

ASSESSMENT OF CORRELATED ERRORS IN CHEMICAL MEASUREMENT

TREBALL DE FI DE GRAU

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Degree in Chemistry



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Tarragona, June 2019

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ACKNOWLEDGEMENTS

I would like to express my very great appreciation to Dr Quentin Hanley for his valuable and constructive suggestions during the planning and the development of this project. As well as for his patience and encouragement.

I would also like to thank Nigel Mould and Diego Lo Destro for their assistance and help in offering me resources in running the experiments.

Finally, I wish to thank my parents and my friends for their support and encouragement throughout my study.

1. ABSTRACT

1.1 English Abstract.

In this project covariance is assessed. Covariance is the correlation between two or more variables. For this reason, to study it, concentration of zinc, calcium and magnesium in sea salt and mineral water were analysed by ICP-OES. Then, using the mean and the standard deviation of the data obtained, covariance was calculated by two different methods.

The results obtained exhibited that there was correlation between the metals concentration and sea salt or mineral water samples mass. Moreover, sea salt sample results presented correlation between the mass measured and the instrument's baseline.

In the end, it was concluded that covariance is important and it must be considered in error propagation.

1.2 Catalan Abstract.

En aquest projecte la covariància és avaluada. La covariància és la correlació entre dos o més variables. Per aquest motiu, per estudiar-la, la concentració de zinc, calci i magnesi en mostres de sal marina i aigua mineral va ser determinada per mitjà de ICP-OES. Seguidament, utilitzant la mitjana i la desviació estàndard dels valors obtinguts, la covariància va poder ser calculada mitjançant dos mètodes diferents.

Els resultats recollits mostren l'existència de correlació entre la concentració dels metalls i la massa mesurada de sal mineral o d'aigua mineral. A més a més, les mostres de sal mineral també presentaven correlació entre la massa mesurada i la línia base de l'instrument.

Finalment, es va concloure que la covariància és important i que ha de ser considerada en el càlcul de propagació d'errors.

2. AIMS AND OBJECTIVES

The objective of this project is to improve uncertainty calculation in correlated variables. It is suspected that considering covariance in error propagation could make an improvement. For this reason, the aims are to find out if covariance exists in ratio concentrations, to learn how to calculate it and to assess its importance. To do it, an apparently simple experiment was performed. Zinc, calcium and magnesium concentrations in sea salt and mineral water were measured by ICP-OES applying the sampling analysis method.

3. INTRODUCTION

This project was performed in the laboratories of Nottingham Trent University under the supervision of Dr. Quentin Hanley, who is very concerned about the covariance treatment in error propagation.

It is impossible to study a given property of a single molecule, which is surrounded by millions of other molecules. For this reason, statistical methods are applied in chemistry measurements¹. Therefore, the results obtained from a chemical experiment are estimated averages of a range which contains all the possible outcomes. The unit of measure that limits the range is uncertainty. Thus, one definition of uncertainty could be the range where the true analytical value is expected to be found².

According to Heijungs and Lenzen (2014)³, there are four main ways that uncertainty can turn up. Those are input data, which variates depending on how accurate the measurements are; assumptions that can be discussed, error propagation and interpretation of uncertain results.

The complexity of calculating uncertainty made scientists took some approaches to manage it. One of them is considering that there is no relation between variables. In other words, that there is no covariance³.

Some examples that calculate uncertainty of independent variables are Rasul and others (2018)⁴, Keene and others (1986)⁵ and Oksanen and Sarjakoski (2005)⁶.

Rasul and others (2018) wanted to introduce the concepts of data quality evaluation in analytical chemistry and the use of uncertainty in Bangladesh. Because their scientists report results without an uncertainty assigned. To show how uncertainty is calculated, they use the error propagation equation for uncorrelated variables.

Keene and others (1986) study the composition of sea salt collected from precipitation. They are interested in if there are non-sea salt components in sea salt samples, and to test some assumptions made for sea salt corrections. For example, no fractionation and considering a purely marine source. In doing so, they compare the ratios of different

components in sea salt. In the end, they concluded that the assumptions made are not always satisfied and that uncertainty needs to be minimized.

Oksanen and Sarjakoski (2005) aim was to make a consistent analysis of the DEM (digital elevation model) error propagation in topography. To test this, they studied how random errors are propagated on two constrained derivatives and one unconstrained. Eventually, they concluded that there was a very strong correlation between one of the two constrained derivatives.

All the previous articles have two variables related and those variable are looked at separately. Therefore, they neglect covariance between variables.

The conclusion they reached, considering that the neglected covariance, it leads to question what covariance is, how to detect it and when it should be considered.

Covariance can be defined as the correlation between two or more variables⁷. For this reason, to analyse it, some relation between variables is needed. There are two ways that can be used to identify covariance. The first one is by linear regressions and the second by random behaviour.

Longford (2010)⁸ is an example of the first case. It studies two variables in four different groups of students. Different interactions to each group were applied. Next, he plotted the results into linear regressions and he compared them. When interactions between variables were not applied, the linear regressions obtained from each group were parallel. However, when interactions were added, the linear regressions of each group started to lose their parallelism. To sum up, when there were no interactions between variables, the linear regressions were parallels; whereas when there were interactions, the linear regressions were not parallel.

Longford (2010) can be used to find covariance between different groups. If only one group is used, then random behaviour can be used.

Random effect is defined as a factor that differs from one replication to the other⁸. When the different factors follow a tendency, it is suspected that covariance is present. Knowing this, random errors can be used to identify covariance in data.

Once the covariance existence is known, its importance should be studied.

For instance, the two areas of chemistry that covariance usually appears are geochemistry⁹ and life cycle assessment (LCA), which is defined as the environmental impact of one product during its entire life³.

One of the reasons is that geochemistry needs to determine isotope ratios⁹. Ratio is defined as the relation between two numbers or amounts associated to one another⁷. Moreover, correlated uncertainties are known as mutual relationship or the connection between two or more things¹⁰. In conclusion, ratio and correlated uncertainties are closely tied, therefore causing covariance.

Schmitz and Schoene (2007), as Rasul and others (2018), want to provide a useful tool to help geochronology students to clarify the general method of error propagation. However, Schmitz and Schoene (2007) consider error correlation.

Schmitz and Schoene (2007) are looking for appropriate methods to measure U-Pb and Pb-Pb ratios, with different isotope combinations and to determine their derivative ages. In the end, they conclude that the ratios between the different isotopes of Pb and U are strongly correlated except for $^{204}\text{Pb}/^{206}\text{Pb}$, which supports that covariance cannot always be neglected.

For LCA different procedures have been applied in order to calculate error propagation. In Groen and others (2014)¹¹, they compare five different methods of calculating error propagation or, as they call it, uncertainty propagation. These methods are Monte-Carlo sampling (MCS), Latin hypercube sampling (LHS), quasi Monte-Carlo sampling (QMCS), analytical uncertainty propagation (AUP) and fuzzy interval arithmetic (FIA).

Among other things, they concluded that LHS and QMCS were more accurate in determining means than MCS, and they converged faster. Also, FIA used less memory than the other sampling methods.

Moreover, sampling method is the one used in this project for running samples and this article has been supportive in understanding how it works.

In summary, the conclusions Schmitz and Schoene (2007) and Groen and others (2014) reached are that for normally correlated parameters, correlation must be considered. However, for parameters in some nonlinear functions, nonnormality is pronounced. It

can often match or exceed the error confidence limits. For this reason, they aborted this way to calculate error propagation for nonnormality cases.

Heijungs and Lenzen (2014) combines the two articles that have been discussed above. They compare two different techniques to study error propagation, sampling method and analysis method.

Sampling procedure requires running the same samples repeatedly to get a model of results. Subsequently, they are analysed and various uncertainty indicators are obtained. Therefore, tests on correlation can be put into practise.

However, the principal disadvantage of this method is that it requires a large amount of time to be completed. Due to obtain small standard deviations; large numbers of simulations need to be done.

As an alternative solution, the analytical approach is proposed. It defines how inputs are converted into outputs by implementing local derivatives. For this reason, a more mathematical background is demanded. Even though this approach only estimates the mean and the standard deviation, it considerably reduces the computing time.

In the end, they conclude that both approaches are equitably important due to they give different sets of information. The sampling procedure gives more information than the analytical approach, however it takes more calculating time.

For this reason, the utilization of one approach or the other, it depends on how accurate the results must be and how much time is available.

Schmitz and Schoene (2007), Groen and others (2014) and Heijungs and Lenzen (2014) reached the conclusion that calculating covariance is difficult, and sometimes large amounts of time are required. This might be why few scientists do not give importance to it. Also, it might be due to the small knowledge about it. In consequence, it is normally neglected, as the first three articles discussed above: Rasul and others (2018), Keene and others (1986) and Oksanen and Sarjakoski (2005).

If a closer look at them is taken, it can be noticed that all of them are studying ratio between masses. So, covariance should be considered.

In Rasul and others (2018), the reason it might be neglected is because they are trying to explain to laboratories in Bangladesh how to calculate uncertainties in a simple way, due to they never used uncertainties before.

However, in Keene and others (1986) and Oksanen and Sarjakoski (2005), they do not use error correlation in their error propagation. Though they do conclude that either the uncertainty must be minimised or that either there is a strong correlation in the data.

Therefore, the aim of this work is to study covariance in more detail, and try to find out if it must be considered or not in error propagation.

To do this, a simple experiment was performed. Zinc, calcium and magnesium concentrations were measured repeatedly in different weights of sea salt and mineral water samples. In other words, sample mass and metal concentration are supposed to be related. Thus, many measurements of the same sample are done to create a model of results, from which mean and standard deviation would be extracted.

The reason of analysing metals' concentration in samples is due to needing two correlated magnitudes in order to study error correlation. The instrument used for this purpose is ICP-OES.

Determination of Zn, Ca and Mg in sea salt and mineral water by ICP-OES has been studied before. However, as Hwang and others (2016) state, few methods have been reported to determine salt minerals by atomic absorption spectrometry. And none of the papers that have been found, relate their experiments to error correlation. They are focused on extracting, concentrating, separating and determining various minerals from different samples of salt or water¹²⁻¹⁵. Basically, they are looking for if the concentration of different minerals in salt and water are within the legal limits¹², or for the best method to determine trace elements¹³⁻¹⁵.

The principal reason that different sources are interested on minerals is due to the fact that some of them are essential at human nutrition such as zinc, calcium and magnesium¹⁴⁻¹⁸.

Nevertheless, the excess or lack of them can produce several damages to the human body. For instance, weight loss and anorexia^{13,14}, osteoporosis¹⁸, Alzheimer, Parkinson, diabetes, hypomagnesemia and hypocalcemia^{16,17}.

Because of these diseases, the importance of identifying zinc, calcium and magnesium content in various samples is being considered from viewpoints of quality control and food safety^{13,15}.

To sum up, an accurate detection of zinc, calcium and magnesium concentrations in sea salt and mineral water is important for health care. For this reason, to know if covariance is present between them is important in order to have more precise results and a better quality control.

4. THEORATICAL PART

Most presentations of chemical data analysis neglect the covariance term^{19–22}. The objective of this project is to assess it and conclude if it must be considered in error propagation or not.

Tellinghuisen (2001)²³ had already questioned himself about it. So, his objective was to test if inclusion of a covariance term in error propagation improved the analysis. To do it, he presents a general method for obtaining error propagation equation that includes the covariance term. He concluded that least-squares parameters were normally correlated, such as $y = ax + b$. So, when functions were normally distributed, correlation must be considered, and hence covariance. His formalism was used in this project. Tellinghuisen (2001) started with the error propagation matrix.

$$\sigma_f^2 = g^T V g \quad (1)$$

In which σ_f^2 is the variance in some function f of a set of parameters β with the i th element in the vector g being $\partial f / \partial \beta_i$. V is the variance-covariance matrix of those parameters. And g^T the transpose of g .

Then, he applied this approach to several functions. However, the one that was interesting for this project was equation 2 due to the concentration of metals being a ratio of the analyte to the mass of sea salt and mineral water weighed.

$$f = b/a \quad (2)$$

To build equation 1 from 2, he did the partial derivatives of f and obtained g^T vector. Which was $g^T = (-\frac{b}{a^2}, \frac{1}{a})$. Then, he completed the equation 1 transforming it into equation 3.

$$\sigma_f^2 = \begin{bmatrix} -\frac{b}{a^2} & \frac{1}{a} \end{bmatrix} \begin{bmatrix} \sigma_a^2 & \sigma_{ab}^2 \\ \sigma_{ab}^2 & \sigma_b^2 \end{bmatrix} \begin{bmatrix} -\frac{b}{a^2} \\ \frac{1}{a} \end{bmatrix} \quad (3)$$

Finally, he developed equation 3 and divided it by equation 2 and he obtained equation 4.

$$\left(\frac{\sigma_f}{f}\right)^2 = \left(\frac{\sigma_a}{a}\right)^2 + \left(\frac{\sigma_b}{b}\right)^2 - \frac{2\sigma_{ab}^2}{ab} \quad (4)$$

Where related to the results obtained from the experiments of this project; σ_f is the standard deviation of the results obtained, σ_a of sea salt mass (or mineral water mass), σ_b of metal concentration and σ_{ab} is the covariance between metal concentration and sample mass. f is the average of the metal and sample ratio, a of the sea salt or mineral water mass and b of the metal. In order to calculate the covariance term two methods are proposed. The first one isolates the covariance term and the second one focus on forming a trend line equation.

This point is where data is used to assess it. The averages and standard deviations of the ratio, sea salt or mineral water mass and metal mass are known. So, the actual variance obtained is compared to the variance of error propagation where covariance is neglected (equation 5).

$$\left(\frac{\sigma_f}{f}\right)^2 = \left(\frac{\sigma_a}{a}\right)^2 + \left(\frac{\sigma_b}{b}\right)^2 \quad (5)$$

The difference between equation 4 and 5 will be the covariance term allowing isolated assessment of covariance (equation 6).

$$\sigma_{ab}^2 = \frac{ab}{2} \left(\frac{\sigma_a}{a}\right)^2 + \frac{ab}{2} \left(\frac{\sigma_b}{b}\right)^2 - \frac{ab}{2} \left(\frac{\sigma_f}{f}\right)^2 \quad (6)$$

On the other hand, if the second method is tracked, the linear function obtained is the following one.

$$\frac{ab}{2} \left(\frac{\sigma_f}{f}\right)^2 = \frac{ab}{2} \left(\frac{\sigma_a}{fa}\right)^2 + \frac{ab}{2} \left(\frac{\sigma_b}{b}\right)^2 - \sigma_{ab}^2 \quad (7)$$

Where σ_{ab}^2 term is the intersection of the trend line with the y-axis.

These are the two ways that the covariance term is calculated in this project. If it is zero or compared to the other sigma terms is very small, it can be neglected. However, if it is different from zero and comparable to the other sigma terms, then it must be considered.

5. EXPERIMENTAL PART

The reagents used for the experiments were zinc solution, calcium solution, magnesium solution, nitric acid, ultrapure deionised water, sea salt and mineral water. Zinc, calcium and magnesium solutions (1000 ppm) are certified standards for AAS (Sigma Aldrich). Nitric acid (70 %) was also from Sigma Aldrich. Ultrapure deionised water (18 M Ω) was obtained from the laboratory sources (manufacturer Del system). Sea salt (Smart Spice Coarse Sea Salt) and mineral water (Carrick Glen) samples were obtained from local shops (Mineral water was obtained from Lidl).

The material used was volumetric flasks of 500 ml, 50 ml and 10 ml (class B); one graduated cylinder and micropipettes of 0.1-2 μ l, 0.5-10 μ l, 10-100 μ l, 100-1000 μ l, 20-200 μ l (BioPette Plus) and 0.5-5 ml (Finnipipette F2). All glassware material was cleaned, rinsed with deionised water, and then rinsed with ultrapure deionised water (18 M Ω).

The instrument used was ICP-OES (Optima 2100 DV) from Perkin-Elmer. The wavelengths used were 206.200 nm for zinc, 317.933 nm for calcium and 285.213 nm for magnesium.

In order to determine error correlation, five different experiments were set and stock solutions of zinc (10 ppm), calcium (100 ppm) and magnesium (100 ppm) were performed.

In the first one zinc in sea salt was analysed. Fifteen standard solutions were prepared (0 ppm to 3 ppm) in dilute 1 % nitric acid. Also, four sets of sea salt samples were performed (0.01 g, 0.1 g, 0.5 g and 1 g) with five replicates each.

For the second experiment, fifteen standard solutions were prepared with calcium (0 ppm to 27.5 ppm) and magnesium (0 ppm to 57.5 ppm) together. The same four sets of samples with their replicates as before were performed, and then diluted 1000 times each.

For the third experiment, four different blanks were analysed in order to determine if sea salt concentration in samples affects the base-line. Four samples of sea salt from 0 ppm to 1000 ppm were studied.

As a result of the matrix effect for the fourth experiment four sets of six sea salt standards were performed for calcium and magnesium (0 ppm to 2.5 ppm). Each set of standards had a different concentration of sea salt as internal pattern (10 ppm, 100 ppm, 500 ppm and 1000 ppm). Samples were prepared as in the third experiment.

For the fifth experiment, mineral water samples were used due to a simpler matrix. Eight standards were prepared for calcium (0 ppm to 10 ppm) and magnesium (0 ppm to 3 ppm). Samples were performed as sea salt samples changing the initial mass of mineral water (0.1 g, 0.5 g, 1 g and 2 g).

All standards and samples were analysed by ICP-OES. For each trial 10 replicate measurements were completed to assess the mean and standard deviation using MS Excel.

6. RESULTS AND DISCUSSION

The aims of the project are to learn how to calculate error covariance and assess if it is relevant to consider it or not in error propagation. To do it, five experiments were needed to be run. They were labelled in chronological order from experiment 1 to 5.

Experiment 1 consisted in the analysis of zinc concentration in sea salt sample by ICP-OES in order to determine if there is a relation between them. For this reason, four sets of samples were performed. During the sample analysis, from ICP-OES window it was observed that the plasma colour changed from green to orange due to the presence of sodium in sea salt. The data obtained is collected in table 1.

Salt (g)	Zn (mg)
0.0102	8.57E-04
0.1019	-1.41E-04
0.5022	-5.60E-04
1.0103	-8.48E-04

Table 1. Averages of the results obtained in zinc detection analysis by ICP-OES in sea salt samples.

It can be noticed that while sea salt mass is increasing, zinc abundance is decreasing. This fact is not logical. What was suspected was that the measurements were done near to the detection limit, as zinc is a trace element in sea salt. The aim of the project is not to detect zinc in sea salt samples, but to study covariance between two analytes. As a result, the experiment needed to change, which leads to experiment 2.

Salt (g)	Ca (mg)	Mg (mg)
0.0108	-1.18E+01	-2.30E+02
0.1011	6.22E+01	-2.49E+02
0.5022	4.43E+02	-2.21E+02
1.0103	9.04E+02	-1.86E+02

Table 2. Averages of the results obtained in calcium and magnesium detection by ICP-OES in sea salt samples.

During the second experiment zinc detection was changed to calcium and magnesium, which are more concentrated elements in sea salt. The results obtained are condensed in table 2.

In this case, calcium values seem reasonable, where calcium concentrations and sea salt masses increase simultaneously. However, it does not happen for magnesium, where the values are roughly constant. Once more, focusing on the aim of the project, a perfect calcium and magnesium detection is not required. Thus, given that the values of calcium seemed reasonable, they were used to calculate the covariance term. The results obtained are discussed in more detail further on this section.

Still, the negative value issue was producing problems to continue with the covariance analysis. Therefore, a further explanation about what was happening was investigated. The wavelength behaviour was checked. The spectra obtained are collected in figures 1, 2 and 3.

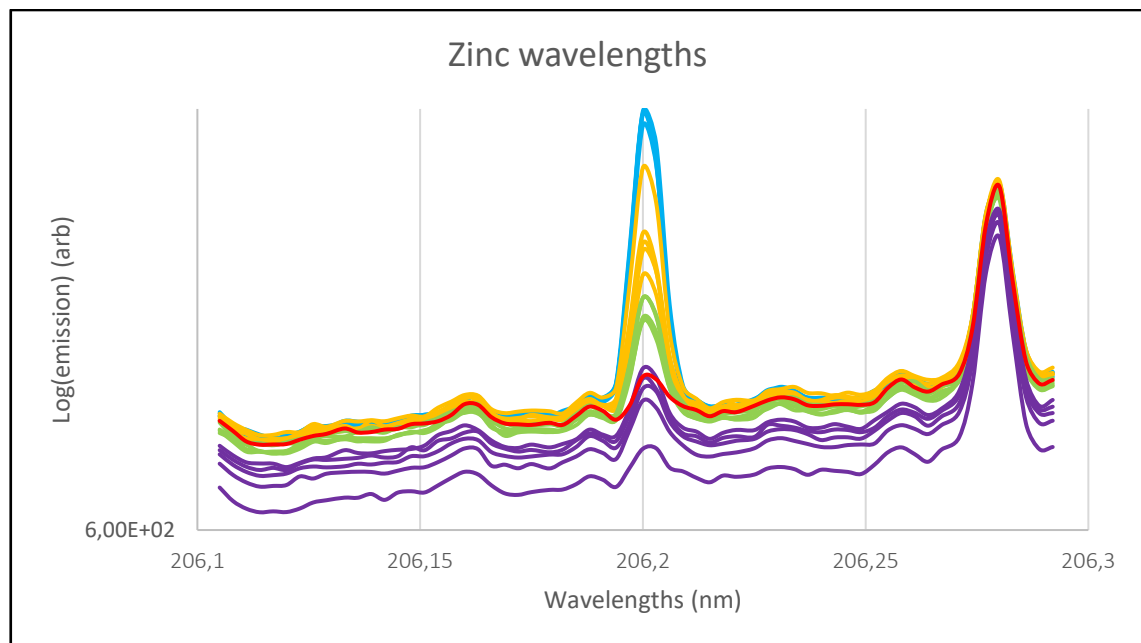


Figure 1. Spectra of logarithmic emission of zinc concentration in sea salt samples. Blank base-line is coloured in red. 0.01 g sea salt masses are coloured in blue. 0.1 g sea salt masses are coloured in orange. 0.5 g of sea salt masses are coloured in green. 1 g sea salt masses are coloured in purple.

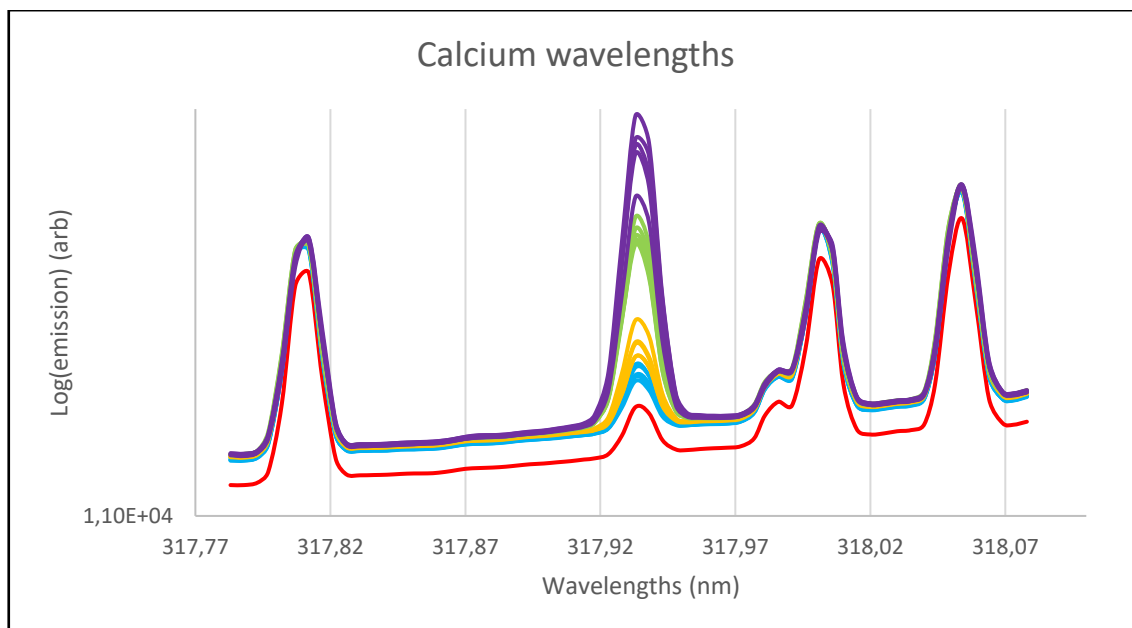


Figure 2. Spectra of logarithmic emission of calcium concentration in sea salt samples. Blank base-line is coloured in red. 0.01 g sea salt masses are coloured in blue. 0.1 g sea salt masses are coloured in orange. 0.5 g of sea salt masses are coloured in green. 1 g sea salt masses are coloured in purple.

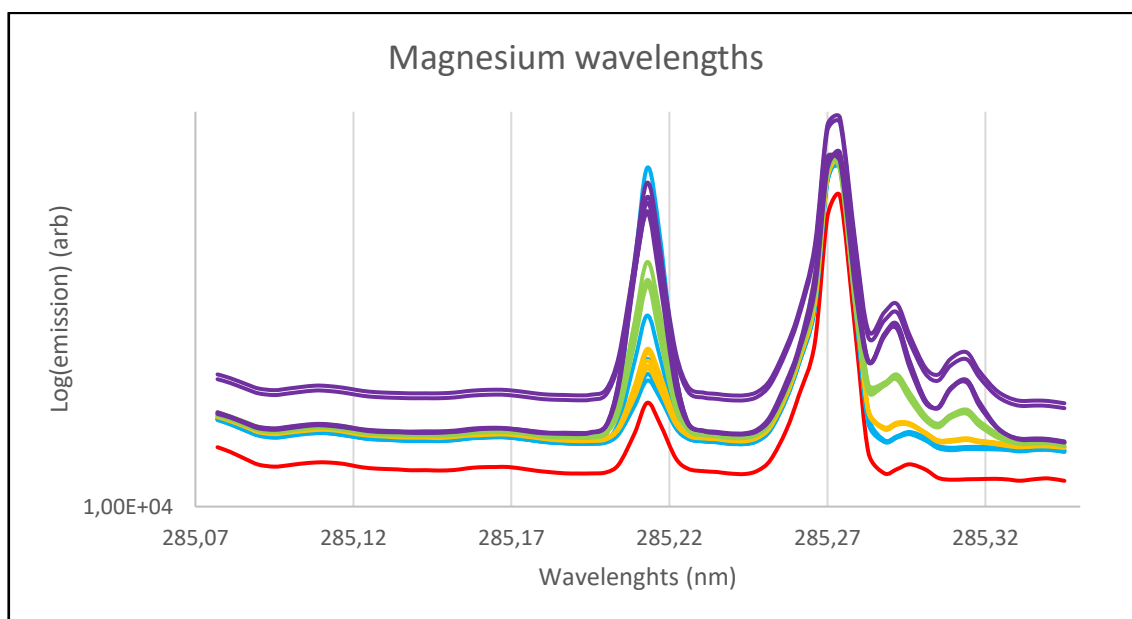


Figure 3. Spectra of logarithmic emission of magnesium concentration in sea salt samples. Blank base-line is coloured in red. 0.01 g sea salt masses are coloured in blue. 0.1 g sea salt masses are coloured in orange. 0.5 g of sea salt masses are coloured in green. 1 g sea salt masses are coloured in purple.

As it can be observed, the base-lines have different heights. It was suspected that this caused zinc and magnesium to have negative values. So, it was thought that there might be a matrix effect that affect the results. Moreover, it was questioned if there was correlation between the base-line and the amount of sea salt analysed.

For these reasons, a third experiment was performed to check if sea salt matrix effect was present. Experiment 3 consisted of measuring four different solutions with different concentrations of sea salt (0 ppm, 10 ppm, 100 ppm and 1000 ppm). The ion measured in that experiment was sodium. Due to 1000 ppm sea salt solution being too concentrated, it could not be determined. The spectra obtained for the other three concentrations are concentrated in figure 4.

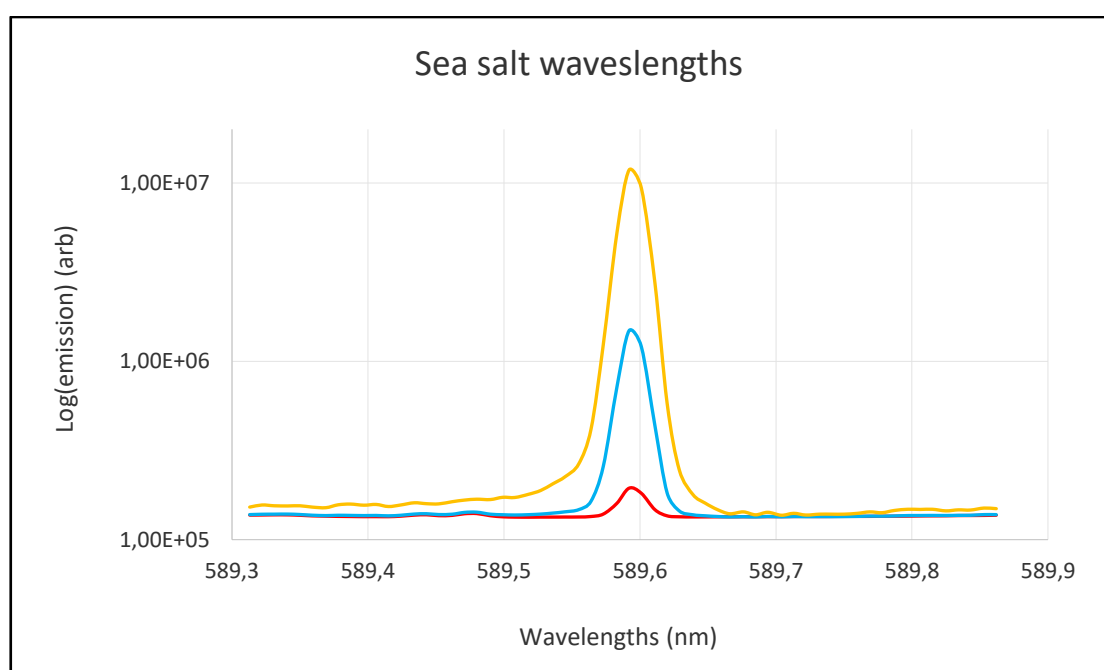


Figure 4. Spectra of logarithmic emission of sodium concentration in sea salt samples. 0 ppm sea salt concentration is coloured in red. 10 ppm sea salt concentration is coloured in blue. 100 ppm sea salt concentration is coloured in orange.

Studying the data obtained, it can be observed that there is a relation between sea salt concentration and instrumental base-line. To find out if that relation is defined or not, the results were plotted. Figure 5 shows that a linear relation between them exists, hence, they are proportionally related. Moreover, it can be concluded that sea salt

matrix affects ICP-OES plasma temperature. Still, it was not analysed in more detail due to the lack of time for looking for more information.

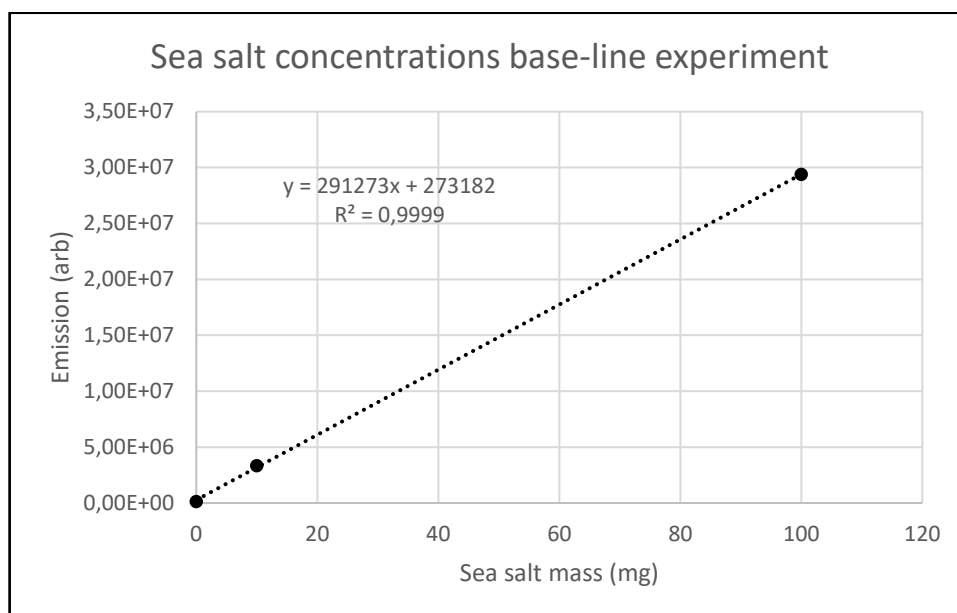


Figure 5. Linear regression of emission versus sea salt masses prepared for experiment 3.

However, as highlighted above, the aims of this project are not related to the matrix effect. Nevertheless, the matrix effect was considered to perform in the next experiments. Due to the short time left in laboratory, two experiments were set and completed at the same time.

Experiment 4 was carried out by splitting the standards for each mass of sea salt. Each set of standards contained an internal pattern of sea salt in order to reduce the matrix-effect, and to have the instrumental base-line at the same level as the samples.

Figures 6, 7, 8 and 9 show magnesium concentration spectra in sea salt samples. Except for 0.1 g sea salt samples, the correlation was not corrected at all.

Calcium graphs are not included; however, they show the same trend as magnesium's.

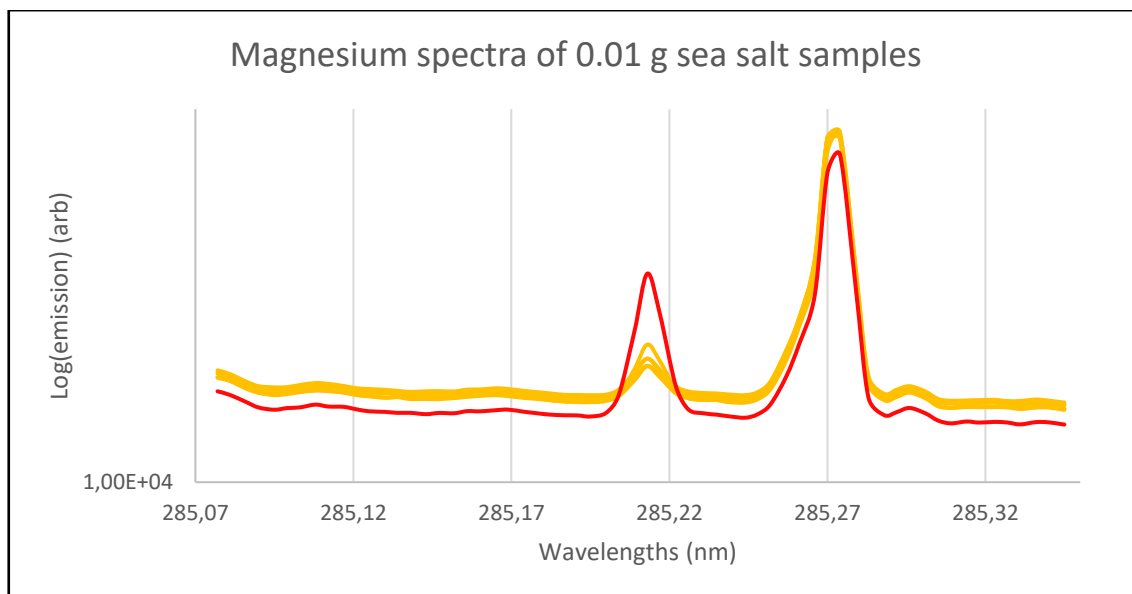


Figure 6. Spectra of logarithmic emission of magnesium concentration in sea salt samples. Blank is coloured in red. 0.01 g sea salt masses are coloured in orange.

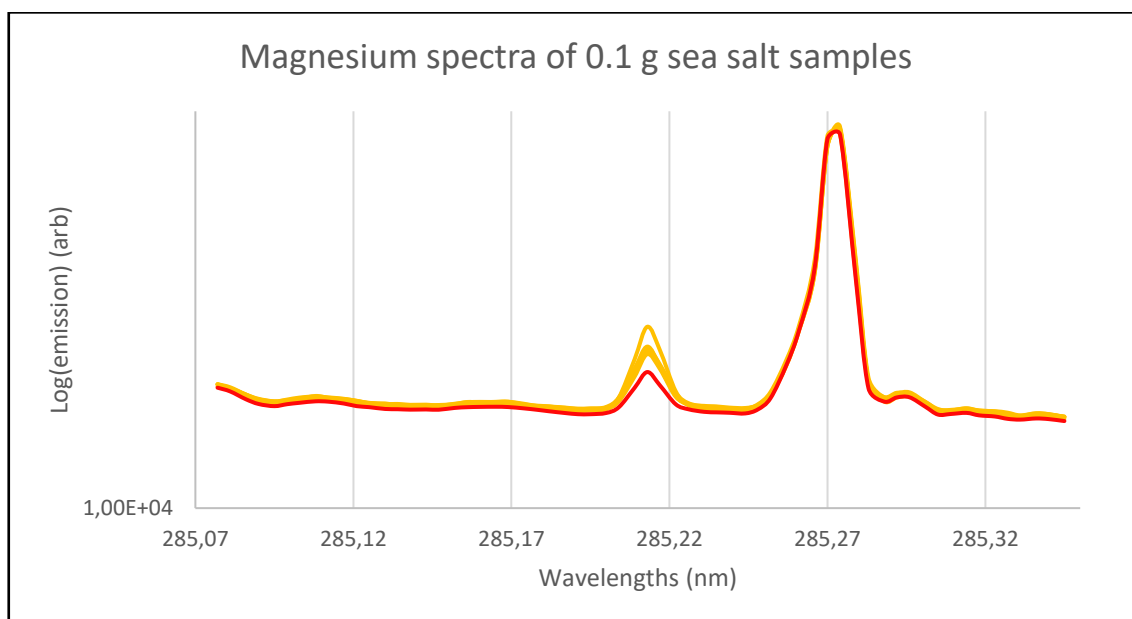


Figure 7. Spectra of logarithmic emission of magnesium concentration in sea salt samples. Blank is coloured in red. 0.1 g sea salt masses are coloured in orange.

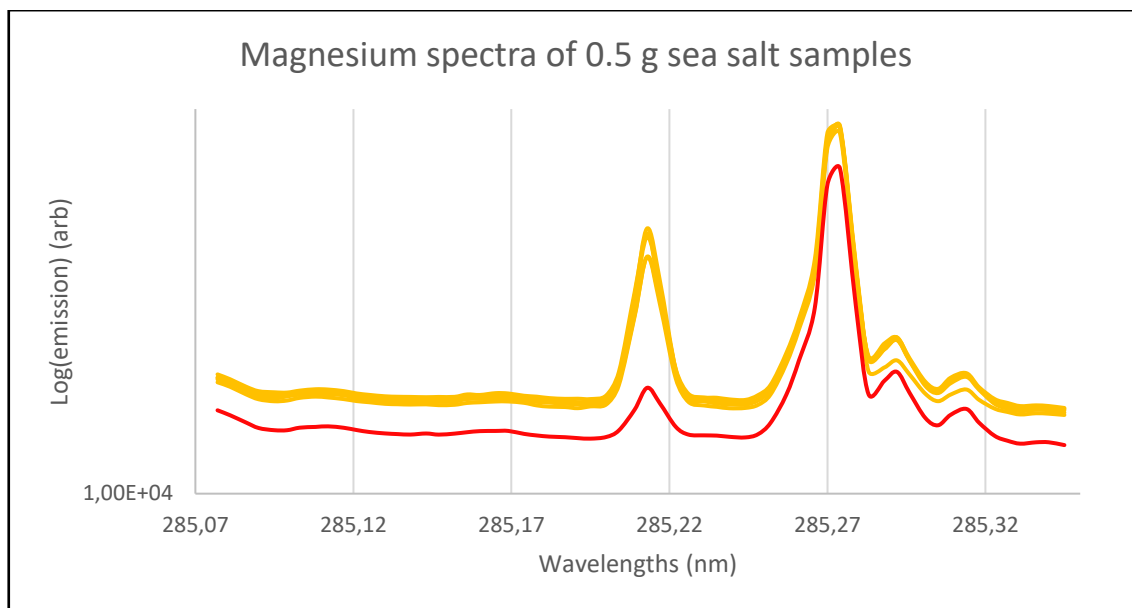


Figure 8. Spectra of logarithmic emission of magnesium concentration in sea salt samples. Blank is coloured in red. 0.5 g sea salt masses are coloured in orange.

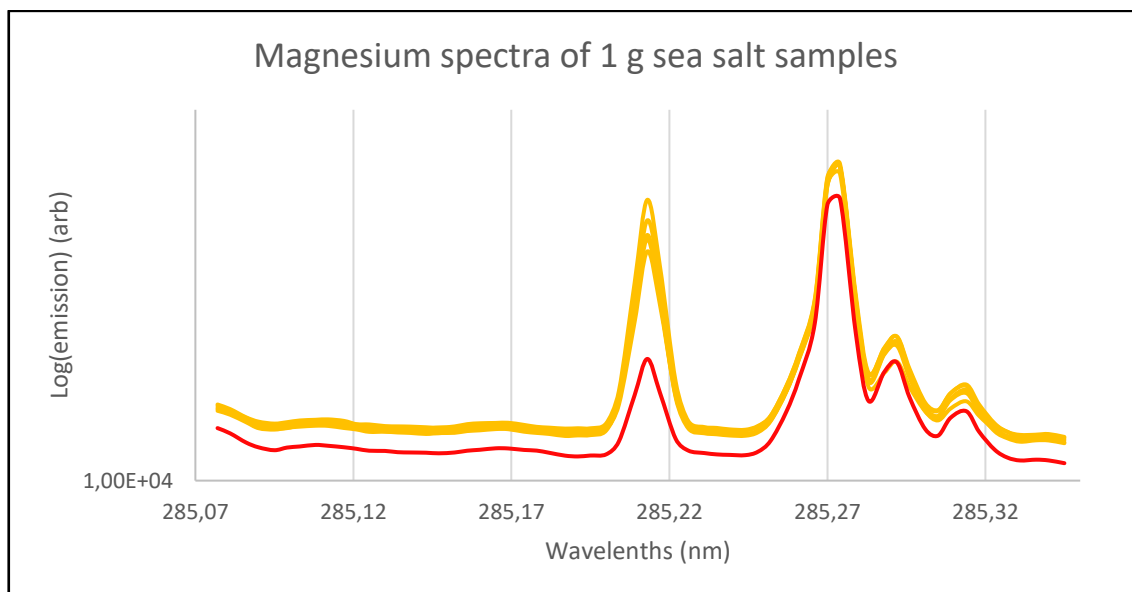


Figure 9. Spectra of logarithmic emission of magnesium concentration in sea salt samples. Blank is coloured in red. 1 g sea salt masses are coloured in orange.

Even though the results were not very good, covariance was been able to calculate for both elements. Even though it is not a good analysis of sea salt, the data can be used because the focus of the project is the covariance term. For this reason, despite of 0.01 mg/g sea salt samples were negative, error correlation was calculated. In case calcium and magnesium concentration were analysed with other purposes, those values should

be neglected and concluded that for this sea salt mass no calcium nor magnesium were detected. As the previous experiment, the covariance results will be discussed further on.

Experiment 5 was made by changing the sample analysed into mineral water, which has a simpler matrix. Also, the spectra were checked to see if matrix-effect existed or not. The data obtained for calcium concentrations are condensed in figure 10. In this case, correlation is softer and it cannot be appreciated.

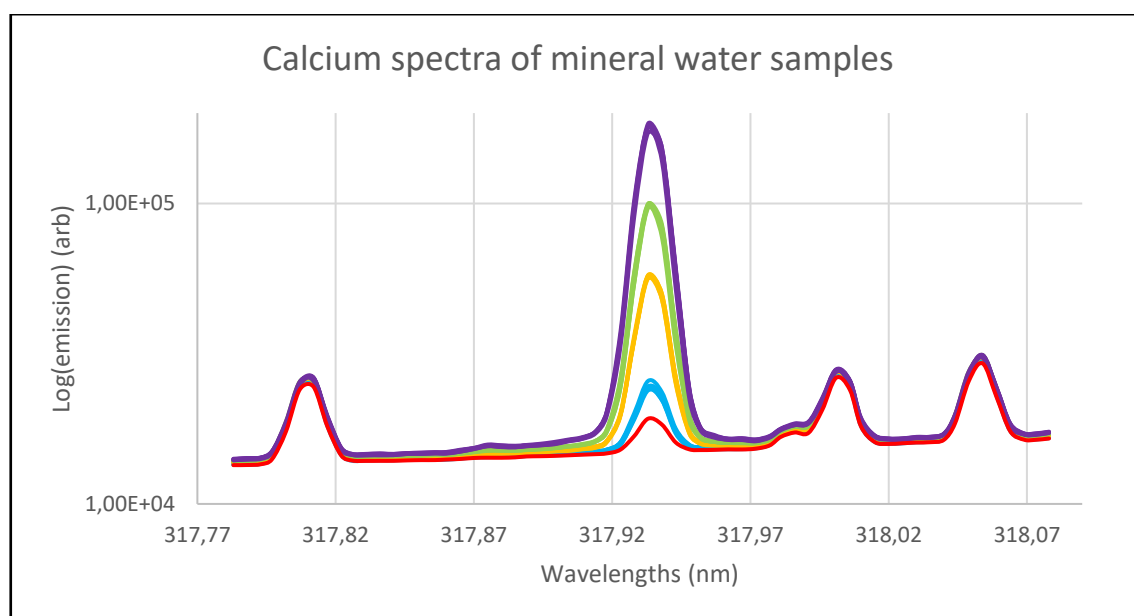


Figure 10. Spectra of logarithmic emission of calcium concentration in mineral water samples. Blank base-line is coloured in red. 0.1 g mineral water mass is coloured in blue. 0.5 g mineral water mass is coloured in orange. 1 g of mineral water mass is coloured in green. 2 g mineral water mass is coloured in purple.

Magnesium's spectra were similar to calcium's. Thus, covariance term was been able to calculate for both elements.

As it was clarified previously, no further importance was given to the base-line problems. The objective of this project is not based on the quantification of metals in sea salt or water, but on the covariance between two variables. For this reason, from now on, the discussion will be focused on covariance.

As explained in the theoretical section, two methods were applied to calculate σ_{ab}^2 , which is the covariance term. The data of the previous experiments are collected in tables and figures, which can be found further on and in the appendix.

The first covariance term calculated was the one related to the calcium results from experiment 2. The data obtained using the first and second methods are collected in table 3. It includes the propagated error without considering covariance, the actual error propagation and the difference between them, which is the covariance term (σ_{ab}^2) calculated by the first method. Moreover, the propagated error was plotted against the actual error and the other way around. The intersection between the trend line and the y-axis gives the covariance term values. To see the plots, go to the appendix (figures 11 and 12).

Salt (g)	Ca (mg)	Propagated error	Actual error	Individual σ_{ab}^2	Trend line σ_{ab}^2 (prop vs actual)	Trend line σ_{ab}^2 (actual vs prop)
0.0108	-0.0118	-2.54E-04	-2.58E-04	3.98E-06	1.30E-04	-1.39E-04
0.1011	0.0622	1.74E-03	1.73E-03	1.34E-05		
0.5022	0.4426	2.17E-03	2.02E-03	1.44E-04		
1.0103	0.9038	1.51E-02	1.62E-02	-1.06E-03		

Table 3. Table for Ca/Salt results of experiment 2 using method 1 and 2.

The results obtained from experiment 4 are condensed in the subsequent tables, which include the same information as in experiment 2. Plots were also made, see appendix (figures 13 – 18). The ratios that are studied for this experiment are Ca/Salt, Mg/Salt and Mg/Ca.

Salt (g)	Ca (mg)	Propagated error	Actual error	Individual σ_{ab}^2	Trend line σ_{ab}^2 (prop vs actual)	Trend line σ_{ab}^2 (actual vs prop)
0.0098	-0.0408	-3.17E-05	-3.20E-05	2.34E-07	-3.52E-05	3.49E-05
0.1008	0.0713	5.10E-04	5.15E-04	-5.60E-04		
0.5003	0.4838	5.96E-03	5.98E-03	-2.30E-04		
1.0032	0.8681	2.01E-02	1.98E-02	3.00E-03		

Table 4. Table for Ca/Salt results of experiment 4 using method 1 and 2.

Salt (g)	Mg (mg)	Propagated error	Actual error	Individual σ_{ab}^2	Trend line σ_{ab}^2 (prop vs actual)	Trend line σ_{ab}^2 (actual vs prop)
0.0098	-0.0051	-7.60E-06	-7.60E-06	-1.43E-07	-1.16E-06	1.15E-06
0.1008	0.0080	2.71E-05	2.71E-05	-3.87E-08		
0.5003	0.0320	1.48E-04	1.48E-04	-4.32E-07		
1.0032	0.0425	3.77E-04	3.68E-04	8.68E-06		

Table 5. Table for Mg/Salt results of experiment 4 using method 1 and 2.

Ca (mg)	Mg (mg)	Propagated error	Actual error	Individual σ_{ab}^2	Trend line σ_{ab}^2 (prop vs actual)	Trend line σ_{ab}^2 (actual vs prop)
-0.0408	-0.0051	4.83E-05	3.88E-05	9.51E-06	-	-
0.0713	0.0080	5.96E-05	4.65E-05	1.31E-05		
0.4838	0.0320	5.24E-04	2.06E-04	3.18E-04		
0.8681	0.0425	1.18E-03	7.02E-04	4.74E-04		

Table 6. Table for Mg/Ca results of experiment 4 using method 1 and 2.

For experiment 5, the same ratios were studied. The tables that contain the data related to them are collected below. Moreover, plots were performed and they can be found in the appendix (figures 19 - 28).

Water (g)	Ca (mg)	Propagated error	Actual error	Individual σ_{ab}^2	Trend line σ_{ab}^2 (prop vs actual)	Trend line σ_{ab}^2 (actual vs prop)
0.0982	3.4036	1.22E-03	7.99E-04	4.25E-04	1.19E-03*	-1.94E-03*
0.4995	20.2571	1.39E-03	2.40E-04	1.15E-03		
0.9957	41.0638	2.03E-03	1.50E-03	5.29E-04		
1.9997	83.9694	4.04E-03	4.64E-03	-5.95E-04		

Table 7. Table with error propagation for Ca/Water results of experiment 5 using method 1 and 2. (*) 0.0982 g of water sample errors were not used to calculate the trend line terms.

Water (g)	Mg (mg)	Propagated error	Actual error	Individual σ_{ab}^2	Trend line σ_{ab}^2 (prop vs actual)	Trend line σ_{ab}^2 (actual vs prop)
0.0982	1.4102	1.52E-04	8.92E-05	6.33E-05	4.23E-04*	-6.02E-04*
0.4995	7.5575	5.14E-04	1.08E-04	4.06E-04		
0.9957	15.1484	7.64E-04	5.27E-04	2.37E-04		
1.9997	30.8631	1.25E-03	1.17E-03	7.91E-05		

Table 8. Table with error propagation for Mg/Water results of experiment 5 using method 1 and 2. (*) 0.0982 g of water sample errors were not used to calculate the trend line terms.

Ca (mg)	Mg (mg)	Propagated error	Actual error	Individual σ_{ab}^2	Trend line σ_{ab}^2 (prop vs actual)	Trend line σ_{ab}^2 (actual vs prop)
3.4036	1.4102	2.10E-02	3.94E-03	1.70E-02	-	-
20.2571	7.5575	3.16E-02	1.50E-03	3.01E-02		
41.0638	15.1484	6.02E-02	2.41E-02	3.60E-02		
83.9694	30.8631	1.13E-01	1.85E-01	-7.20E-02		

Table 9. Table with error propagation for Mg/Ca results of experiment 5 using method 1 and 2.

For Ca/Water and Mg/Water ratios, when covariance was calculated using trend lines a Horwitz curve was detected. It might have appeared in consequence of working near the detection limit and background noise interferes²⁴. If 0.0982 g of water is neglected a straight-line is obtained and Horwitz curve disappears. For this reason, this point was neglected in order to calculate the covariance term. The plots related to it can be found at the appendix (figures 20, 22, 24 and 26). For Mg/Ca ratio, the same happens, however when the first point is neglected, a straight-line does not appear. For this reason, covariance term could not be calculated by this way.

Using one method or the other can be spotted some differences, due to the first method gives more than one result for the covariance term, whereas the second just gives one value. However, if using the data obtained by the first method and an absolute range is provided, it can be noticed that the absolute values obtained by the second method are included in each range.

Moreover, when the second method is used and the propagated error is plotted against the actual error gives a different value rather when they are plotted the other way around. This difference might be related to the heteroscedasticity of linear regression.

The only two ones trend line σ_{ab}^2 that could not be calculated are Mg/Ca ratios of both experiment 4 and 5. Since the graphic shapes are not straight-lines (see figures 7, 8, 17 and 18). Their shape seems to follow an exponential approach.

From the data obtained, it can be concluded that the results that follow a linear regression approach have a constant covariance term (σ_{ab}^2), whereas the other ones the covariance term still has an effect, but it is not constant. Both ways, σ_{ab}^2 has an important effect on error propagation and it must be considered.

7. CONCLUSIONS

7.1 English Conclusions.

Zinc, calcium and magnesium detection of sea salt and mineral water samples by ICP-OES helped to demonstrate that covariance must be considered in error propagation. Hence, it confirms covariance existence in correlated variables or in ratio concentrations.

Furthermore, this project is an example that can be followed to calculate covariance in simple experiments with two variables using two different ways to calculate the covariance term.

One of the reasons that there have been some problems in sea salt samples is because sea salt concentration changes plasma emission base-lines. It might be for this reason that Escudero and others (2010) and Kagaya and others (2009) do pre-treatments before sea salt analysis. Another cause could be due to the laboratory material not being clean enough and traces of calcium and magnesium from water might have contaminated sea salt samples. For this reason, experiment 5 sample was changed to mineral water, which is a simpler system.

If extra time could have been used to improve the project, a better study of sea salt matrix effect in ICP-OES could have been performed. By doing experiments in sodium, calcium and magnesium special material. Or by studying in more detail what effect the sea salt has on the plasma that makes it change its base emission line.

Moreover, more sets of diverse masses of sea salt or mineral water would have been measured to fill and improve the straight-line obtained, that relates propagated and actual error.

For a future investigation, the difference between individual covariance and trend line covariance can be studied in more detail. In addition, a more complicated experiment could be performed, like three variables related between them, such as in Longford (2010).

Few scientists use covariance to calculate uncertainty. Most of them are related to geochemistry or to life cycle assessment (LCA)^{3,9}. Looking at the results obtained, it would be important to extend its knowledge in other chemical fields. This way, where more accurate results are needed, they will be obtained, such as in Oksanen and Sarjakoski (2005) or Keene and others (1986).

Moreover, it would be important to introduce covariance to chemistry students. When error propagation is taught usually error covariance is ignored, and sometimes, not even explained its existence. One example of the previous affirmation is that in most books, covariance is neglected¹⁹⁻²². Another example is Rasul and others (2018), because they want to introduce error propagation in Bangladesh and they do not mention covariance.

However, there are few books that explain what covariance is and how it should be calculated^{10,25}. Also, some articles want to teach covariance to students, like Schmitz and Schoene (2007).

To sum up, covariance exists in ratio concentrations and it can be calculated by at least two different ways. Therefore, if covariance is included in error propagation, more accurate uncertainty calculation will be.

7.2 Catalan Conclusions.

La detecció de zinc, calci i magnesi en mostres de sal marina i aigua mineral mitjançant ICP-OES ha ajudat a demostrar que la covariància ha de ser considerada en la propagació d'errors. Per tant, es confirma l'existència de la covariància en variables correlatives o en la relació de concentracions.

Altrament, aquest projecte es pot fer servir com una guia a seguir per calcular la covariància en experiments senzills amb dues variables utilitzant dos mètodes diferents, per tal de calcular el terme de la covariància.

Una de les raons per la qual hi ha hagut problemes en les mostres de sal marina és degut a que la concentració de sal canvia les línies bases dels espectres d'emissió. És possible que per aquest motiu que Escudero and others (2010) i Kagaya and other (2009) fan

pretractaments a les mostres de sal marina abans dels anàlisis. Una altra causa podria ser deguda a què al material del laboratori no estigui prou net. Pot ser que traces de calci i magnesi de l'aigua, que es fa servir per rentar el material, hagin contaminat les mostres. Per aquestes raons, en el cinquè experiment, la mostra es canviada per aigua mineral, que és una matriu més senzilla.

Si s'hagués tingut més temps per millorar el projecte, un millor estudi de l'efecte de la matriu de la sal marina en l'ICP-OES s'hagués efectuat. Una opció hagués sigut l'anàlisi de sodi, calci i magnesi utilitzant material especial expressament destinat a experiments d'aquests elements. O bé, estudiant en més detall quin efecte té la sal marina en el plasma que li fa canviar la línia base d'emissió.

A més a més, si s'hagués disposat de més temps, més sets de diverses masses de sal marina o aigua mineral es podrien haver mesurat per tal de completar i millorar la recta de regressió que relaciona l'error propagat (propagated error) i el real (actual error).

Per investigacions futures, la diferència del càlcul de la covariància entre els dos mètodes pot ser estudiada en més detall. Per altra banda, un experiment més complex es podria dur a terme, com per exemple, estudiar la relació entre tres variables tal com Longford (2010) realitza.

Pocs científics utilitzen la covariància en el seu càlcul de la incertesa. La majoria d'ells estan relacionats en el camp de la geoquímica o de l'anàlisi del cicle de la vida (ACV) ^{3,9}. Analitzant els resultats obtinguts en el projecte, és important expandir la importància de la covariància en altres camps de la ciència. D'aquesta manera, on es necessitin resultats més precisos podran ser obtinguts, com per exemple, en Oksanen and Sarjakoski (2005), o bé, Keene and others (1986).

Per altra banda, també seria important introduir la covariància en els estudiants de química ja que, normalment, quan s'ensenya la propagació d'error, la covariància és ignorada i, a vegades, ni tant sols es nombra. Exemples que sostenen l'afirmació anterior són, que en molts llibres, la covariància és negligida^{19–22}. Un altre exemple és Rasul and others (2018), on es vol introduir la propagació d'errors en els laboratoris de Bangladesh, però en el seu article la covariància no és mencionada.

Tot i així, hi ha alguns llibres que sí que expliquen que és i com la covariància pot ser calculada^{10,25}. A més a més, s'han escrit alguns articles amb la intenció d'introduir la covariància en estudiants, com Schmitz and Schoene (2007).

En resum, la covariància existeix en les relacions de concentració i pot ser calculada seguint al menys dos mètodes. Per tant, si la covariància es inclosa en el càlcul de la propagació de l'error, la incertesa dels resultats obtinguts serà més precisa.

REFERENCES

- (1) Menger, F. M. Uncertainty in Chemistry. *Nat. Chem.* **2010**, 2 (9), 698-700. <https://doi.org/10.1038/nchem.799>.
- (2) Wernick, B. The Issue with Tissue-Does Size (of Uncertainty in Chemistry Data) Matter? *Integrated Environmental Assessment and Management.* **2012**, 8, 196-197. <https://doi.org/10.1002/ieam.1262>.
- (3) Heijungs, R.; Lenzen, M. Error Propagation Methods for LCA-a Comparison. *Int. J. Cycle Assess* **2014**, 19, 1445-1461. <https://doi.org/10.1007/s11367-014-0751-0>.
- (4) Rasul, S.; Kajal, A. M.; Khan, A. Quantifying Uncertainty in Analytical Measurements. *J. Bangladesh Acad. Sci.* **2018**, 41 (2), 145-163. <https://doi.org/10.3329/jbas.v41i2.35494>.
- (5) Keene, W. C.; Pszeny, A. A. P.; Galloway, J. N.; Hawley, M. E. Sea-Salt Corrections and Interpretation of Constituent Ratios in Marine Precipitation *J. Geophysiolocal Research* **1986**, 91, 6647-6658.
- (6) Oksanen, J.; Sarjakoski, T. Error Propagation of DEM-Based Surface Derivatives. *Comput. Geosci.* **2005**, 31, 1015-1027. <https://doi.org/10.1016/j.cageo.2005.02.014>.
- (7) Cambridge Dictionary. <https://dictionary.cambridge.org/dictionary/english/ratio> (accessed Jan 30, 2019).
- (8) Longford, N. T. Analysis of Covariance Introduction and Essentials. **2010**, 18-24.
- (9) Schmitz, M. D.; Schoene, B. Derivation of Isotope Ratios, Errors, and Error Correlations for U-Pb Geochronology Using ^{205}Pb - ^{235}U -(^{233}U)-Spiked Isotope Dilution Thermal Ionization Mass Spectrometric Data. *Geochemistry, Geophys. Geosystems* **2007**, 8 (8), 1-20. <https://doi.org/10.1029/2006GC001492>.
- (10) ProQuest Ebook Central - Reader <https://ebookcentral.proquest.com/lib/ntuuk/reader.action?docID=691865> (accessed Apr 15, 2019).

- (11) Groen, E. A.; Heijungs, R.; Bokkers, E. A. M.; De Boer, I. J. M. Methods for Uncertainty Propagation in Life Cycle Assessment. *Environmental Modelling & Software* **2014**, 62, 316-325. <https://doi.org/10.1016/j.envsoft.2014.10.006>.
- (12) Min Hwang, I.; Yang, J.-S.; Hyun Kim, S.; Jamila, N.; Khan, N.; Su Kim, K.; Seo, H.-Y.; Hwang, M. Elemental Analysis of Sea, Rock, and Bamboo Salts by Inductively Coupled Plasma-Optical Emission and Mass Spectrometry. *Anal. Lett.* **2016**, 49, 2807-2821. <https://doi.org/10.1080/00032719.2016.1158831>.
- (13) Kagaya, S.; Mizuno, T.; Tohda, K. Inductively Coupled Plasma Atomic Emission Spectrometric Determination of 27 Trace Elements in Table Salts after Coprecipitation with Indium Phosphate. *Talanta* **2009**, 79, 512-516. <https://doi.org/10.1016/j.talanta.2009.04.025>.
- (14) Escudero, L. A.; Martinez, L. D.; Salonia, J. A.; Gasquez, J. A. Determination of Zn(II) in Natural Waters by ICP-OES with on-Line Preconcentration Using a Simple Solid Phase Extraction System. *Microchemical Journal* **2010**, 95, 164-168. <https://doi.org/10.1016/j.microc.2009.11.003>.
- (15) Tabrizi, A. B. Analytical, Nutritional and Clinical Methods Cloud Point Extraction and Spectrofluorimetric Determination of Aluminium and Zinc in Foodstuffs and Water Samples. *Food Chemistry* **2007**, 100, 1698-1703. <https://doi.org/10.1016/j.foodchem.2005.10.015>.
- (16) Dead Sea Bromine Company Ltd.; Researchers Submit Patent Application, "Magnesium Rich Drinking Water", for Approval. *Atlanta* **2012**.
- (17) Rajizadeh, A.; Mozaffari-Khosravi, H.; Yassini-Ardakani, M.; Dehghani, A. Effect of Magnesium Supplementation on Depression Status in Depressed Patients with Magnesium Deficiency: A Randomized, Double-Blind, Placebo-Controlled Trial. *Nutrition* **2017**, 35, 56-60. <https://doi.org/10.1016/j.nut.2016.10.014>.
- (18) Topolska, K.; Radosław, & Radzki, P.; Filipiak-Florkiewicz, A.; Florkiewicz, A.; Leszczyńska, T.; Cieślik, E. Fructan-Enriched Diet Increases Bone Quality in Female Growing Rats at Calcium Deficiency. *Plants Foods for Human Nutrition* **2018**, 73, 172-179. <https://doi.org/10.1007/s11130-018-0671-4>.

- (19) Currell, G. *Analytical Instrumentation*; Ando, D. J., Ed.; JOHN WILEY & SONS, 2000.
- (20) Jeffery, G. H.; Bassett, J.; Mendham, J.; Denney, R. C. *Quantitative Chemical Analysis*, 5th ed.; Vogel, Arthur Israel, 1989.
- (21) Harris, D. *Quantitative Chemical Analysis*, 9th ed.; Murphy, B., Bristow, A., Eds.; Parker, Kate, 2016.
- (22) Skoog, D.; West, D.; Holler, J.; Crouch, S. *Fundamentals of Analytical Chemistry*, 8th ed.; Kiselica, A., Ed.; Harris, David, 2004.
- (23) Tellinghuisen, J. Statistical Error Propagation. *J. Phys. Chem.* **2001**, *105*, 3917-3921.
- (24) Holland, R.; Rebmann, R.; Williams, C.; Hanley, Q. S. Fluctuation Scaling, Calibration of Dispersion, and Detection of Differences. *Anal. Chem.* **2017**, *89* (21), 11568-11575. <https://doi.org/10.1021/acs.analchem.7b02909>.
- (25) Series, P. S. *Vector Network Analyzer (VNA) Measurements and Uncertainty Assessment*.

APPENDIX

The plots obtained in the experiments can be found in this section.

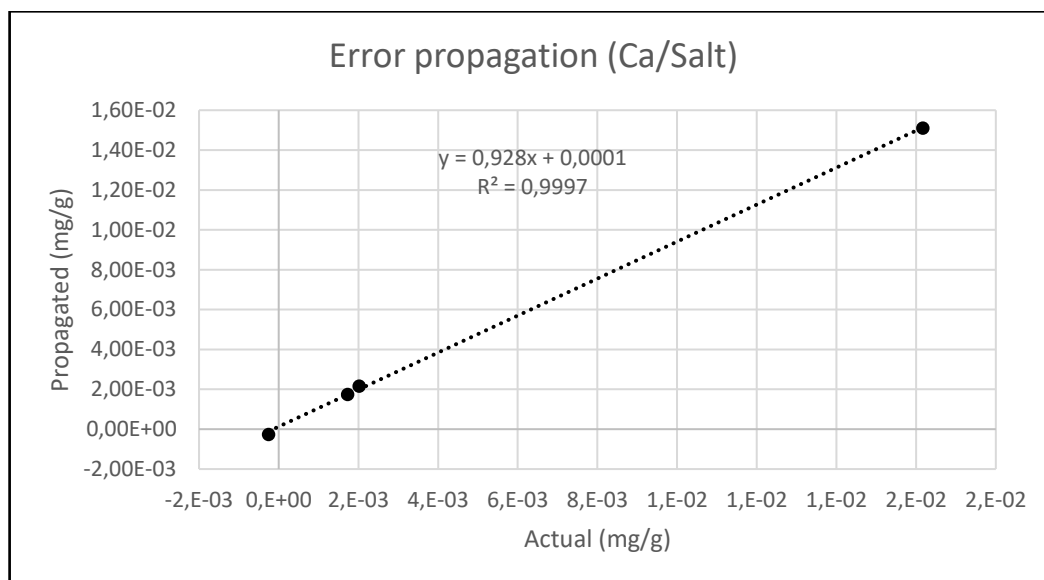


Figure 11. Trend line from Ca/Salt results of experiment 2 using method 2. Propagated error is plotted against actual error.

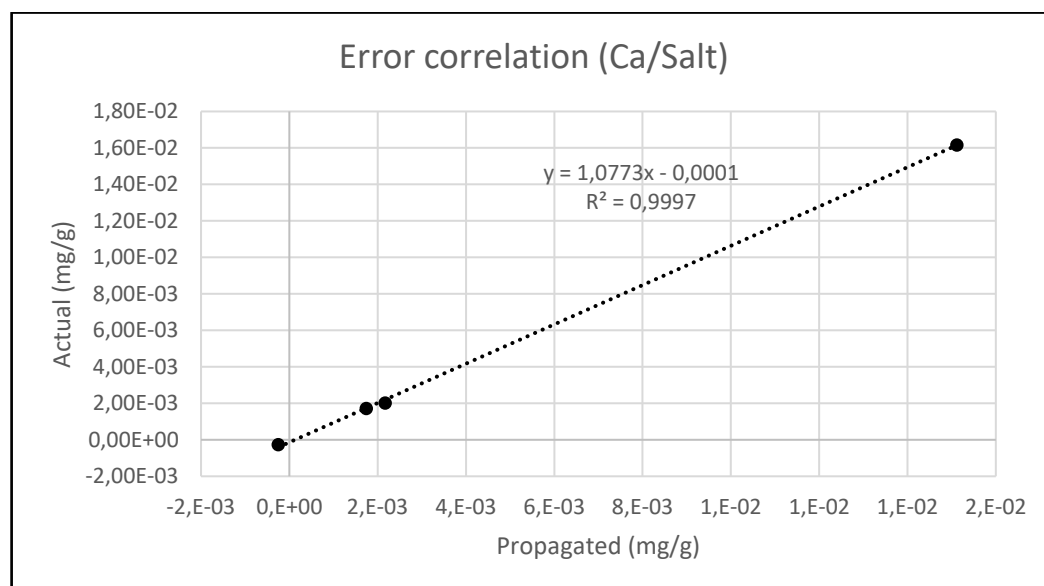


Figure 12. Trend line from Ca/Salt results of experiment 2 using method 2. Actual error is plotted against propagated error.

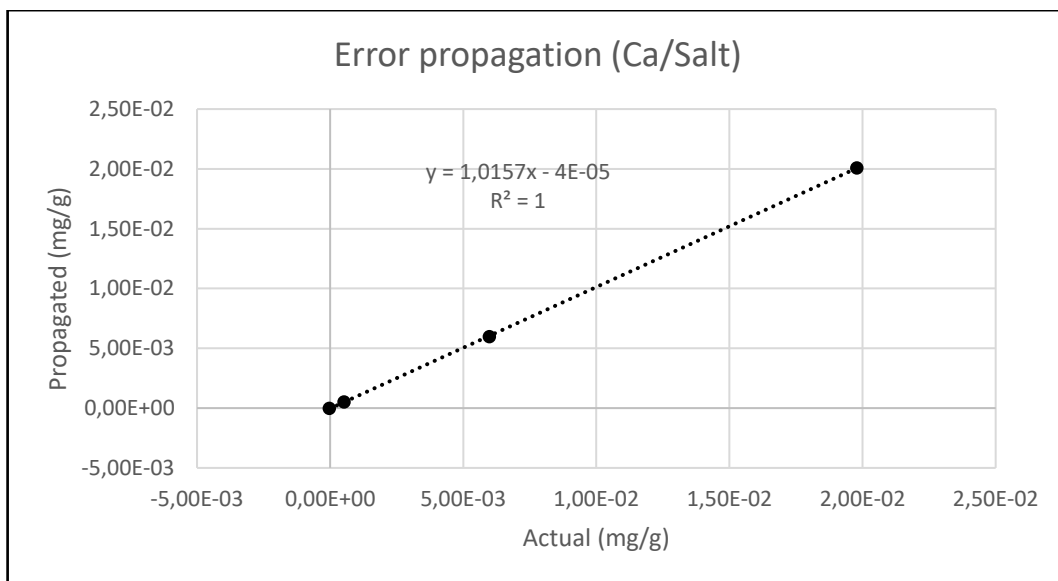


Figure 13. Trend line from Ca/Salt results of experiment 4 using method 2. Propagated error is plotted against actual error.

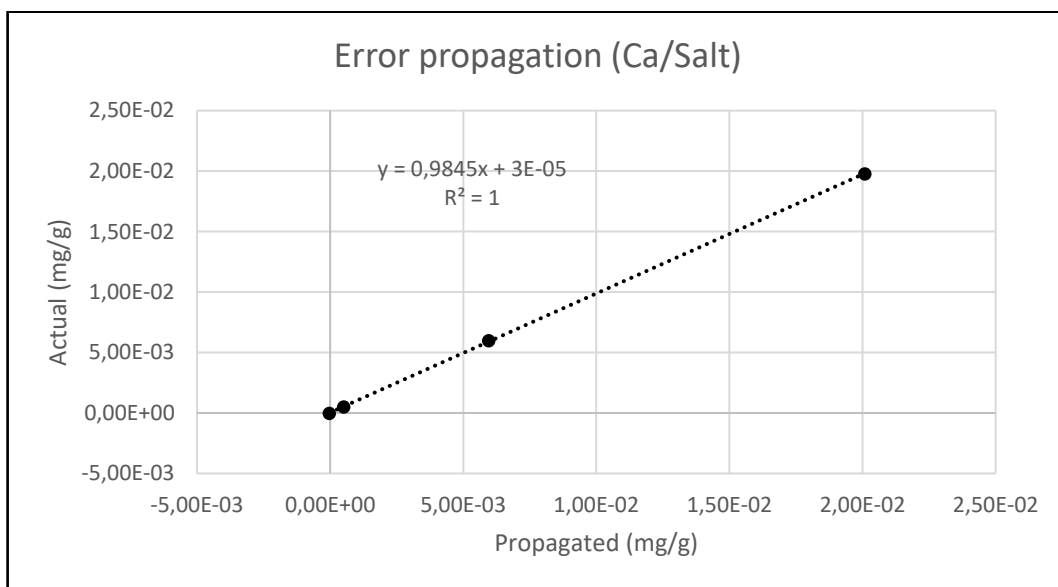


Figure 14. Trend line from Ca/Salt results of experiment 4 using method 2. Actual error is plotted against propagated error.

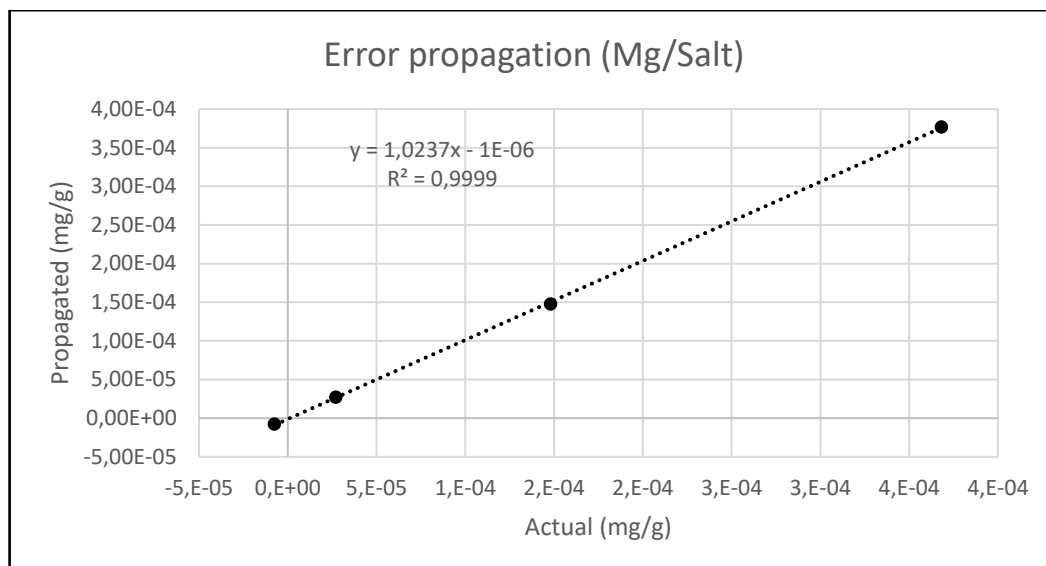


Figure 15. Mg/Salt results plot of experiment 4 using method 2. Propagated error is plotted against actual error.

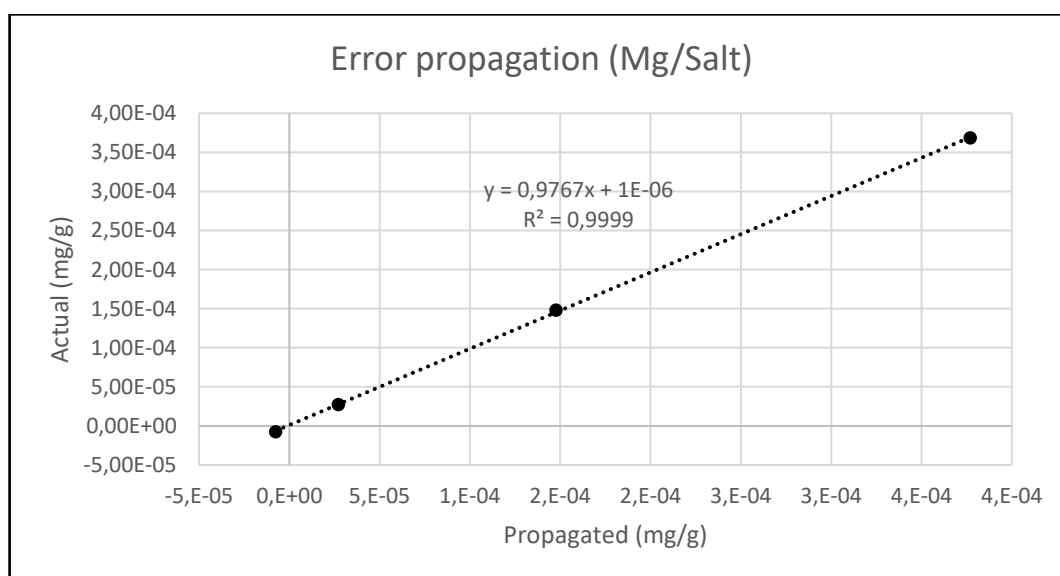


Figure 16. Mg/Salt results plot of experiment 4 using method 2. Actual error is plotted against propagated error.

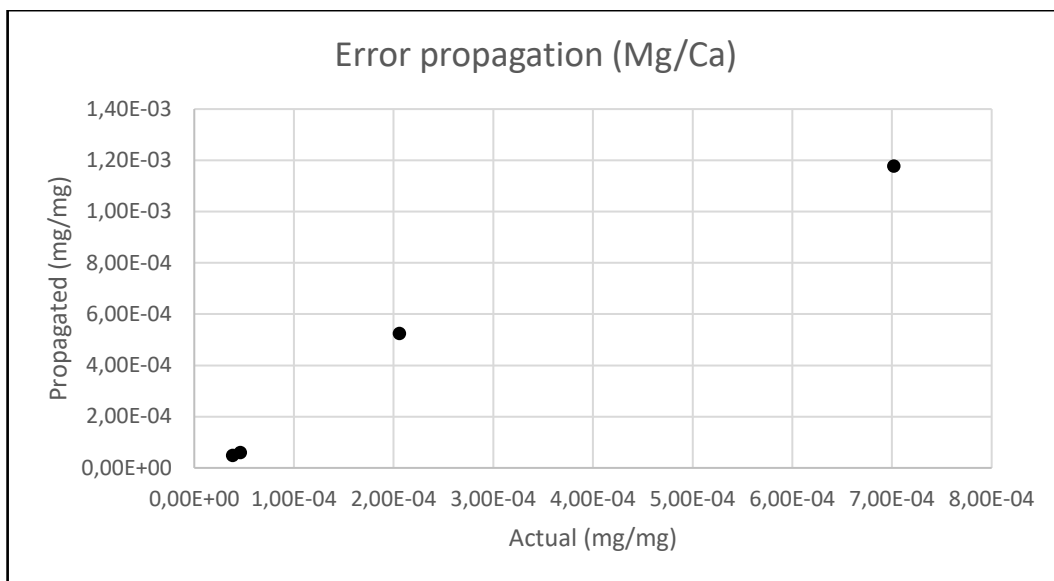


Figure 17. Mg/Ca results plot of experiment 4 using method 2. Propagated error is plotted against actual error.

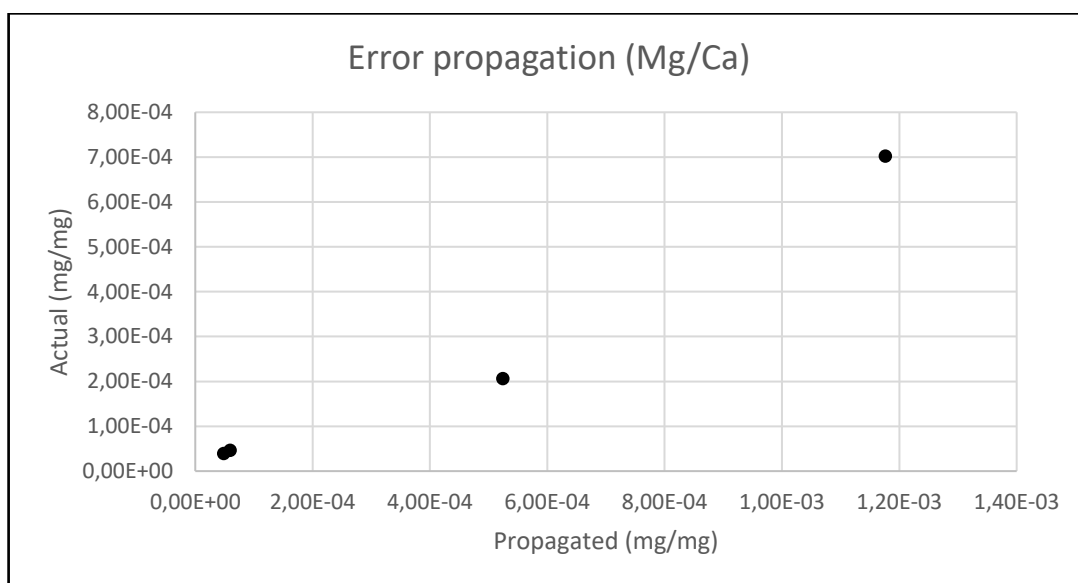


Figure 18. Mg/Ca results plot of experiment 4 using method 2. Actual error is plotted against propagated error.

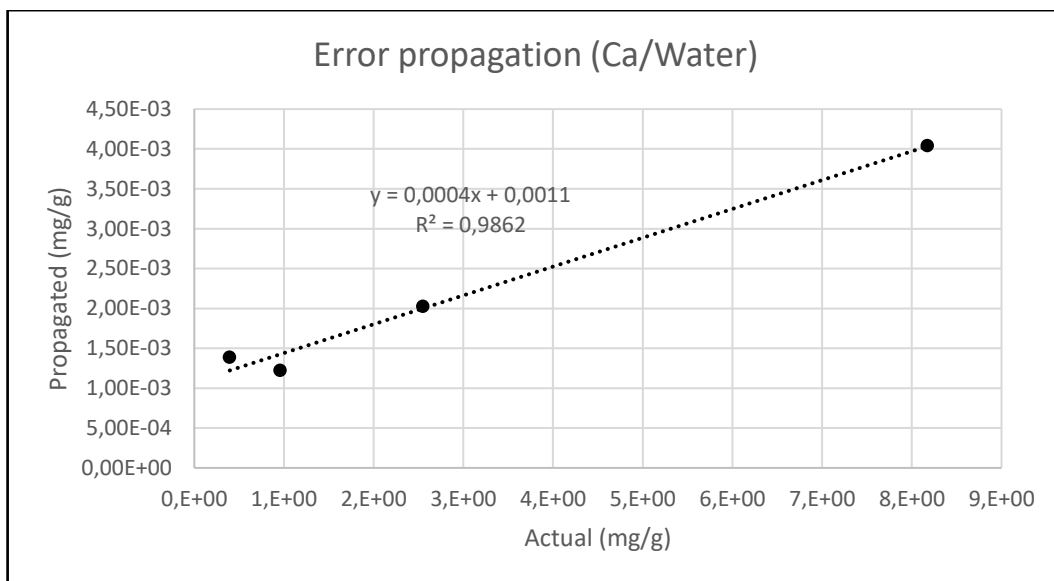


Figure 19. Trend line from Ca/Water results of experiment 5 using method 2. Propagated error is plotted against actual error.

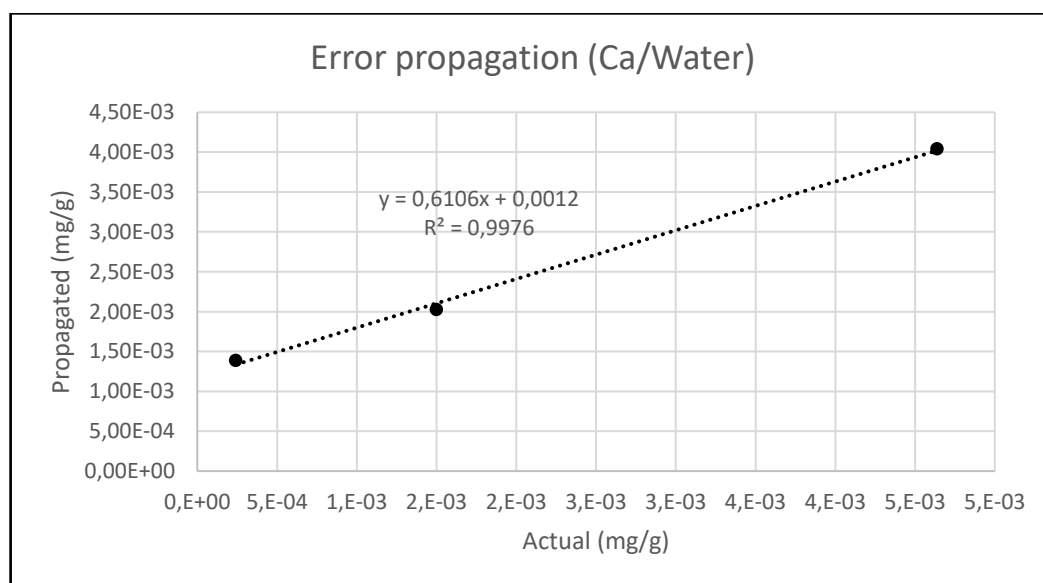


Figure 20. Trend line from Ca/Water results of experiment 5 using method 2 neglecting the first point. Propagated error is plotted against actual error.

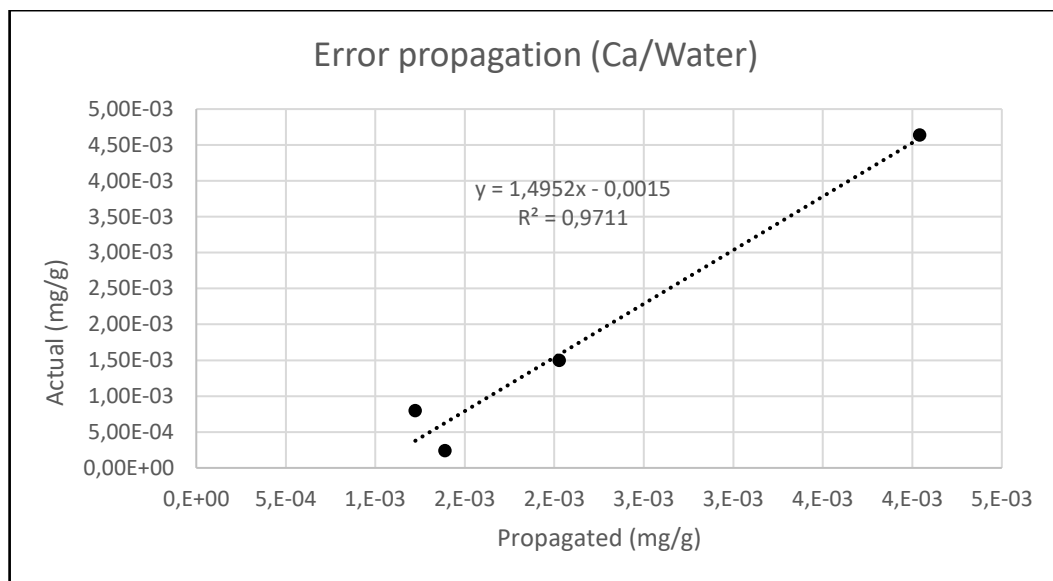


Figure 21. Trend line from Ca/Water results of experiment 5 using method 2. Actual error is plotted against propagated error.

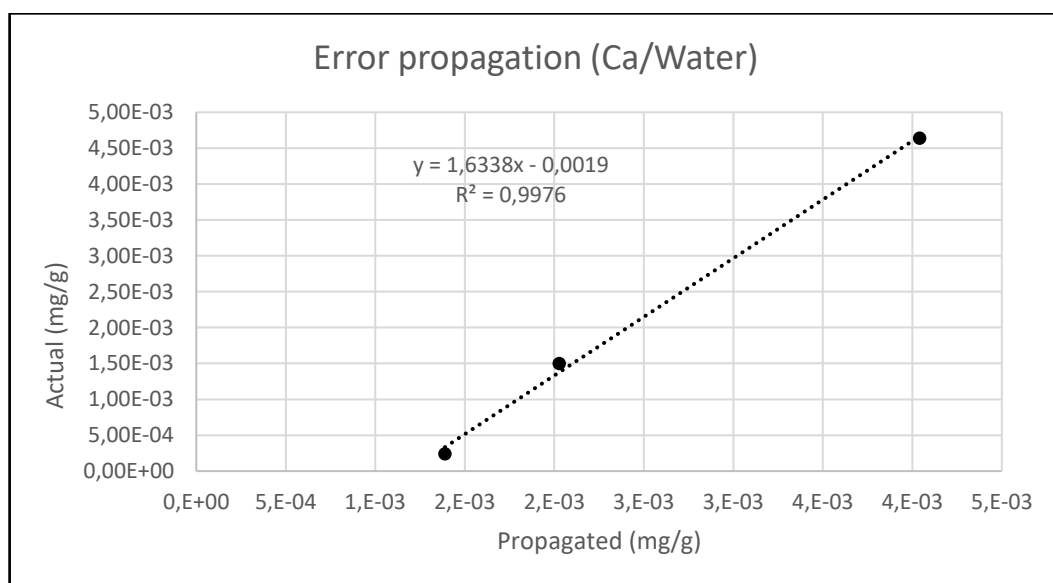


Figure 22. Trend line from Ca/Water results of experiment 5 using method 2 neglecting the first point. Actual error is plotted against propagated error.

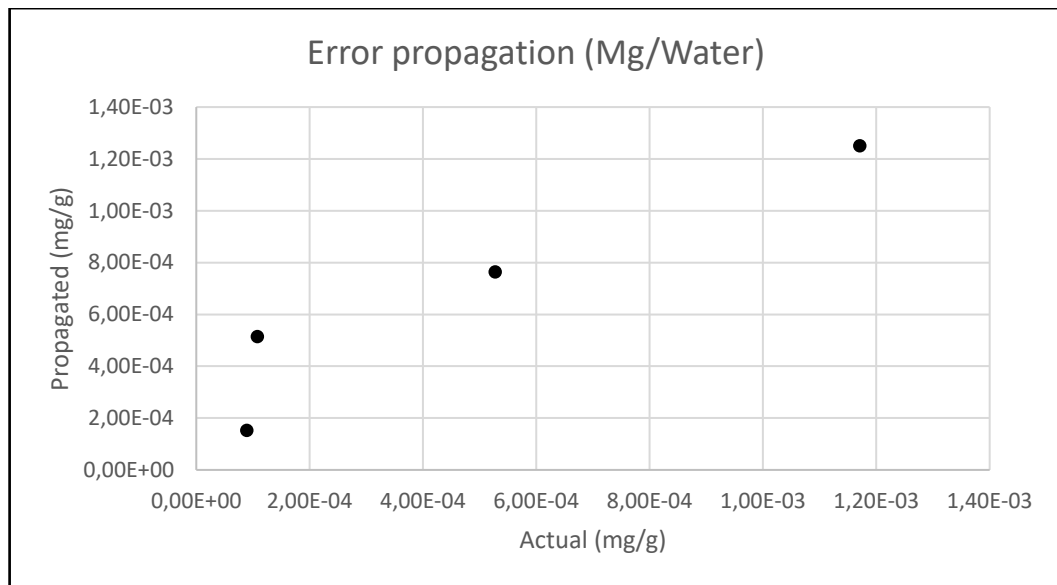


Figure 23. Mg/Water plot results of experiment 5 using method 2. Propagated error is plotted against actual error.

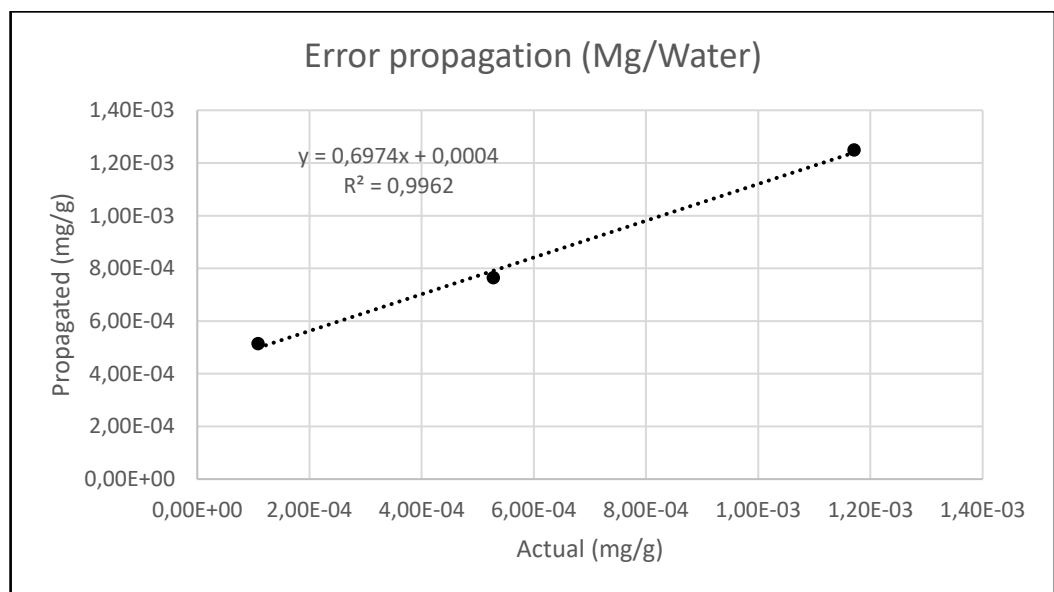


Figure 24. Trend line from Mg/Water results of experiment 5 using method 2 neglecting the first point. Propagated error is plotted against actual error.

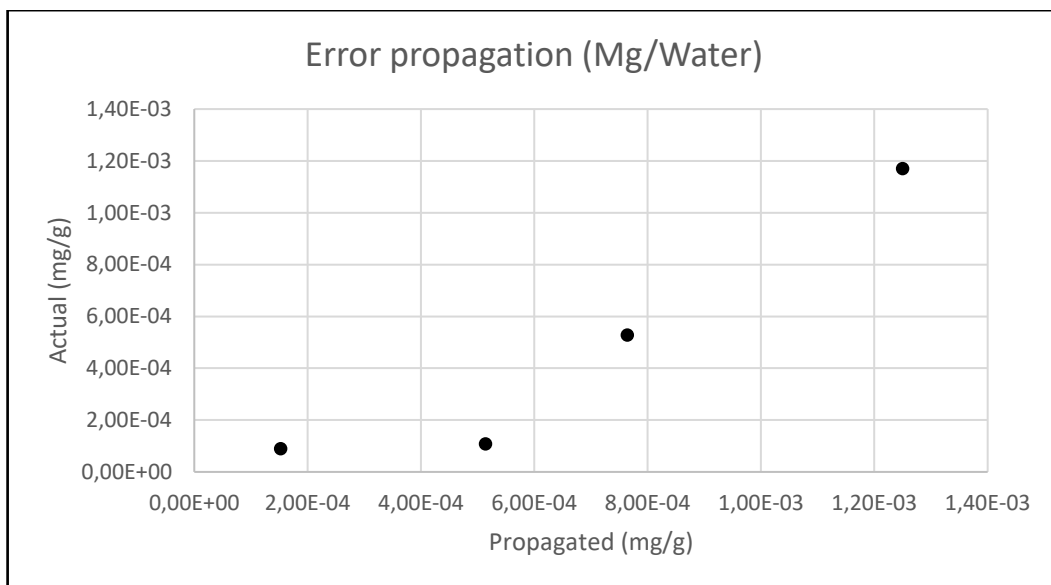


Figure 25. Mg/Water plot results of experiment 5 using method 2. Actual error is plotted against propagated error.

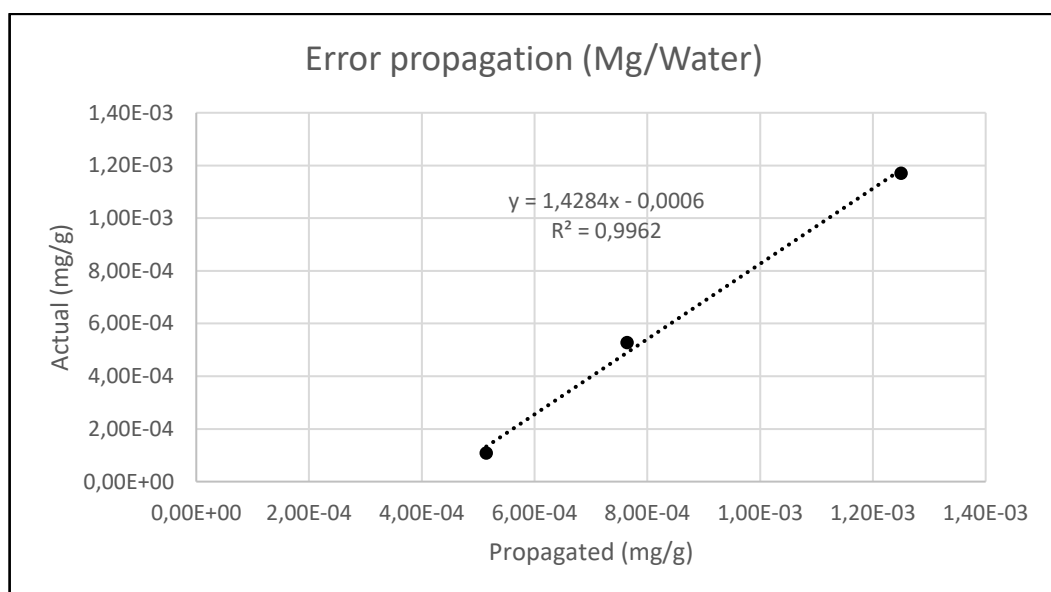


Figure 26. Trend line from Mg/Water results of experiment 5 using method 2 neglecting the first point. Actual error is plotted against propagated error.

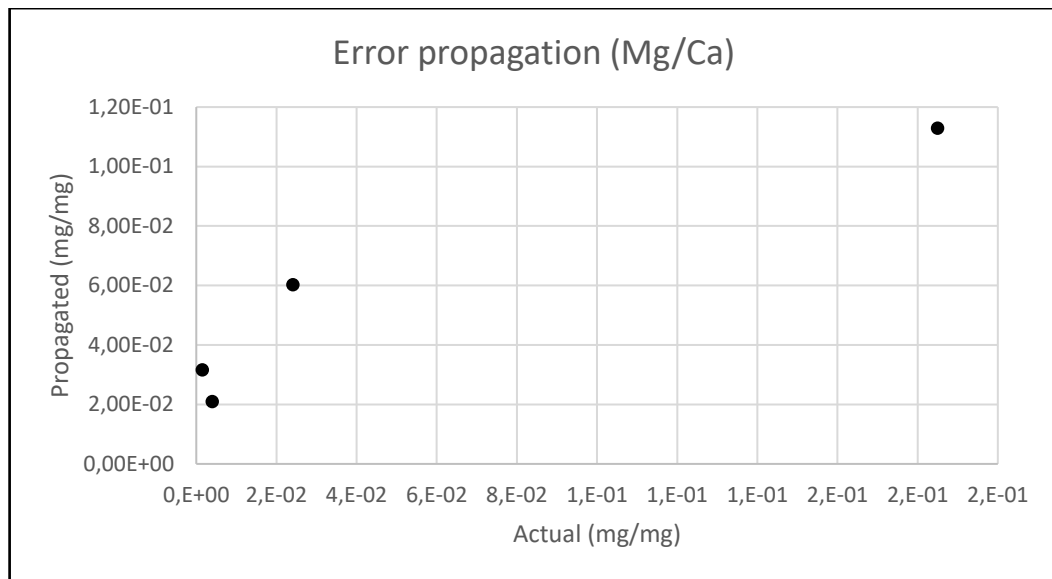


Figure 27. Mg/Ca plot results of experiment 5 using method 2. Propagated error is plotted against actual error.

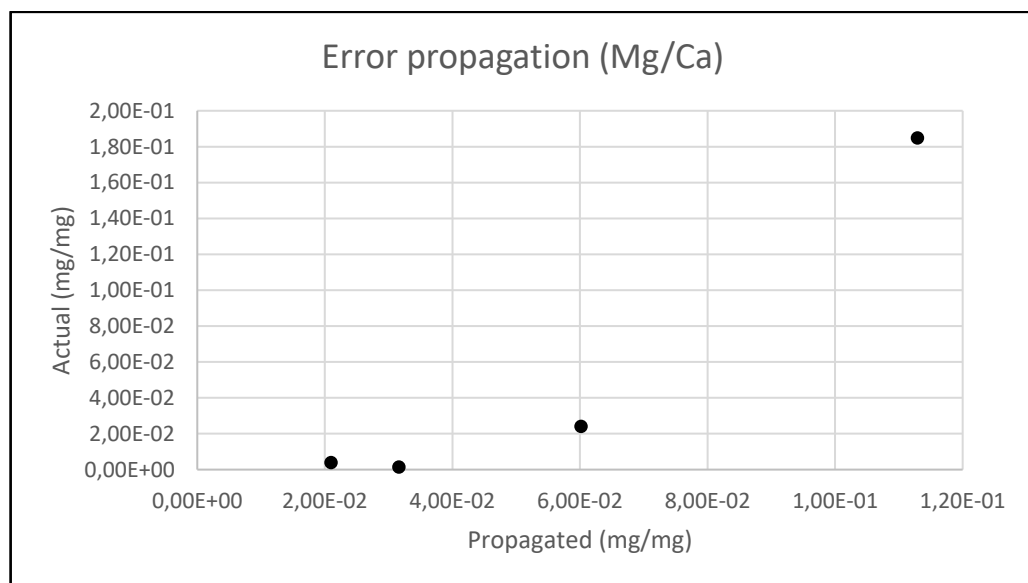


Figure 28. Mg/Ca plot results of experiment 5 using method 2. Actual error is plotted against propagated error.

