

Determination of the total hardness in tap water using acoustic wave sensors

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Abstract

The determination of hardness in water is a useful parameter to control the quality of water for households and industrial uses. The present work proposes a new methodology as an alternative to the conventional EDTA titration. The determination of Ca^{2+} and Mg^{2+} is performed using two different coated piezoelectric quartz crystals. Poly(vinyl chloride) membranes, incorporating a plasticizer and a Mg or Ca ionophore were used to coat the piezoelectric quartz crystals.

Results obtained by this new methodology shows that the tap water found in Portugal can be considered soft in Gouveia ($9.4 \pm 0.8 \text{ mg L}^{-1} \text{ CaCO}_3$) and in Vila Praia Àncora ($15 \pm 1 \text{ mg L}^{-1} \text{ CaCO}_3$), slightly hard in Leiria ($59 \pm 1 \text{ mg L}^{-1} \text{ CaCO}_3$), moderately hard in Aveiro ($74 \pm 1 \text{ mg L}^{-1} \text{ CaCO}_3$) and in Esposende ($104 \pm 1 \text{ mg L}^{-1} \text{ CaCO}_3$) and very hard in Tomar ($225 \pm 1 \text{ mg L}^{-1} \text{ CaCO}_3$). The results obtained by the proposed method are not significantly different ($\alpha = 0.05$), both in terms of accuracy and precision, from the ones obtained by the conventional EDTA titration method. Besides providing individual concentration of Ca^{2+} and Mg^{2+} , this new methodology also has the advantage of being less reagent, sample and time consuming.

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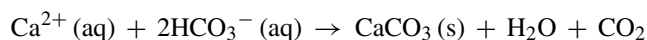
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1. Introduction

Calcium and magnesium dissolved in water are the two most common minerals that make water “hard”. The degree of hardness becomes higher as the calcium and magnesium content increases, and is related to the concentration of multivalent cations dissolved in the water. Hardness is most commonly expressed as milligrams of calcium carbonate equivalent per litre. Water containing less than 17.1 mg of calcium carbonate per litre is generally being considered as soft, slightly hard with less than 60 mg L^{-1} , moderately hard from 60 to 120 mg L^{-1} , hard from 120 to 180 mg L^{-1} and very hard with 180 or more mg L^{-1} of calcium carbonate.

Hard water does not present a health risk, as long as the minerals are not heavy metal salts [1,2]. Therefore, why is hardness such a matter of concern? The answer is that extremely hard water may shorten the life of plumbing and less the effectiveness of certain cleaning agents. Calcium reacts with bicarbonate

ions to form insoluble calcium carbonate (scale).



Therefore, depending on pH, hard water may cause scale deposition in the distribution system, heat exchange equipment and boilers. Besides, soap is less effective in hard water because it reacts to form the calcium or magnesium salt of the organic acid of the soap. These salts are insoluble and form grayish soap scum, but no cleansing lather.

Hard water can also leave an unpleasant film on hair, fabrics, and glassware.

In contrast, soft or moderate hard water, with hardness less than about 100 mg L^{-1} , has a greater tendency to cause corrosion of pipes, which may result in the presence of certain heavy metals, such as cadmium, copper, lead and zinc, in drinking-water. The degree to which this corrosion and solubility of metals occurs also depends on the pH, and dissolved oxygen concentration. Some hardness is therefore needed in plumbing systems to prevent corrosion of pipes.

Hardness of water has traditionally been determined by a complexometric titration with ethylene diaminetetraacetic acid (EDTA). Using the indicator Eriochrome Black T, magnesium and calcium will be determined together. Indicator change colour

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slowly at the end point and thus titration should be performed slowly and carefully.

As the complexometric titration is a laborious and time consuming methodology, there has been attempts to employ a semi-automatic end point detection [3] as well as to develop a flow-batch photometric system which classifies water in the four hardness categories, by monitoring the absorbance at a fix wavelength after the addition of fixed amounts of titrant [4].

Traces of iron and copper block the indicator, and masking agents may be necessary. Fritz et al. [5] recommended a change of indicator.

Ion selective electrodes seem to be an interesting alternative to titration, and Numata et al. [6] used an electrode sensitive both to Ca^{2+} and Mg^{2+} . In 2002, Saurina et al. [7] have published a potentiometric sensor array for total hardness determination in natural waters. Ion selective electrodes respond to the logarithm of activity rather than concentration and activity coefficients depend on ionic strength. In order to work with concentration, ionic strength must be kept constant, which is usually achieved adding an electrolyte, both to standards and samples. As support electrolyte adds, typically K^+ , Li^+ or amine compounds, Saurina et al. [7] did avoid it.

As acoustic wave sensors respond to mass and ionic strength maintenance is not an issue, they can be an excellent alternative to ion selective electrodes. Besides, acoustic wave sensors can be used without a reference, while ion selective electrodes cannot. Frequency changes are proportional to metal sample concentrations and do not exhibit a logarithm dependence as potentiometric sensors, which is clearly another advantage.

An array of acoustic wave sensors to measure water hardness will be presented here, and results will be compared with those obtained, for the same water samples, by complexometric titrations.

2. Experimental

2.1. Reagents

Tetrahydrofuran (THF, Merck 8114), magnesium ionophore 1,3,5-tris [10(1-adamantyl)-7,9-dioxo-6,10-diazaundecyl] benzene (Fluka 63112), dioctyl sebacate (Fluka 84818), calcium ionophore 10,19-bis[bis(octadecylcarbomoyl) methoxyacetyl]-1,4,7,13,16-penta-oxa-10,19-diaza cycloheicosane (Fluka 21203), poly vinyl chloride (PVC, Fluka 81388) and *o*-nitrophenyloctyl ether (Fluka 73732) were used. Potassium tetrakis (*p*-chlorophenyl) borate (KTpCIPB, Fluka 60591) was added to the membrane composition as lipophilic salt. Standard stock solutions were prepared by weighting the appropriate amount of magnesium chloride (Fluka 260793) or calcium chloride (Panreac 131221), previously dried at 110 °C for 2 h, and dissolving it in Milli-Q water.

For the complexometric titration all reagents were p.a. grade. Ammonium chloride (Merck 1145) and ammonia solution (Riedel-deHäen 30501, 25% (w/w)) were used to prepare the buffer solution to which disodium–magnesium salt of EDTA (Aldrich 317810) was added. Calcium carbonate (Fluka 21060) and hydrochloric acid (Riedel-deHäen 30721, 37% (w/w)) were

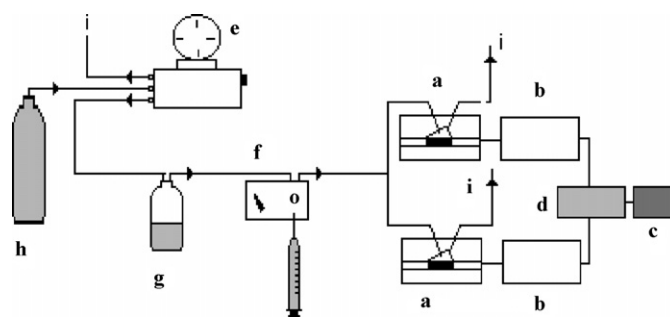


Fig. 1. Experimental layout: (a) crystal cell; (b) oscillator; (c) counter/timer device PXI 6608; (d) BNC 2121 connector blocks; (e) pressure regulator; (f) injection port; (g) Milli-Q water; (h) nitrogen; (i) waste.

used to standardize the disodium salt of ethylenediaminetetraacetic acid (EDTA, Merck 1.08418.0100), used as a titrant. Eryochrome Black T was used as indicator.

2.2. Apparatus

The piezoelectric crystals were 9 MHz, polished, AT-cut, HC-6/U with gold electrodes (ICM—International Crystal Manufacturing Co., Inc., Oklahoma City, OK, USA). Both oscillator circuits, based on TTL inverter gates, and power supply were laboratory-made. The frequencies were monitored with a Counter/Timer Device PXI 6608 from National Instruments and recorded on a PC, with data acquisition software written in LabView.

The analysis of magnesium and calcium in water were performed by flow injection analysis, using two-coated quartz crystals as sensitive detectors. Fig. 1 shows the FIA methodology used, where water carries the metal solution into the crystal cells. A constant nitrogen pressure of 0.1 bar was maintained inside the Milli-Q water bottle, by a pressure regulator (OMNIFIT 3101), and forces the water to move from the bottle to the crystal cells. The sample was injected into the water carrier through an injection valve (OMNIFIT 1106) with a sample loop of 0.5 cm³.

The experiments were performed at controlled temperature. A thermostated water bath was used to maintain the bottle of Milli-Q water, the tubes that carry the solution to the crystal cells, the standard solutions and the samples at 28.0 °C.

2.3. Procedure

The same procedure was used for preparation and deposition of both calcium and magnesium membranes. Ionophore material, PVC, plasticizer and lipophilic salt were dissolved in ~5 mL tetrahydrofuran (THF). The solution mixture was vigorously shaken to ensure thorough mixing.

The quartz crystals were coated on one side with the ionophore solution. THF was allowed to evaporate slowly at room temperature, for 48 h, giving semitransparent membranes.

In order to perform the analysis, the crystals were inserted into the cells and the coated faces were under a constant flow of Milli-Q water. Fixed quantities of 0.5 mL of magnesium solutions, or calcium solutions, of several concentrations were injected. The differences in the frequency of the crystals before injec-

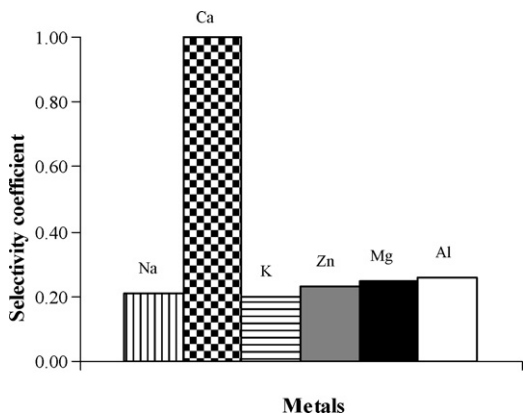


Fig. 2. Selectivity coefficients for the calcium sensor over some other metals, calculated by the fixed interference method.

tion, while Milli-Q water was flowing through the cells, and the minimum frequency observed after each sample injection, were recorded. Baseline stability and complete recover from previous experiment were assured, and no standard or sample was injected before a constant reading, corresponding to the baseline frequency was attained, for each sensor.

All the glassware, as well as the plastic bottles used to store the standards and samples for short periods before the analysis, were treated with HNO_3 and rinsed first with distilled water and finally with Milli-Q water.

All samples were also analyzed by the conventional method. Water hardness is commonly determined by the titration of a water sample with a standardized solution of the disodium salt of EDTA using Eriochrome Black T as an indicator [8]. The EDTA was dried for 2 h at about 80°C before use. The EDTA solution was standardized with a standard calcium solution prepared with calcium carbonate that has been previously dried at 105°C for 4 h.

3. Results and discussion

The sensor for calcium was prepared with one of the membrane compositions previously reported [9]: PVC (34.5%, w/w), DOS (62.1%, w/w), calcium ionophore (3.4%, w/w) and KTpCIPB in a relative molar proportion of salt/ionophore of 60%. Fig. 2 shows the selectivity coefficients for the calcium sensor over some other metals, calculated by the fixed interference method.

A new magnesium acoustic wave sensor is here reported for the first time. The sensor for magnesium was coated with a THF solution of PVC (33%, w/w), NPOE (66%, w/w), magnesium ionophore (1%, w/w) and KTpCIPB in a relative molar proportion of salt/ionophore of 150%. This membrane composition was based on the work of Spichiger-Keller on magnesium-selective membranes for ion selective electrodes [10]. In an attempt to improve selectivity and sensitivity, two other membranes were prepared for magnesium, with KTpCIPB in a relative molar proportion of salt/ionophore of 50% and 250%, respectively.

Fig. 3 shows the selectivity coefficients for the magnesium sensors prepared with those three membrane compositions, over

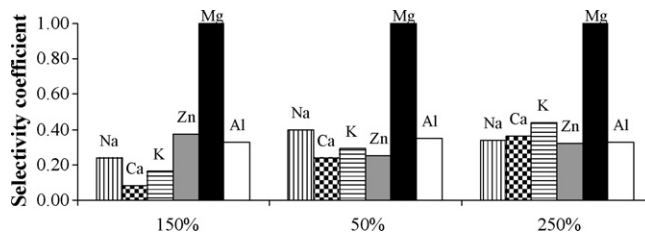


Fig. 3. Selectivity coefficients for the magnesium sensor over some other metals, calculated by the fixed interference method.

some other metals, calculated by the fixed interference method. From Fig. 3 we can conclude that, in fact, the composition of membrane which had been recommended by Spichiger-Keller [10], with KTpCIPB in a relative molar proportion of salt/ionophore of 150%, showed less interference from sodium, potassium and calcium. Therefore this composition was chosen for the magnesium sensor used in the following work.

From Figs. 2 and 3 one can conclude that, as expected, the membranes are not 100% selective to each metal, but selectivity is only important if the interfering metals are present in the sample in significant amounts, in which case sensors for other metals already developed [11–13] should be added to the array. As higher amounts of others cations, besides Ca^{2+} and Mg^{2+} , are not expected in tap waters, analyses have been performed for the moment just with two sensors: one for Ca and one for Mg.

Analysis have been carried out using the two sensors, the magnesium sensor and the calcium sensor with coating amounts which produced a frequency decrease around 20 kHz, on each crystal. Both sensors were calibrated, using standard solutions of magnesium and calcium.

Fig. 4 shows the response of the magnesium sensor to a standard solution of magnesium. Baseline frequency corresponds to Milli-Q water flowing through the crystal cell and the posterior increase in the frequency is a perturbation caused by the injection of the standard solution. As the standard solution must flow through a coil of tube (kept short enough to limit dispersion) before reaching the cell, frequency returns to baseline before it begins to decrease, when the metal reaches the crystal sensitive membrane. The decrease of the frequency is the analytical signal

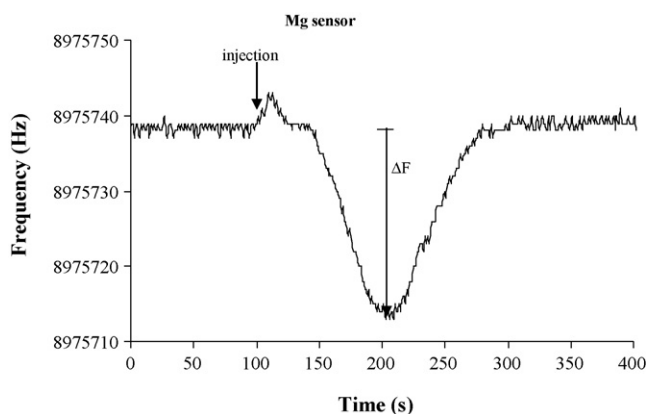


Fig. 4. Frequency of the quartz crystal coated with the membrane for magnesium, before and after the injection of a magnesium standard solution.

Table 1

Magnesium and calcium concentrations, obtained with the new quartz crystal methodology (five replicates for each sample), for several tap water samples

Water samples location	[Ca] (mg L ⁻¹)	[Mg] (mg L ⁻¹)
Water sample 1 (Aveiro)	21 ± 1	5.2 ± 0.8
Water sample 2 (Leiria)	6.8 ± 0.6	10.3 ± 0.9
Water sample 3 (Gouveia)	1.8 ± 0.6	0.8 ± 0.2
Water sample 4 (Tomar)	32 ± 1	37 ± 1
Water sample 5 (Vila Praia de Âncora)	1.0 ± 0.3	3.0 ± 0.8
Water sample 6 (Esposende)	2.2 ± 0.5	24 ± 1

used in the calibration. Complete recover of the sensor is shown, as frequency returns to baseline.

Responses of the calcium sensor have a similar shape and have been already shown elsewhere [9].

For the magnesium standard solutions analysis, a linear calibration line for magnesium sensor of $\Delta F = 0.8795[\text{Mg}^{2+}] + 15.83$, where ΔF is expressed in Hz and Mg^{2+} concentration in mg L^{-1} , and with $r^2 = 0.9994$, was obtained. The sensor for calcium showed also sensitivity to magnesium solutions, with a linear calibration line of $\Delta F = 0.4825[\text{Ca}^{2+}] + 3.4729$ and $r^2 = 0.9989$.

For the calcium standard solutions analysis, a linear calibration line for calcium sensor of $\Delta F = 0.9961[\text{Ca}^{2+}] + 22.087$, where ΔF is expressed in Hz and Ca^{2+} concentration in mg L^{-1} , and with $r^2 = 0.999$, was obtained. The sensor for magnesium showed also a significant sensitivity to calcium solutions, with a linear calibration line of $\Delta F = 0.5773[\text{Mg}^{2+}] + 3.8106$ and $r^2 = 0.999$. Using multiple linear regression (MLR) it is possible to calculate calcium and magnesium in water and finally to compute total hardness. Table 1 shows the calcium and magnesium concentration, respectively, of several tap water samples from different places in Portugal. Using these values it is possible to calculate total hardness.

The same tap water samples were also analyzed with the conventional complexometric titration. The WHO recommends the hardness water determination by a titration of calcium and magnesium with an aqueous solution of the disodium salt of EDTA at pH 10. This method requires a manual procedure subjected to human error as visual transitions associated with volume readings are performed. The method is laborious and time consuming, and consumes and discards large amount of chemicals.

Table 2

Total hardness results obtain with piezoelectric sensors and with the conventional titration method (five replicates for each sample)

Water samples location	Quartz crystal array CaCO ₃ (mg L ⁻¹)	EDTA titration CaCO ₃ (mg L ⁻¹)
Water sample 1 (Aveiro)	74 ± 1	73 ± 1
Water sample 2 (Leiria)	59 ± 1	59 ± 1
Water sample 3 (Gouveia)	9.4 ± 0.8	9.4 ± 0.7
Water sample 4 (Tomar)	225 ± 1	225 ± 1
Water sample 5 (Vila Praia de Âncora)	15 ± 1	15 ± 1
Water sample 6 (Esposende)	104 ± 1	104 ± 1

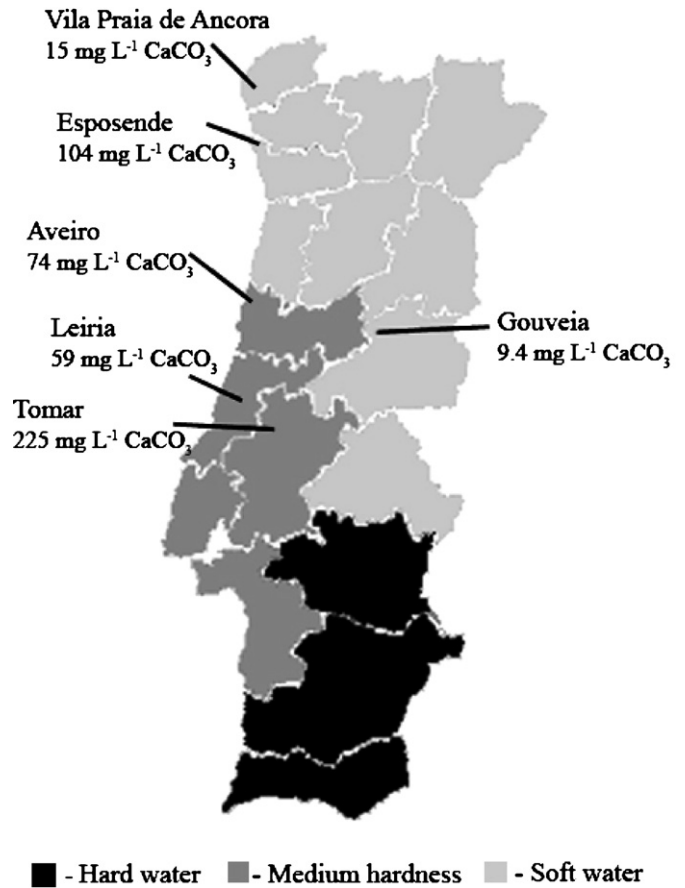


Fig. 5. National distribution of the hardness of water in Portugal, as displayed in a detergent package, along with the results of the analysis and geographic localization.

Table 2 shows the results of tap water hardness obtained with both methodologies. Average of five replicates of each sample are shown, as well as confidence intervals ($\alpha = 0.05$). The results from both methodologies were statistically compared and no differences were found both in the precision and accuracy of the results ($\alpha = 0.05$).

As we can see from Table 2, different water hardness could be found in Portugal. At the North Vila Praia Âncora ($15 \text{ mg L}^{-1} \text{ CaCO}_3$) and countryside Gouveia ($9.4 \text{ mg L}^{-1} \text{ CaCO}_3$) with soft water, Esposende ($104 \text{ mg L}^{-1} \text{ CaCO}_3$) and Aveiro ($74 \text{ mg L}^{-1} \text{ CaCO}_3$) with moderately hard water. At the Center of Portugal, we can found slightly hard water in Leiria ($59 \text{ mg L}^{-1} \text{ CaCO}_3$), and very hard water in Tomar ($225 \text{ mg L}^{-1} \text{ CaCO}_3$).

Fig. 5 shows the national hardness distribution information present in the laundry detergents. We can observe that the north of the country usually presents soft waters, the littoral centre presents medium hardness, and the south of the country presents the hardest waters. The locations of sampling collection points and mean values found have been added to the map. A few exceptions to the national trend have been detected, with Tomar clearly above the expected hardness.

As a conclusion of this work, it can be said that this new methodology is less reagent, sample and time consuming than the complexometric titration, but capable of producing results that are not statically different ($\alpha = 0.05$).

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