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PII: S0039-9140(18)30658-1
DOI: <https://doi.org/10.1016/j.talanta.2018.06.055>
Reference: TAL18797

To appear in: *Talanta*

Received date: 18 April 2018
Revised date: 13 June 2018
Accepted date: 16 June 2018

Cite this article as: Lígia V.L. Venâncio, Andreia S.F. Farinha and M. Teresa S.R. Gomes, Analysing sulphate and chloride in mineral drinking water by flow injection analysis with a single acoustic wave sensor, *Talanta*, <https://doi.org/10.1016/j.talanta.2018.06.055>

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Analysing sulphate and chloride in mineral drinking water by flow injection analysis with a single acoustic wave sensor

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Abstract:

Sulphate is a very hydrophilic anion, and, therefore, difficult to be selectively determined in aqueous solution with a coated sensor. Zinc(II) 2,3,9,10,16,17,23,24-Octatosylaminophthalocyanine was used for the first time as a sensitive coating. Selectivity to sulphate regarding chloride was not enough to ignore its contribution in mineral waters, and, therefore, an analytical protocol was carefully designed to allow the determination of both anions with this sensor. Results displayed on the label of eight commercial bottles of mineral waters are within the confidence interval of the values obtained with the FIA-sensor system, both for chloride and sulphate. However, results for chloride obtained by titrimetry are, in half of the cases, statistically different from the ones obtained by the sensor, and in 7 out of 8 of them more precise. There is an evidence of a systematic error in the chloride titrimetric analysis, consistent with a small overtaking of the equivalence point. Precision of the results obtained by the titrimetric analysis of sulphate were in 6 out of 8 of the analysis less precise than with the sensor, probably due to losses of the barium sulphate precipitate, which is consistent with the occurrence of lower values.

Keywords: acoustic wave sensor, sulphate, chloride, Zinc(II) 2,3,9,10,16,17,23,24-octatosylaminophthalocyanine, piezoelectric quartz crystal

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1. Introduction

Sulphate taste threshold is 250-500 mg L⁻¹ for sodium sulphate, 250-1000 mg L⁻¹ for calcium sulphate and 400-600 mg L⁻¹ for magnesium sulphate. Although high sulphate concentrations are unpleasant, the addition of 270 mg L⁻¹ of calcium sulphate and 90 mg L⁻¹ of magnesium sulphate, but not sodium sulphate, were found to improve drinking water organoleptic properties. Cathartic effects have been reported in people consuming drinking water with sulphate concentrations exceeding 600 mg L⁻¹. Dehydration and diarrhoea have also been reported associated to high levels of sulphate in drinking water, although there is not an established level of sulphate that causes adverse health effects to humans [1].

Chloride in excess of 250 mg L⁻¹ is organoleptically detected, although taste threshold is dependent on the associated cation [1-2]. Chloride also plays a role in metal pipes corrosion. Besides other sources, chloride can experience a marked increase after disinfection treatments, and its concentration is a key parameter in drinking water analysis [2].

Based on aesthetic effects (i.e., taste and odour), the EPA Secondary Drinking Water Regulations recommend a maximum concentration of 250 mg L⁻¹ for chloride ions and 250 mg L⁻¹ for sulphate ions. Home water treatments, for chloride and sulphate, based on ion exchange, are currently available.

Several analytical methodologies based on titrimetric and colorimetric analyses are available for chloride analysis [3], while sulphate is most often determined by gravimetry or titrimetry after its precipitation, or by turbidimetry [4]. Ion chromatography is another possibility [5], but it is expensive.

The availability of chemical sensors depends on the existence of anion receptors, and most of them are based on H-bonding functionality. Searching the literature, shows that the majority of the reported molecules are only tested in organic solvents, as, when in water, competition for H-bond with the hydrogen of water becomes dominant. This problem is more important for the most hydrophilic anions, the ones at the end of the Hofmeister series, where sulphate belongs. Previously, bis(thiourea) [6], a derivative of imidazole [7], a zwitterionic bis(guanidinium) [8], Schiff base complexes of transition metal ions [9], and metalphthalocyanines [10] have all been used as ionophores for potentiometric sulphate sensing. Among them, the zinc phthalocyanine, used by Ganjali et al. [10], is the most selective. Later, the same group reported a sulphate sensor based on a different ionophore [11], 3,5-triphenyloxyridinium perchlorate, but the interference due to chloride ions was higher. Eleven years later, Liu et al. [12] used a squaramide-based tripodal ionophore, but,

again, selective coefficient over chloride was higher than the one reported for zinc phthalocyanine.

In the present work, and in order to increase sensitivity, eight N-tosil groups were attached to the periphery of the phthalocyanine molecule. Places prone to anion interaction due to the possibility of Hydrogen bonding formation, which were before limited to pi-anion interactions, did increase significantly. The chromogenic properties of this molecule in organic solution of several anions have already been tested [13], but not for sulphate, and its behaviour as an ionophore in aqueous solutions have, as far as we know, not been tested before. Therefore, an initial study of the new compound sensitivity and selectivity for sulphate detection was mandatory.

After these tests, the finding that chloride was an interfering anion in sulphate determination opened the possibility of quantifying both ions, sulphate and chloride, with the same sensor. Other sensors for chloride reported in the literature are also prone to interferences from more lipophilic anions and many ionophores have been reported so far [14-17]. As sulphate is the most hydrophilic, it makes sense to start to optimise the ionophore for sulphate sensing and using it for quantifying both anions. The determination of both anions in mineral drinking sulphated waters dictated the need to establish an analytical protocol.

Afterwards, the reliability of the analytical procedure using the new sensor was evaluated by comparing the obtained results with the concentrations displayed on the labels, as well as those obtained by titrimetric analysis.

The option for piezoelectric acoustic sensors over potentiometric ones is both based on simplicity of construction, and on the fact that sensitivity do not depend on the ion charge, and on the linearity of the analytical signal *vs.* concentration. Potentiometric sensors with Nernstian responses detect double charged ions with half the sensitivity of the mono charged ions and respond linearly to the logarithm of concentration. For potentiometric measurements, besides the ionophore, other compounds are used in the electrode membrane: polyvinylchloride, a plasticizer, and a cationic additive to reduce the ohmic resistance. Although a membrane of similar composition could be used in acoustic sensors, the phthalocyanine can be solely applied on the piezoelectric quartz crystal.

Given the preference for an acoustic wave sensor optimized for sulphate determination, the use of a sensitive layer composed of a selective ionophore, is preferred to the phosphorylated 11-mercapto-1-decanol, which served as an interfacial layer for the immobilization of barium sulphate crystals. The monitorization of gravimetric surface change was done after a period of 10 min [18], which would render the methodology heavily time-consuming.

2. Experimental

2.1 Reagents

Fig. 1 shows the structure of Zinc(II) 2,3,9,10,16,17,23,24-Octatosylaminophthalocyanine ($\text{ZnPc}(\text{Tos})_8$). This compound has been synthesized according to [13]. Chloroform (BDH Prolabo 22711.324) was used to dissolve the above-mentioned compound before coating the piezoelectric quartz crystals.

Stock solutions of several salts were prepared by dissolving the p.a dried solid salts in Milli-Q water. Salts used were sodium acetate (Panreac 131633), sodium bromide (Panreac 131646), calcium carbonate (Flika 21060), ammonium chloride (Merck 8564623), sodium chloride (Merck 1.06404), sodium dihydrogen phosphate monohydrated (Panreac 131965), sodium fluoride (Fluka 71522), sodium formate (Panreac 131676), sodium iodide (Alfa Aesar 941), sodium nitrate (Fluka 31440) and sodium sulfate (Aldrich 12110088). Standard solutions were prepared by appropriate dilution of the stock solutions.

Hydrochloric acid (Riedel-de-Haën) was used to adjust pH. Calcium hydroxide (Panreac 142001211) and barium chloride (Merck 0096389) were used to precipitate interfering anions, or in standard methodologies, along with and Triplex II (Merck 8421), ammonium hydroxide (Fluka 30501), sodium hydroxide (Panreac 131687), silver nitrate (Absolve 50008), and magnesium chloride (Carlo Erba 459337), Nitrogen was Alphagaz from "Arliquido".

2.2 Samples

Eight bottles of sulphated mineral waters of different brands were purchased at local supermarkets. All of them presented information about sulphate concentration on the label.

2.3 Apparatus

The piezoelectric crystals were 9 MHz, polished, AT-cut, HC-6/U, with gold electrodes (ICM - International Crystal Manufacturing Co, Inc.).

A spin-coater DELTA 10TT was used to spread the coating solution on one of the faces of the piezoelectric quartz crystal.

All the analyses were performed by flow injection analysis (FIA). Fig. 2 shows a diagram of the FIA-sensor analytical system, which has already been described elsewhere [19].

2.4 Analytical procedures

2.4.1 Coating the piezoelectric quartz crystal

A drop of a chloroform solution of the $\text{ZnPc}(\text{Tos})_8$ was applied onto one side of the quartz crystal and it was then spread by spinning at 340 rpm for 45 s. Sensor was left to dry for two days, before being used. A piezoelectric crystal with a frequency decrease due to coating of 23.5 kHz was used in the present work. Coating is rigid enough and spin coating allowed obtaining a uniform thickness, so that Sauerbrey equation could be used to obtain an estimate of the mass of phthalocyanine on the active area of the quartz crystal (25 μg).

2.4.2 Obtaining the analytical signal by FIA-sensor system

Following the diagram on Fig.2, Milli-Q water flowing at 0.9 mL min^{-1} reached the crystal cell and contacted with the coated face of the piezoelectric quartz crystal (active area = 0.196 cm^2). After frequency stabilization, baseline value was recorded. A valve with an injection loop of 0.5 mL was used to inject standards or samples into the water flowing stream. The interaction between coating and the analyte allowed observing a decrease in the frequency, as soon as the solution reached the coated quartz crystal. The observed minimum frequency value was registered and the difference between the minimum and the baseline frequency was computed. A new injection could only take place after complete recovering and baseline stabilization.

2.4.3 Procedure for determining chloride by the FIA-sensor system

Samples were degassed under vacuum. Fig. 3 presents a simplified plan of the first sample treatment for bicarbonate elimination, showing the detectable ions, along with their origin. Bicarbonate from an aliquot of 50.00 mL was precipitated with calcium hydroxide, filtered by paper Whatman n° 42, on a Büchner funnel, washed (pH=8) and discarded. pH of filtered solution was adjusted with a known volume of HCl to pH 6.35. In order to determine chloride, sulphate must be eliminated, and, for this purpose, a second treatment, schematically shown on Fig. 4 was implemented. An exact volume of the barium chloride was added, and solution was heated. The solution was later on filtered under vacuum through a Waterman n° 42 paper on a Büchner funnel. The precipitate was washed with cold Milli-Q water and allowed to stand until all the liquid was collected on the flask. The content of the flask was transferred into a 100.00 mL volumetric flask and filled to the mark with Milli-Q water. This solution was injected in the FIA analytical system. The obtained signal was used to know the amount of chloride with the aid of the chloride calibration line. Depending on the

frequency decrease, further sample dilutions may have been needed, to obtain a value as close as possible to the centroid of the calibration line. The chloride concentration corresponds to the amount of chloride present in 50,00 mL of water plus the chloride added in the acidification step and the chloride added as BaCl_2 , which are both known and can be subtracted later on.

2.4.4 Procedure for determining sulphate by the FIA-sensor system

Injecting the sample after the elimination of bicarbonate, (Fig. 3), allowed obtaining a frequency decrease signal that was produced by both chloride and sulphate. The part of the signal corresponding to the chloride in the sample and the chloride added in the acidification step was found by entering with the correspondent chloride concentration in the chloride calibration line. Fig. 5 demonstrates that subtracting the calculated frequency value to the one obtained in the analysis allows having the frequency decrease correspondent to sulphate ions. The correspondent sulphate concentration was found through the sulphate calibration line.

2.4.5 Determination of chloride and sulphate by standard titrimetric methods

Chloride was determined by the Mohr method, which used potassium chromate as indicator in the titration with standard silver nitrate [3].

Sulphate was precipitated as barium sulphate after sample acidification. The precipitate was then filtered and dissolved in an excess of a standard EDTA solution in the presence of ammonia. The excess of EDTA was then titrated with a standard solution of magnesium chloride at $\text{pH}=10$ [4].

3. Results and Discussion

3.1 Reversibility of the interaction between coating and the anions

Frequency decrease, observed injecting chloride or sulphate standard solutions, or samples, quickly returned to baseline, after the solution been swept to waste by the water carrier. Fig. 6 shows the signal obtained when injecting a sulphate solution $5.005 \times 10^{-4} \text{ mol dm}^{-3}$. Frequency started decreasing as soon as the sample reached the sensor, and attained the minimum 45 s later. Complete recover was obtained in 55 s (Fig. 6).

3.2 Calibration curves for chloride and for sulphate

Injecting solutions of sulphate with concentrations between $2.018 \times 10^{-5} \text{ mol dm}^{-3}$ and $2.002 \times 10^{-3} \text{ mol dm}^{-3}$ allowed obtaining a calibration line plotting the frequency decrease vs.

concentration. Slope of the calibration line was $85678 \text{ Hz dm}^3 \text{ mol}^{-1}$. Detection limit was $42 \mu\text{mol dm}^{-3}$.

Analysing standard chloride solutions with concentrations between $2.018 \times 10^{-5} \text{ mol dm}^{-3}$ and $2.514 \times 10^{-3} \text{ mol dm}^{-3}$ allowed obtaining the calibration line for chloride with a slope of $52992 \text{ Hz dm}^3 \text{ mol}^{-1}$. Detection limit was $50 \mu\text{mol dm}^{-3}$.

3.3 Study of interfering anions

Regarding a series of other anions, the sensor detects sulphate with the highest sensitivity. Fig. 7 shows the selectivity coefficients of the sensor over various other anions relative to sulphate. Coefficients were determined by the fixed interference method. The frequency decrease was measured for solutions with a constant concentration of an interfering anion B, $Conc_B$, while varying the concentration of the sulphate ion. The frequency changes obtained were plotted vs. the concentration of the primary ion. The intersection of the extrapolated linear portions of this plot led to a value, $Conc_A$, which was then divided by $Conc_B$, to calculate the selectivity coefficient, K. The highest the value of K the highest is the interfering effect of the tested anion. It can be seen that chloride, which is ubiquitous in water, was also detected, although selectivity coefficient was only 0.318. Interference from bicarbonate was even more severe and it needed to be eliminated before the analysis. Concentrations of other anions were not high enough to produce a significant signal. pH strongly influences sulphate signal, and therefore, before sulphate analysis, pH of the sample was carefully adjusted to 6.35.

3.4 Comparison of the results obtained with the sensor with results obtained by titrimetric methods and displayed on the bottles' label.

Tables 1 and Table 2 show the results for chloride and sulphate, respectively, obtained with this new FIA-sensor method, and by titrimetry, as well as the value displayed on the label of the water bottles.

Comparing the precision of the new method with the one obtained with titrimetry, F test showed that for 7 of the 8 samples, the results for chloride obtained with the sensor were less precise than the ones obtained by titrimetry ($\alpha=0.05$). For sulphate the results from the sensor were statistically as precise as the titrimetric ones in 6 cases, while in 2 analysis the results of the sensor were more precise than the titrimetric ones ($\alpha=0.05$).

Fig. 8 shows the plot of the mean values obtained with the sensor and by titrimetry *vs.* the label values, both for chloride and sulphate. Comparing the results obtained by each method with the values displayed on the label, it is possible to infer that results of the sensor are closer to the ones on the labels than the titrimetric ones, and Table 1 and Table 2 show that the values on the label are always within the confidence interval ($\alpha=0.05$) of the sensor values.

The slopes obtained for the regression of the experimental data *vs.* label values are further from 1 for the titrimetric methods than for the sensor, but also the intercept is further from the ideal value of 0 for the titrimetric results *vs.* label values. In particular, the high value obtained on the intercept for chloride, evidences the occurrence of a systematic error on the titrimetric determinations, attributed to an overtaking of the equivalence point in the titration, probably due to difficulties in visualising the colour change. The lower precision of sulphate titration results regarding sensor results, as well as the fact that results from titrimetric analysis of sulphate were always lower for than the ones on the label and the ones obtained with the sensor, can be attributed to the loss of barium sulphate precipitate.

3.4 Sensor lifetime

The coated quartz crystal was kept inside the cell for 6 weeks, within the system, at ambient temperature and wet, and used during this period without changing its position. Several calibration curves were obtained along these six weeks. Although sensitivity did randomly change along time, the sensor continued to be used with reliable results until the 5th week. By the 6th week, the coated crystal stopped vibrating and became useless.

Conclusion

The lack of selectivity of the sensor allowed determining both chloride and sulphate in mineral waters. The extensive analytical work, precipitating interfering anions, and in some assays also primary anions, in order to have separate signals with and without them, were a source of random errors, and degraded precision, which was in some analysis worse than the one achieved with titrimetry. However, the values of chloride and sulphate concentrations displayed on the water labels were always within the confidence interval ($\alpha=0.05$) of the results obtained by the sensor. On the contrary, results obtained for sulphate by titrimetry were always lower than the ones on the label, due to difficulties in obtaining and dissolve the barium sulphate precipitate without losses. The acoustic sensor with a sensitive coating of

ZnPc(Tos)₈, used in a simple flow analytical system, and used according to a protocol here presented, allowed to obtain reliable sulphate and chloride concentrations within a period of 5 weeks after coating.

Acknowledgments

Thanks are due for the financial support to CESAM (UID/AMB/50017 - POCI-01-0145-FEDER-007638), to FCT/MCTES through national funds (PIDDAC), and the co-funding by the FEDER, within the PT2020 Partnership Agreement and Compete 2020

Conflicts of interest

There are no conflicts to declare.

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Fig. 1 Structure of Zinc(II) 2,3,9,10,16,17,23,24-Octatosylaminophthalocyanine: ZnPc(Tos)₈

Fig. 2 Flow Injection analysis system including the sensor

Fig. 3 First treatment for bicarbonate elimination, showing that frequency decrease obtained from the injection of the treated sample corresponded to both chloride and sulphate ions.

Fig. 4 Second treatment for sulphate elimination, showing that frequency decrease obtained from the injection of the treated sample corresponded to the total chloride, which has multiple origins

Fig. 5 Determination of sulphate in the sample by analysing the solution after the first pre-treatment. The signal correspondent to the chloride added on the acidification step plus the chloride present in the water sample must be subtracted from the reading. The sulphate concentration is then calculated through the sulphate calibration line.

Fig. 6 Frequency of quartz crystal coated with ZnPc(Tos)₈, before and after the injection of 0.5 mL of a sulphate solution $5.005 \times 10^{-4} \text{ mol dm}^{-3}$

Fig. 7 Selectivity coefficients of the sensor over various anions relative to sulphate

Fig. 8 Comparison of the results obtained by the new FIA-sensor methodology and by titrimetry with the values displayed on the label.

Supplementary material: Photograph of the experimental setup

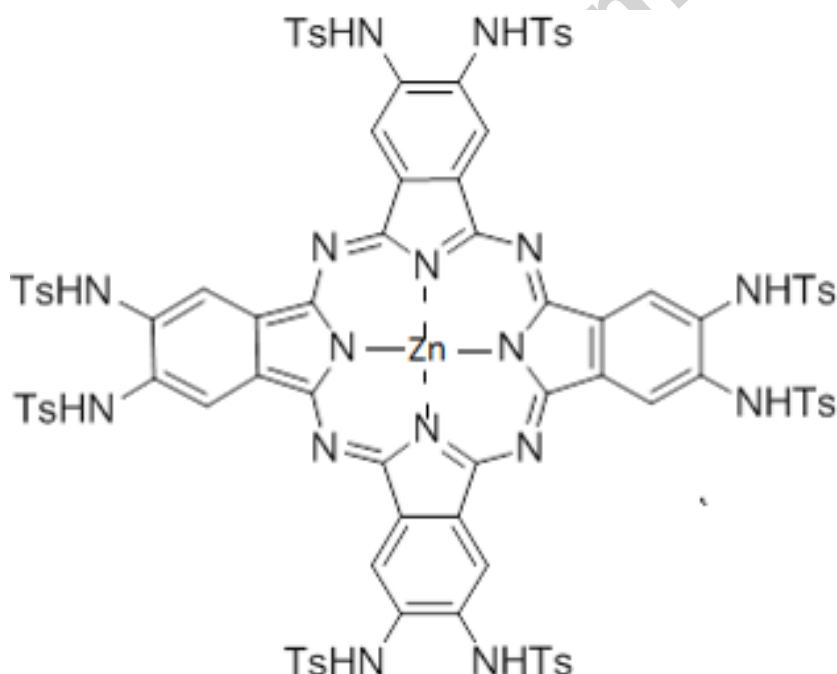


Fig. 1

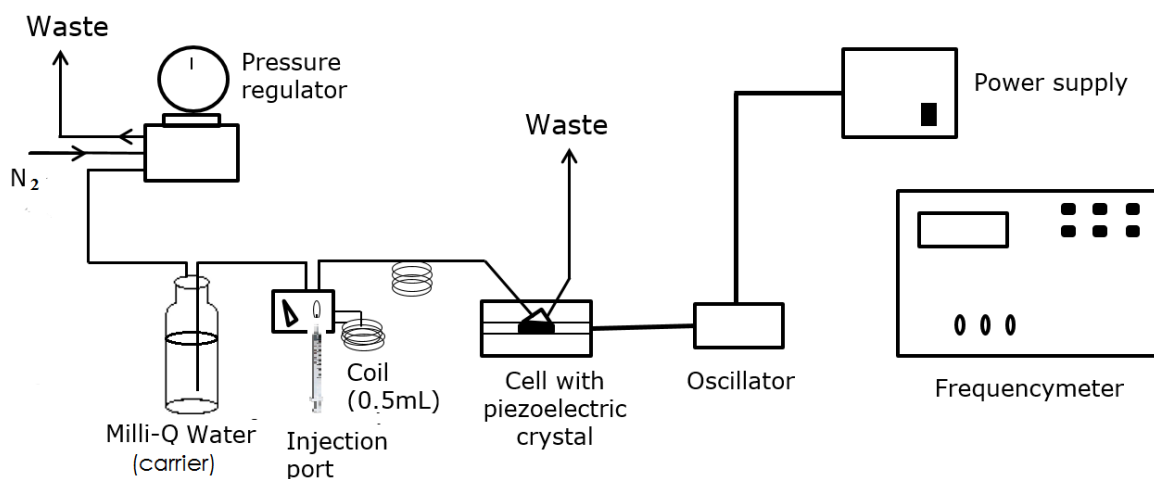


Fig. 2

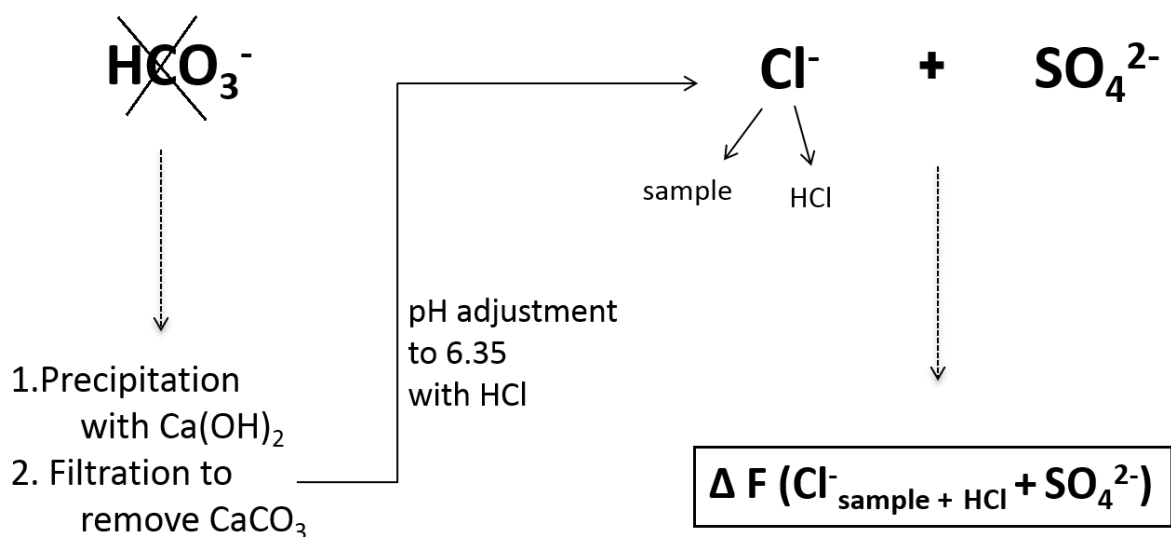


Fig. 3

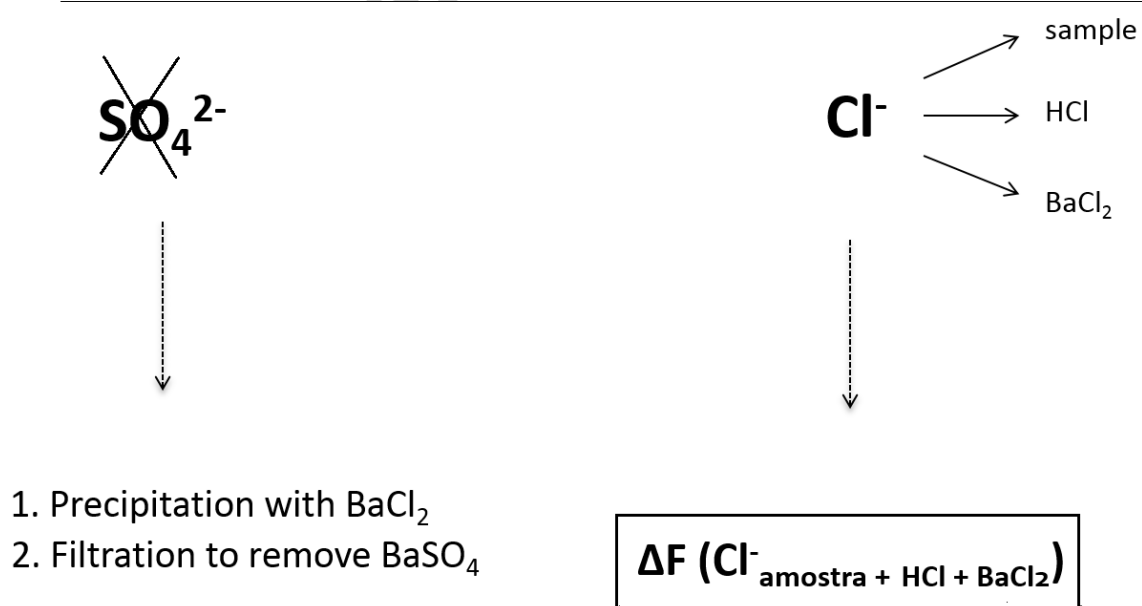


Fig. 4

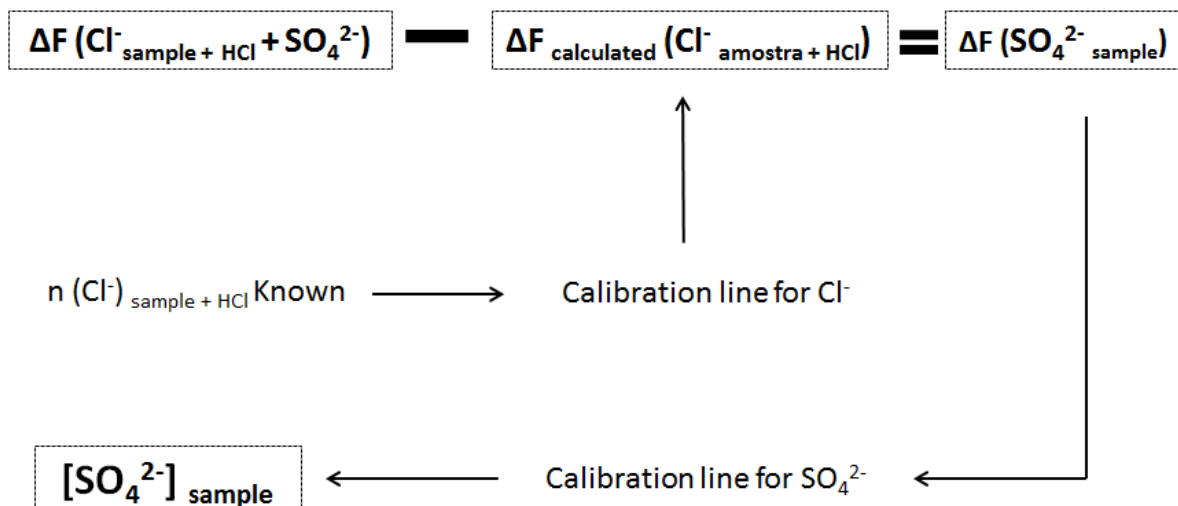


Fig. 5

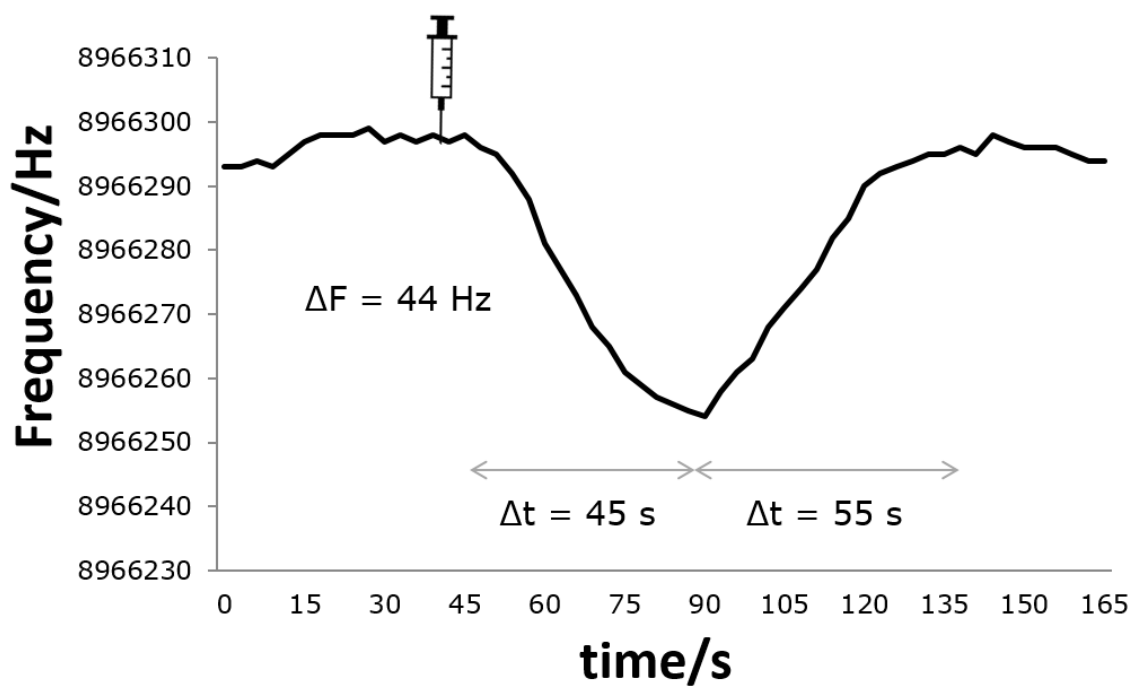


Fig. 6

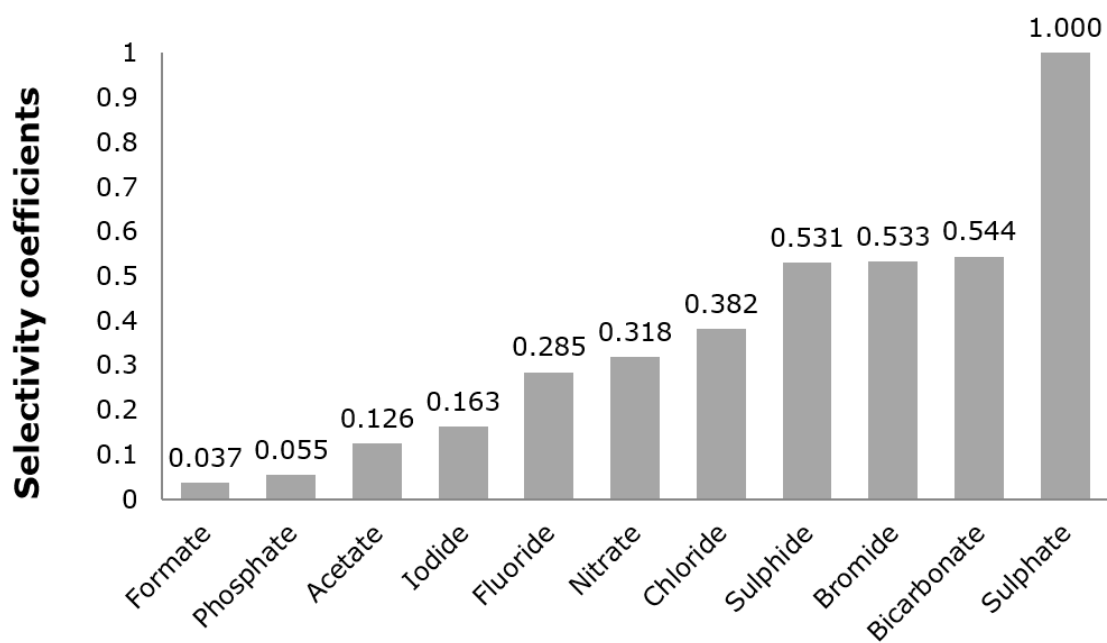


Fig. 7

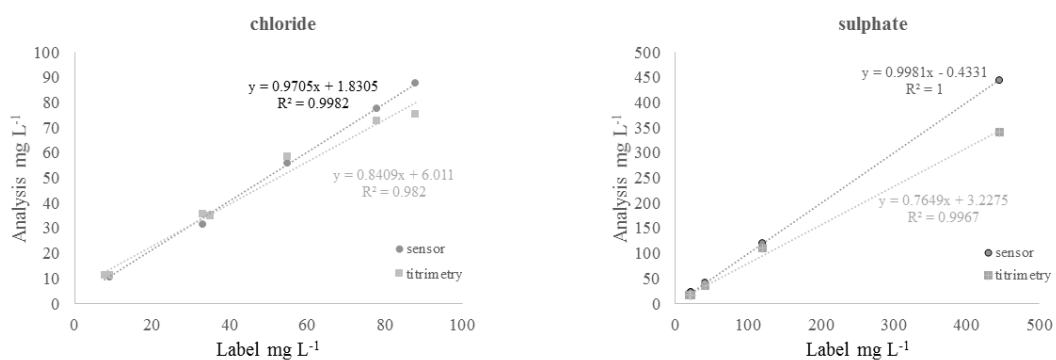
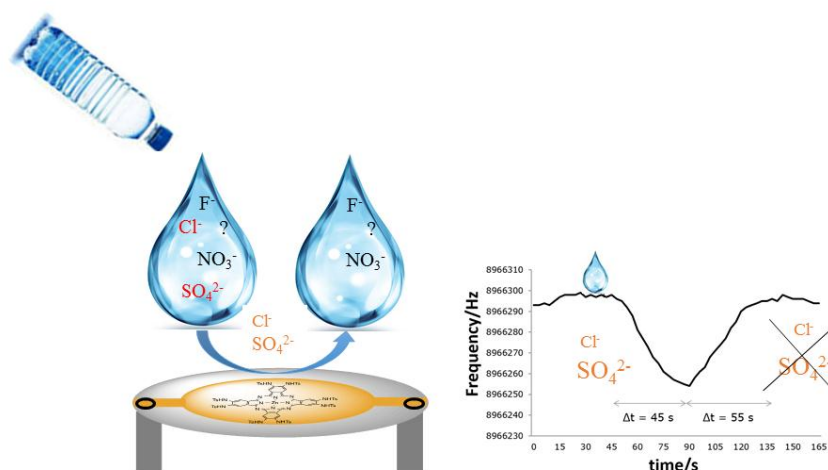


Fig. 8



Graphical Abstract

Table 1 Results for chloride (mg L^{-1}) obtained with this new method and by titrimetry (four replicates were analysed by each method), along with values displayed on the label of the bottles.

Source/Brand	S. Pellegrino	Castello	Saskia	Acqua Panna	Valtorre	Vittel	Castello Finna	Solander Cabras
Sensor	59 ± 12	78 ± 2	31 ± 1	10 ± 1	35 ± 2	9.7 ± 0.9	88 ± 2	11.2 ± 0.9
Titrimetry	58.5 ± 0.2	72.60 ± 0.07	35.60 ± 0.09	11.4 ± 0.1	34.9 ± 0.2	9.9 ± 9.3	75.1 ± 0.8	11.1 ± 0.1
Label	54.8	78	33.0	9.0	35.1	----	88	7.8

Table 2 Results for sulphate (mg L^{-1}) obtained with this new method, and by titrimetry (four replicates were analysed by each method), along with values displayed on the label of the bottles.

Source/Brand	S. Pellegrino	Castello	Saskia	Acqua Panna	Valtorre	Vittel	Castello Finna	Solan de Cabras
Sensor	444 ± 6	22 ± 1	41 ± 2	19 ± 2	18 ± 2	120 ± 1	19 ± 1	22 ± 1
Titrimetry	340 ± 32	16 ± 4	34 ± 3	17 ± 5	16 ± 4	111 ± 6	16 ± 3	17 ± 2
Label	445.0	22	40.8	21.0	18.7	120	20	21.9

Highlights:

- Sulphate, being a hydrophilic molecule, was determined with a sensor in water.
- The sensor showed some selectivity to sulphate over other common anions.
- Following an established protocol, both sulphate and chloride were determined
- Results were not statistically different from the values printed on the bottles.
- Sensor maintained sensitivity for 5 weeks.