0,2064	60,01
0,688	1,17	1,1473	1,0984	0,4104	59,65
0,688	1,69	1,2174	1,1618	0,4738	68,87
0,688	1,77	1,1641	1,1136	0,4256	61,86
1,032	1,17	0,5080	0,5194	0,5126	49,67
1,032	1,69	0,8267	0,8080	0,2240	21,70
1,032	1,77	0,7362	0,7261	0,3059	29,64

From Table 12, it can be verified that the presence of free chlorine in a water sample does not interfere in the chlorine dioxide concentration since the absorbance of the patterns does not increase as the free chlorine concentration increases. It should be noted that a series of results have been obtained that were not as expected. It can see how the relative errors, in the patterns that only present chlorine, are very high, reaching a relative error of 225 %. Below it can see a graph where it is analyzed that, for each case, the concentrations differ a lot from each other. In addition, it is observed that for the samples that only contains free chlorine, there is a value in which a very high absorbance is obtained for the fact that it does not contain chlorine dioxide. This problem has only been encountered when using the extraction method. For this reason, more studies would be needed to find the reason why the patterns that do not contain chlorine dioxide, once the extraction is done, have a blue color characteristic of the reaction between leuco-methylene blue reagent and chlorine dioxide. Another option would be not to continue studying this method since it has found a method, the precipitation of sulfates, which works and is not harmful to health, as the fact of working with organic solvents can be harmful to health.

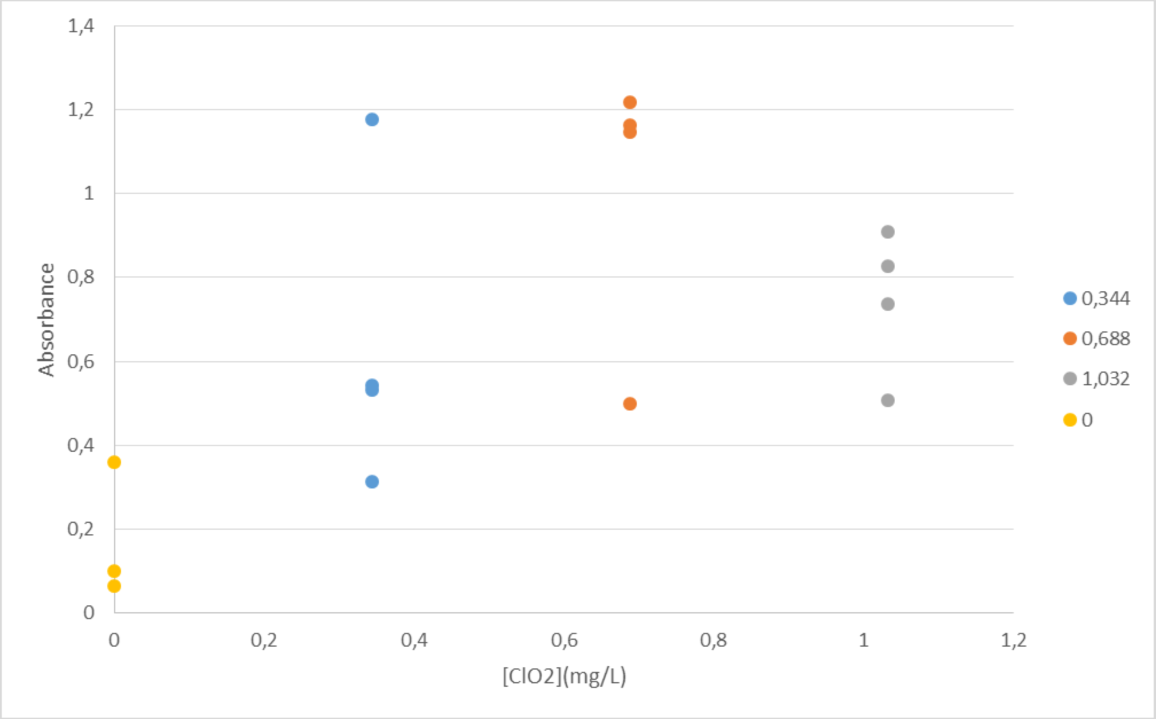

Figure 13. Interference study. Method: Extraction with 1,2-dichloroethane (with tap water).

5.4. Conductivity influence

For the sulfates precipitation method, it is studied if the conductivity of a water influences the precipitation of the sulfates. The samples of tap water come from Sant Andreu de la Barca and Bellvitge, in addition to a sample of mineral water. The conductivity of each water is:

Table 13. Conductivities.

Water area	Conductivity (µS/cm)
Sant Andreu de la Barca	365
Bellvitge	866
Mineral water with low mineralization	258

The results obtained are:

Table 14. Results.

Water area	$[ClO_2]_{expected}$ (mg/L)	Absorbance	$[ClO_2]_{obtained}$(mg/L)	Relative error (%)
Mineral water with low mineralization	0,6	0,5322	0,5691	5,15
Sant Andreu de la Barca	0,6	0,5223	0,5591	6,81
Bellvitge	0,6	0,4297	0,4668	22,20

It can be observed that as the conductivity of a water increases, the error in the determination of the chloride dioxide concentration also increases.

5.5. Presence of chlorine dioxide in different waters

For the sulfates precipitation method, it is studied if the real water contains chlorine dioxide. The samples of real water come from Sant Andreu de la Barca, Bellvitge, Granollers and Papiol, in addition to a sample of mineral water with low mineralization. The conductivity of each water is:

Table 15. Conductivities.

Water area	Conductivity (µS/cm)
Sant Andreu de la Barca	365
Bellvitge	866
Granollers	361
Papiol	965
Mineral water with low mineralization	258

The results obtained are:

Table 16. Results.

Water area	$[ClO_2]_{expected}$ (mg/L)	Absorbance	$[ClO_2]_{obtained}$(mg/L)
Sant Andreu de la Barca	0	0,0742	0,1119
Bellvitge	0	0,0746	0,1124
Granollers	0	0,0565	0,0942
Papiol	0	0,0511	0,0889
Mineral water with low mineralization	0	-0,0041	0,0337

In Table 16, it can be verified that the absorbance of all waters is approximately zero. Therefore, it is concluded that the waters of different areas, whether tap water or mineralized water, do not contain chlorine dioxide.

SECOND PART: SENSORY ANALYSIS

6. Sensory analysis of chemical compounds

6.1. Introduction to sensory analysis of drinking water

In the introduction section, it has been commented that one of the aspects to take into account in the quality of water for human consumption is the absence of substances that transmit unpleasant sensations, such as color, turbidity, taste and smell.

The regulations of the countries regarding the substances that may be present in the water and the quantity of each of them, regulate the minimum quality controls to guarantee the health of the consumers. The level of demand in terms of water quality, however, has been increased, which has caused humans to develop a study on the organoleptic properties of certain compounds in water.

Aigües de Barcelona, carries out a series of studies on the sensory analysis of substances present in drinking water. The method on which it is based is the Flavor Profile Analysis (FPA). This method is carried out from a group of panelists, chosen in a selection process, where the detection capacity of certain substances present in drinking water is evaluated. Once chosen, they carry out a training period, which normalize the description of the smells and flavors they detect.

6.2. FPA method

The FPA method is a technique to identify flavors and odors in samples of drinking water. The present project will only focus on the olfactory part.

The odor threshold is the minimum concentration at which a person detects the presence of a certain substance in water. Each substance has a different threshold, which is why each component is individually characterized and assigned its own classification of intensity.

The FPA method uses a group of four or five trained panelists to examine the sensory characteristics of a water sample. Panelists should be able to detect and recognize various odors present in the sample. The reproducibility of the results depends on the training and experience of the panelists. In a panel session, the different members should write down the perceptions they receive. Once each individual has carried out an independent evaluation of the sample, the results are shared.

In a panel session should be taken into account the factor exerted by fatigue, which causes a decrease in the sensory acuity of the analyst as a result of continuous exposure to olfactory or gustatory stimulation. Fatigue occurs due to mixtures of odors present in a water sample. It also influences the

intensity of the odor, the type of compound that is present (compounds such as geosmin and chlorine cause greater fatigue compared to other substances), the number of samples to analyze and the rest interval between one sample and another.
The odor intensity is judged from the following scale:

Table 17. Odor intensity scale.

Intensity	Description
-	Odor-free
T	Threshold
2	Very weak
4	Weak
6	
8	Moderate
10	
12	Strong

Panelists should not smoke or drink 15 to 30 minutes before the panel session. The use of cologne or the washing of hands with perfumed soap are not allowed.

6.2.1. Drinking water wheel

In the Aigües de Barcelona laboratory, the next drinking water wheel is used. This wheel is divided into three parts:

- In the upper right part are the tastes: sweet, salty, bitter and sour. The salty taste is related to the presence of minerals in the water while, the rest of tastes are related to low mineralization waters.
- Then, following in a clockwise direction, there are the sensations: rough, spicy, etc.
- Finally, the smells are found. There is a very high variety of odors in a drinking water and its origin may be due to:
    - Chemical compounds, such as geosmin, which is produced by the presence of algae.

- Disinfection treatments, which cause the odor of chlorine.
- Products formed in the distribution system.

The odors are classified into two groups: natural and chemical. The classification of odors is a very subjective discipline, so it generally happens that the same compound is identified or qualified differently between several tasting panels.

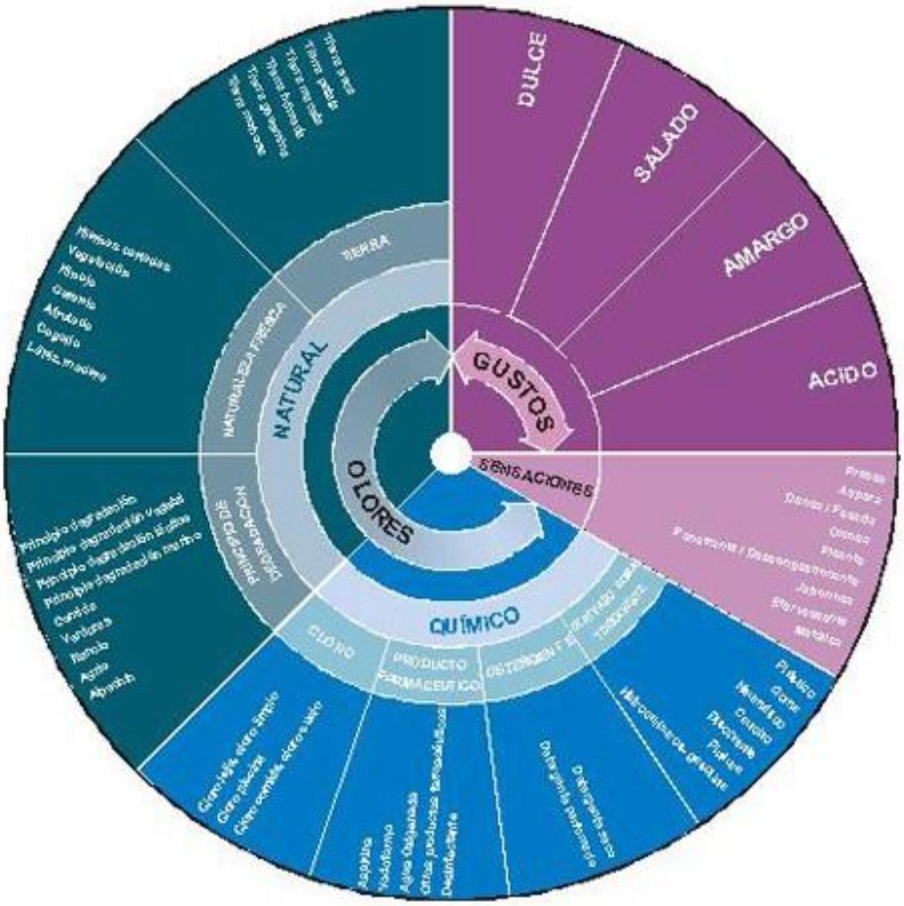

Figure 14. Drinking water wheel. Source: AGBAR.

6.2.2. Characteristics of the panel room

It is important that the panel room has a series of characteristics to guarantee the comfort of the panelists. These characteristics are:

- The temperature of the room should be around 21-23 °C in order to guarantee the thermal comfort of the panelists.
- The room should have enough natural light to guarantee the luminous comfort of the panelists.

- Striking colors should not be used on the walls of the room or as decoration (cupboards, tables, etc.), neutral colors should be used (preferably white).

6.2.3. Sensory procedure

Erlenmeyers of 500 mL are used, where a sample volume of 200 mL is introduced. Erlenmeyers should be heated to a temperature of 45 °C.

The panelist, when performing the analysis, should shake gently (do not shake) the erlenmeyer in a circular way to ensure that the volatile compounds are released in the space left free in the Erlenmeyer flask. Then, the Erlenmeyer is brought to the nose, the cap is removed and the sample is smelled.

When the analysis is finished, the impressions of the smell attributes in the perceived order and the evaluation of the intensity of each attribute are recorded. In the taste and odor analysis, each panelist determines intensity classifications by comparing the intensity of the perceived odor with the reference intensities that have been previously smelled.

The first perception received is the most important because, if you smell the same sample twice, it may have decreased its concentration due to the high volatility of the odorant. It should rest at least 2 minutes between samples and not analyze more than five or six.

Finally, when all the panelists have examined the sample, each one indicates the impression they have perceived and the leader of the panel records the results.

6.3. Geosmin

Geosmin is one of the substances responsible for the smell of wet earth. One of the habitual complaints of the consumers of drinking water is the smell or taste of humid earth, this fact usually occurs in times of summer and autumn, and is due to the presence of algae in the water. This problem is often found in waters with high levels of nutrients and in shallow reservoirs. When blooms occur, bacteria die and release odorous chemicals.

The objective of this study is to find a relationship that identifies the intensity of the odor of a water sample containing geosmin depending on its concentration. The only source of information that is available is an article, where they perform this same study but for the hexanal substance. In this study, achieves a linear relationship between the odor intensity of a sample as a function of the logarithm of the hexanal concentration.

7. Methodology

7.1. Material and reagents

Material:

- 500 mL erlenmeyers.
- 1 L beaker.
- 200 mL and 1 L flasks.
- Automatic pipette.
- Thermal bath.
- Thermostat.
- Ground-glass stoppers.

Reagents:

- Hexanal of 1 mg/L concentration.
- Geosmin of 0,5 mg/L concentration.
- Distilled water.
- Solan de cabras water.
- Tap water from Aigües de Barcelona laboratory.
- Water with code 448, coming from Badalona.

7.2. Preparation of the samples

The panel session consists of five samples that the panelists have to smell. The first two samples represent the intensity references that they have to use to evaluate the intensity of the three remaining samples.

The two intensity references are composed of hexanal because the intensity-concentration relationship for this substance is known. The next three samples are composed of geosmin, which is the substance to be studied.

First, a study should be carried out to detect the threshold at which panelists detect the presence of geosmin in a sample, but that study was done previously by Aigües de Barcelona. The detection threshold of geosmin is 0,2 µS/cm. The series of concentrations studied are:

- 0,2 / 2 / 20 ng/L.
- 0,5 / 5 /50 ng/L.
- 1 / 10 / 100 ng/L.

The procedure to prepare the samples is:

1. Label all erlenmeyers with codes so that the panelists do not know what it contains and, in addition, it serves to have them identified.
2. Introduce approximately 0,5 L of distilled water into a 1 L volumetric flask using a beaker.
3. Introduce, with an automatic pipette, the necessary volume of hexanal or geosmin.
4. Dilute to the mark with distilled water.
5. Using a beaker, introduce 200 mL of the above solution in a 200 mL flask.
6. Pour into a 500 mL Erlenmeyer flask.

Because hexanal and geosmin are highly volatile substances, samples are prepared on the same day as the panel session, preferably about two hours before. In addition, the samples should be placed in the thermal bath half an hour before the arrival of the panelists so that the samples are at 45 °C, temperature at which the perception of the volatile components is greater. The material and the necessary substances have to be used exclusively in the panel to avoid possible contamination, as well as the workspace, which have also be exclusive for that purpose. The series of codes used to identify the different erlenmeyers are the following:

- 372 / 174 / 965 / 967 / 985
- 372 / 174 / 472 / 360 / 990

The first two codes refer to the two hexanal references and the last three codes to the three geosmin samples. These two series of codes alternate between the panelists so that there is no type of influence between them.

7.3. Procedure to carried out in the panel sessions

- Approximately 2 hours before of the panelists arrival, prepare the samples.
- Half an hour before the panel session, the thermal bath is turned on at 45 ºC and the samples are introduced.
- For each panel session, the procedure to be followed have to be explained, without giving any information about the content of the the samples.

8. Results

8.1. Trained panelists

Table 18 shows the average of the results obtained for the different concentrations of geosmin. All the results obtained in the different sessions can be consulted in the section of annexes A.

Table 18. Panel results (Trained panelists).

Geosmin concentration (ng/L)	**Average intensity**
0,2	2,57
0,5	2,63
1	3,66
2	4,39
5	4,27
10	4,88
20	5,42
50	4,91
100	5,59

From these results, and from the logarithm of the geosmin concentration, a graph is obtained where a linear regression of the geosmin intensity as a function of the concentration.

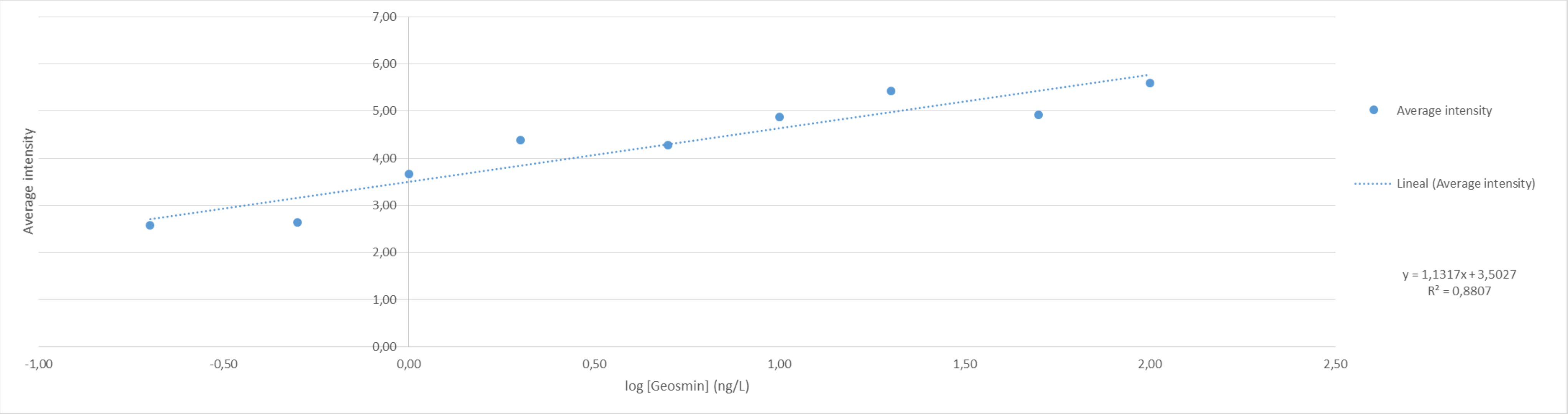

Figure 15. Regression line intensity-concentration (trained panelists).

The R^2 obtained in the linear regression is approximately 0,88. For future projects, the study could continue using higher concentrations of geosmin and also carry out more repetitions of the concentrations that have already been studied to improve the result of this R^2.

Next, a series of tests with different types of water are carried out, adding a known concentration of geosmin, to study if the different substances present in a real water interfere in the intensity that the panelist perceives. High concentrations of geosmin are used to detect their presence and not be masked by the presence of other substances.

Table 19. Panel results with real samples (trained panelists).

Geosmin concentration (ng/L)	**Average intensity**		
	448 (Badalona)	**Solan de cabras**	**Tap water (Aigües de Barcelona laboratory)**
10		5,88	4,63
50	6	7,03	3,50
100	4,63	6,29	4,98

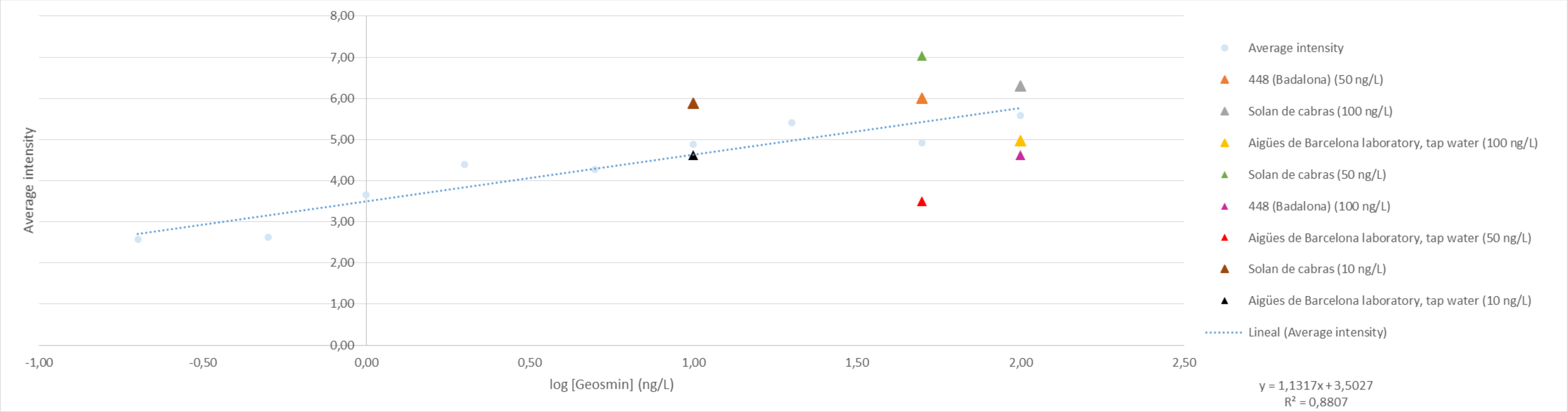

Figure 16. Panel results with real samples (trained panelists).

For a same concentration of geosmin, in the samples prepared with Solan de cabras water, a greater perception of geosmin is obtained than in the samples prepared with tap water from Badalona and the laboratory of Aigües de Barcelona. This is because the tap water contains a higher concentration of chlorine and masks the detection of other substances. Therefore, the substances present in the real water, especially those containing a high concentration of chlorine, interfere in the detection of geosmin.

8.2. Panelists in formation

Table 20 shows the average of the results obtained for the different concentrations of geosmin. All the results obtained in the different sessions can be consulted in the section of Annexes A.

Table 20. Panel results (panelists in formation).

Geosmin concentration (ng/L)	Average intensity
0,2	4,19
0,5	3,13
1	5,52
2	5,31
5	5,48
10	6,08
20	7,38
50	7,04
100	8,29

From these results, and from the logarithm of the geosmin concentration, a graph is obtained where a linear regression of the geosmin intensity as a function of the concentration.

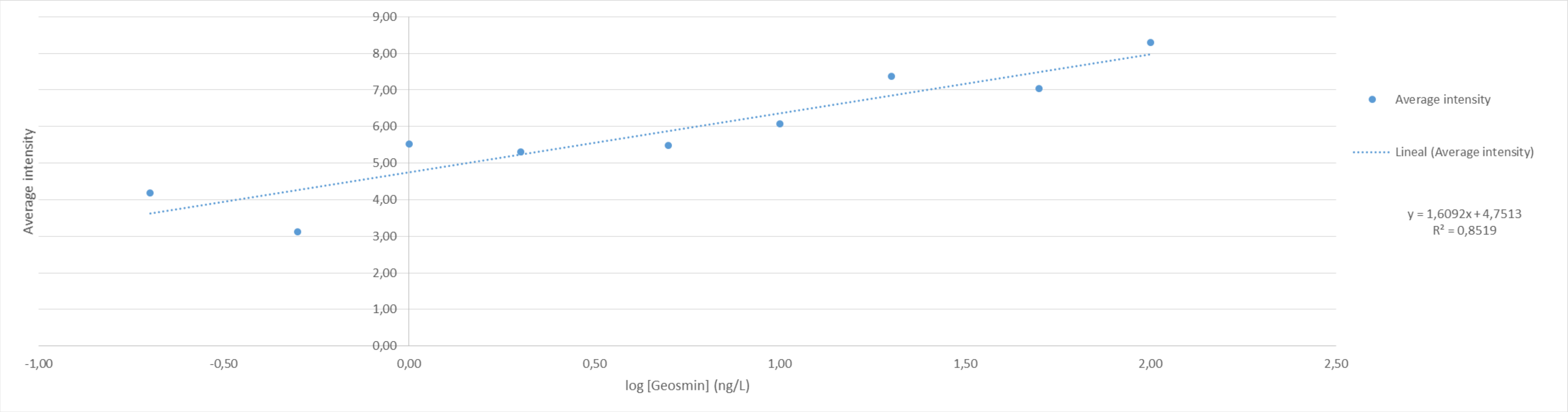

Figure 17. Regression line intensity-concentration (panelists in formation).

The R^2 obtained in the linear regression is approximately 0,85. The value is very similar to the obtained with the trained panel, although it should be noted that, in this case, there is a lower number of repetitions for each concentration of geosmin.

Security and environment

Safety measures in the laboratory

In the laboratory of Aigües de Barcelona it have to follow a series of rules to ensure safety in the laboratory, which are detailed below:

- Use a gown and wear it always fastened.
- Never eat or drink while working in the laboratory.
- Use protective glasses whenever necessary.
- Do not use contact lenses.
- Wear closed shoes.
- The long hair have to be collected.
- Use nitrile gloves when reagents are used.
- Use the extractor hood for the products that require it.
- All emergency exits have to be known.
- Know the meeting point in case of evacuation.
- The location of the extinguishers and the safety elements in the laboratory (eyewash, showers, extinguish fires and first aid kit) have to be known.
- A course should be received from the safety officer in the laboratory, informing about the procedure to be followed in case of emergency.

Hazard of the reagents used

Below are the H and P phrases of the different reagents used.

Table 21. Phrases H and P

Reagent	Hazard phrases	Precautionary phrases
Chlorine dioxide	-	-
Methylene blue	H302	P264;P270;P301+P312;P330;P501
Barium chloride dihydrate	H302;H332	P261;P264;P270;P301+P310;P304+P304;P501
Stannous chloride dihydrate	H332;H302;H314	P280;P261;P302+P352;P305+P351+P338;P304+P340;P501
1,2-dichloroethane	H350;H225;H302;H319;H335;H315	P201;P202;P210;P233;P240;P241;P242;P243;P261;P264;P270;P271;P280;P281;P301+P312;P302+P352;P303+P361+P353;P304+P340;P305+P351+P338;P308+P313;P312;P321;P330;P332+P313;P337+P313;P362;P370+P378;P403+P233;P403+P235;P405;P501
chloroform	H302;H315;H351;H373	P280;P302+P352;P301+P312;P308+P313;P332+P313;P501
Hexane	H315;H373;H411;H304;H360Df;H336;H304	P210;P243;P280;P301+P310;P331;P303+P361+P353;P332+P313;P273;P391;P501
Diethyl ether	H224;H242;EUH019;H302;EUH066;H336	P210;P233;P240;P241;P242;P501;P243;P261;P264;P270;P271;P280;P301+P312;P303+P361+P353;P304+P340;P312;P330;P370+P378;P403+P233;P403+P235;P405

Analysis of the environmental impact

The waste generated in the laboratory have to be treated properly so that it does not damage the environment. For this reason, in the laboratory of Aigües de Barcelona, there is a series of containers for evoke the waste that is generated, which have to be in an extractor hood. There are a total of four containers that are divided in: various aqueous solutions, solutions containing DPD, chlorinated solvents and non-chlorinated solvents.

When they are filled, laboratory technicians transport them to a waste storage room, always using a mask.

Conclusions

Conclusions of the analytical part

- Calibration lines have been made for samples that have a chlorine dioxide concentration of between 0,1 and 1,5 mg/L by the methylene blue colorimetric method.
- The reaction of chlorine dioxide with leuco-methylene blue reagent is immediate and unstable over time. It is decided to apply a time for the reading of the samples in the spectrophotometer.
- The sulfates present in the water react with the leuco-methylene blue reagent forming a precipitate that makes it impossible to read the absorbance in the spectrophotometer.
- The methods proposed to eliminate the turbidity of the samples prepared with real water are:
    - Precipitation of the sulfates by the addition of barium chloride and subsequent filtration with a syringe with a filter for chromatography of 0.45 µm of pores.
    - Extraction with 1,2-dichloroethane.
- In the 1,2-dichloroethane extraction method, the stability of the standards remains constant over time. Therefore, it is not necessary to set a time to read the absorbance.
- For both methods, calibration lines have been made for the reading of samples containing a chlorine dioxide concentration of between 0,1 and 1,5 mg/L by the methylene blue colorimetric method. The reproducibility between the calibration lines is achieved.
- Interferences created by free chlorine are considered insignificant in both methods because, for high concentrations of chlorine, no inconsistent results have been observed. Although, in the case of the extraction method with 1,2-dichloroethane, results have been obtained in which the absorbance has been very high in patterns that did not contain chlorine dioxide. For its validity, more studies should be carried out to verify the reason why in the patterns that do not contain chlorine dioxide, once the extraction is done, have a high absorbance.
- The sulfate precipitation method is valid for the determination and quantification of chlorine dioxide present in a sample by the methylene blue colorimeter method.

Conclusions of the sensory part

- A linear relationship has been obtained between the odor intensity of a sample as a function of the geosmin concentration.
- In the case of the trained panelists group, an R^2 was achieved a little higher than that of the panelists in training. In addition, the trained panelists have made a greater number of panel sessions and, therefore, a greater number of data is available.

- In the tests carried out with real water it has been proved that the presence of other substances in the water, such as chlorine, masks the perception of geosmin.
- For future projects, the study could continue using higher concentrations of geosmin and also carry out more repetitions of the concentrations that have already been studied to improve the result of the R^2.

Economic analysis

In the following section, a recopilation of the costs to be taken into account for the realization of this project are carried out, that are those associated with the material, reagents, equipment, water consumption and the cost of personnel.

Regarding the cost of the equipment that is needed, it is calculated by means of the following formula:

$$Equipment\ cost = \frac{Cost\ (€)}{Useful\ life\ (years) \cdot users} \cdot Activity\ (\frac{months}{years}) \qquad \textbf{(Eq. 10.1)}$$

Regarding personnel costs, they correspond to the salary of a chemical engineer, a veteran chemical engineer and the collaboration of a group of panelists formed by five trained panelists and four panelists in formation. To estimate the salary of the personal, the minimum and maximum contribution bases are taken into account, as well as the type of contribution in the Social Security by the company of the year 2017. The gross salary is calculated as the average between the base minimum and maximum contribution. This salary is the equivalent for a total of 40 hours a week, as in this case the contract is 30, the salary is adjusted equivalently. Table 22 lists all these data.

Table 22. Personnel cost data.

Personnel	**Minimum contribution base (€/month)**	**Maximum contribution base (€/month)**	**Estimated gross salary (€/month)**	**Estimated gross salary (€/month) 30 h weekly**	**Social security business fee (%)**
Chemical engineer	956,10	3751,20	2353,65	1765,24	23,60
Veteran engineer	1152,90	3751,20	2452,05	1839,04	23,60

The cost of the personnel is calculated from the following expression:

$$Coste\ empresa(€) = \left((1 + SSE) \cdot gross\ salary\left(\frac{€}{month}\right)\right) \cdot \frac{dedication\ (h)}{working\ hours\ (\frac{h}{mes})} \qquad \textbf{(Eq. 10.2)}$$

Where:

SSE = Social security business fee.

In the case of the panelists, a temporary contract is made through by an external company. The gross salary of each panelist is: 31,00 €/panel session.

Below is a series of tables that summarize the costs associated in the analytical part and the sensory part of the project.

Economic evaluation of the analytical part

Table 23. Reagents cost.

Reagent	Quantity used	Price/quantity	Cost (€)
Methylene blue	25 mg	40,50 €/25g	0,04
Stannous chloride dihydrate	5,64 g	72,60 €/5g	81,90
Hydrochloric acid	5 mL	38,50 €/100 mL	1,93
Bleach	4 mL	1,40 €/5L	0
Chloroform	40 mL	82,50 €/L	3,30
Chlorine dioxide	-	-	-
1,2- dichloroetane	1,14 L	126 €/L	143,64
Hexane	40 mL	309,50 €/L	12,38
Diethyl ether	40 mL	37,75 €/L	1,51
Barium chloride dihydrate	0,255 g	293 €/100g	0,74

Table 24. Water cost.

Type of water	Quantity used (L)	Price/quantity (€/L)	Cost (€)
Distilled water	10,50	-	-
Tap water	6,6	0,0030	0,02

Table 25. Material cost.

Material	Units	Price/units (€/unit)	Cost (€)
1 mL pipette	1	2,10	2,10
2 mL pipette	1	4,39	4,39
3 mL pipette	1	6,50/3 ud.	2,17
5 mL pipette	1	3,66	3,66
6 mL pipette	1	1,70	1,70
10 mL pipette	1	3,15	3,15
20 mL pipette	1	4,40	4,40
25 mL flask	16	26,61	425,76
50 mL flask	17	27,87	473,79
100 mL flask	1	32,47	32,47
250 mL flask	2	40,13	80,26
1 L flask	3	76,69	230,07
Spatula	1	3,14	3,14
50 mL erlenmeyer	14	8,98	125,72
Cuvette	1	59,75	59,75
Separating funnels	6	2,10	12,60
Funnels	6	52,14	312,84
10 mL graduated cylinder	1	7,18	7,18

Table 26. Equipment cost.

Equipment	Purchase price (€)	Depreciation	Dedication	Users	Cost (€)
Spectrophotometer UV/VIS diode array 8453. Hewlett Packard.	3941	10	3 months	2	49,26
Magnetic stirrer	394	5	3 months	2	9,85
Balance	1600	5	3 months	2	40,00
Automatic stirrer	1429,64	5	3 months	2	35,74

Economic evaluation of the sensory part

In the case of reagents, the volume of hexanal and geosmin used is very small and its cost is not taken into account.

Table 27. Water cost.

Type of water	Quantity used (L)	Price/quantity (€/L)	Cost (€)
Distilled water	52	-	-
Tap water	6	0,0030	0,02
Solan de cabras water	5	1,80	9

Table 28.Material cost.

Material	Units	Price/units (€/unit)	Cost (€)
Automatic pipette	1	49	49
1 L beaker	3	20,89	62,67
200 mL flask	2	45,17	90,34
1 L flask	5	76,69	383,45
500 mL erlenmeyer	25	11,55	288,75

Table 29. Equipment cost.

Equipment	Purchase price (€)	Depreciation	Dedication	Users	Cost (€)
Thermal bath	641,00	5	3 months	1	32,05

Personnel cost

Table 30. Personnel cost.

Type	gross salary (€/month)	Dedication	Cost (€)
Graduated in chemical engineering	1765,24	360 hours	6545,51
Veteran chemical engineer	1839,04	360 hours	6819,16
Panelists	31,00 €/panelist and session	18 sessions	2232,00

Total cost of the project

Table 31. Total cost of the project.

Type of cost	Cost (€)
Reagents and water	254,48
Material	2659,36
Equipment	166,90
Personnel cost	15596,67
TOTAL	**18677,41**

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Annexes

A1. Panel results

The results obtained in all the panel sessions for the different concentrations of geosmin are presented below.

<u>Trained panelists</u>

	0,2 ng/L		
	17-10-17	**27-10-17**	**03-11-17**
	3	2	4
	3	2	2
	2	3	2
		2,50	
Daily average	2,67	2,38	2,67
Average concentration	<u>2,57</u>		

	0,5 ng/L			
	10-10-17	**20-10-17**	**14-11-17**	**19-12-17**
	3	2,50	4,50	5
	1,50	3	2	2
	1	2	3,50	3,50
			2	2,50
				3
Daily average	1,83	2,50	3	3,20
Average concentration	2,63			

	1 ng/L				
	31-10-17	**10-11-17**	**17-11-17**	**21-11-17**	**15-12-17**
	6	3	4	2	2,50
	5	2	4	2	6
	3,50		4		4
	6,50		5,50		
Daily average	5,25	2,50	4,38	2	4,17
Average concentration	3,66				

	2 ng/L		
	17-10-17	**27-10-17**	**03-11-17**
	4	6	2,50
	3,50	4,50	4,50
	3	6	5,50
		5,50	
Daily average	3,50	5,50	4,17
Average concentration	4,39		

	5 ng/L			
	10-10-17	**20-10-17**	**14-11-17**	**19-12-17**
	4	4	6	3,50
	2,50	4,50	6	4
	3,50	4	4,50	5
			3	4
				7
Daily average	3,33	4,17	4,88	4,70
Average concentration	4,27			

	10 ng/L				
	31-10-17	**10-11-17**	**17-11-17**	**21-11-17**	**15-12-17**
	5	4	5,50	5	5
	9	3	6	5	5
	4,50		5,50		5
	4,50		3,50		
Daily average	5,75	3,50	5,13	5	5
Average concentration	4,88				

	20 ng/L		
	17-10-17	**27-10-17**	**03-11-17**
	5	6,50	6
	5,50	4	4
	4	7	7
		5,50	
Daily average	4,83	5,75	5,67
Average concentration	5,42		

	50 ng/L			
	10-10-17	**20-10-17**	**14-11-17**	**19-12-17**
	4	5	4	6,50
	5	5,50	7	7
	5	5	2,50	4
			3,50	5
				7
Daily average	4,67	4,83	4,25	5,90
Average concentration	4,91			

	100 ng/L				
	31-10-17	**10-11-17**	**17-11-17**	**21-11-17**	**15-12-17**
	5	6	6,50	7	5
	10	5	7	4	4
	3		6,50		7
	2,50		6		
Daily average	5,13	5,50	6,50	5,50	5,33
Average concentration	5,59				

Panelists in training

	0,2 ng/L	
	18-10-17	**25-10-17**
	4	4
	4	4,50
	2	6
	5	4
Daily average	3,75	4,63
Average concentration	4,19	

	0,5 ng/L	
	08-11-17	**15-11-17**
	3	1,50
	1	1,50
	3	6
	6	
Daily average	3,25	3
Average concentration	3,13	

	1 ng/L	
	22-11-17	**13-12-17**
	7	2
	7	6,50
	6	3
		6
Daily average	6,67	4,38
Average concentration	5,52	

	2 ng/L	
	18-10-17	**25-10-17**
	6	5
	3	8
	5,50	4
	7	4
Daily average	5,38	5,25
Average concentration	5,31	

	5 ng/L	
	08-11-17	**15-11-17**
	6	4
	3,50	4
	5	8
	8	
Daily average	5,63	5,33
Average concentration	5,48	

	10 ng/L	
	22-11-17	**13-12-17**
	5	6
	3	9
	6	7
		8
Daily average	4,67	7,50
Average concentration	6,08	

	20 ng/L	
	18-10-17	**25-10-17**
	8	7
	6	8
	7,50	7,50
	8	7
Daily average	7,38	7,38
Average concentration	7,38	

	50 ng/L	
	08-11-17	**15-11-17**
	8	3
	5,50	6
	7,50	10
	10	
Daily average	7,75	6,33
Average concentration	7,04	

	100 ng/L	
	22-11-17	**13-12-17**
	9	8
	5	11
	8	8
		10
Daily average	7,33	9,25
Average concentration	8,29	