



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



Lígia V.L. Venâncio<sup>a</sup>, Andreia S.F. Farinha<sup>b,1</sup>, M. Teresa S.R. Gomes<sup>a,\*</sup>

<sup>a</sup> CESAM & Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal

<sup>b</sup> QOPNA & Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal

## ARTICLE INFO

### Keywords:

Acoustic wave sensor  
Sulphate  
Chloride  
Zinc(II) 2  
3  
9  
10  
16  
17  
23  
24-octatosylaminophthalocyanine  
Piezoelectric quartz crystal

## 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.

## 1. Introduction

Sulphate taste threshold is 250–500 mg L<sup>-1</sup> for sodium sulphate, 250–1000 mg L<sup>-1</sup> for calcium sulphate and 400–600 mg L<sup>-1</sup> for magnesium sulphate. Although high sulphate concentrations are unpleasant, the addition of 270 mg L<sup>-1</sup> of calcium sulphate and 90 mg L<sup>-1</sup> 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<sup>-1</sup>. 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<sup>-1</sup> 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<sup>-1</sup> for chloride ions and 250 mg L<sup>-1</sup> 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 metalphtalocyanines [10] have all been used as ionophores for potentiometric sulphate sensing. Among them, the zinc phtalocyanine, 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-

\* Corresponding author.

E-mail address: [mtgomes@ua.pt](mailto:mtgomes@ua.pt) (M.T.S.R. Gomes).

<sup>1</sup> Current address: King Abdullah University of Science and Technology (KAUST), Biological and Environmental Science and Engineering (BESE) Division, Water Desalination and Reuse Center (WDRC), Thuwal 23955-6900, Saudi Arabia.

triphenylpyridinium 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-tosyl 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 sulphate (Aldrich 12110088). Standard solutions were prepared by appropriate dilution of the stock solutions.

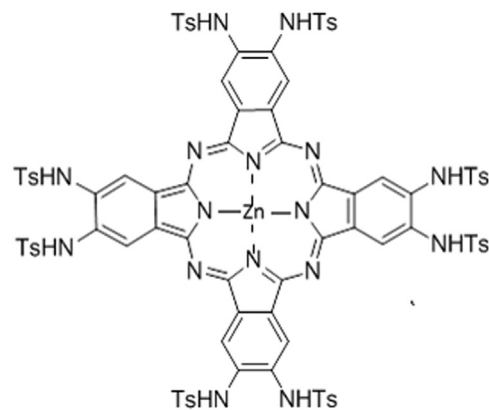


Fig. 1. Structure of Zinc(II) 2,3,9,10,16,17,23,24-Octatosylaminophthalocyanine:  $\text{ZnPc}(\text{Tos})_8$ .

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  $\mu\text{g}$ ).

#### 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  $\text{min}^{-1}$  reached the crystal cell and contacted with the coated face of the piezoelectric quartz crystal (active area = 0.196  $\text{cm}^2$ ). 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

Download English Version:

<https://daneshyari.com/en/article/7675169>

Download Persian Version:

<https://daneshyari.com/article/7675169>

[Daneshyari.com](https://daneshyari.com)