Magnesium optical one-shot sensor based on a coumarin chromoionophore

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Abstract

The characterization of a new irreversible optical absorption-based one-shot sensor for magnesium is described. The magnesium photoactive probe is 7-diethylamino-3-(3,4-ethylendioxybenzoyl)coumarin immobilized in a plasticized polymeric membrane. The magnesium selectivity can be explained in terms of size and charge density of magnesium and charge-separated resonance forms contribution in the excited state of coumarin. The selectivity obtained for magnesium over a variety of naturally occurring species in natural waters meets the requirements for the determination of this ion in water. The one-shot sensor responds between 0.14 and 14 mg L^{-1} with a sensor-to-sensor reproducibility of 1.3% as log $a_{Mg^{2+}}$, at the medium level of the range. The performance of the optical one-shot sensor was tested in the analysis of magnesium in different types of natural waters and soft drinks validating results against a reference procedure.
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1. Introduction

Of the different strategies for cation recognition, chromoionophore molecules are notable for having a recognition moiety for the analyte linked to a signalling moiety to convert the recognition event into an optical signal (absorption, reflection, luminescence). A very interesting signalling moiety is the coumarin nucleus because of its photochemical and photophysical properties when coupled to cryptands [1], crown ethers [2] or calixarenes [3].

Different monoaza- and diazacrowns linked to a coumarin nucleus via a methylene [4,5] or ethylene bridge [6] have been synthesized, demonstrating that the carbonyl group of coumarin moiety participates in the complexation next to the crown ring. The replacement of a methylene bridge by a carbonyl group in a monoaza-15-crow-5 ether improves selectivity against alkaline-earth ions. Here, the amide bridge

participates in the complexation and generates hyperchromaticity [7].

Making the complexing cavity stiffer by connecting the aroyl coumarin with the crown ring through a benzo group [8] or by incorporating the benzo group in the ether crown [9] leads to competition between 3-aroylcoumarin chromophore and crown ether for the metal ion, forming a mixture of two different 1:1 complexes with carbonyl groups and crown ether, respectively [8].

This was demonstrated by preparing a 7-diethylamino-3-(3,4-ethylendioxybenzoyl)coumarin in which the crown ring was substituted for a 1,4-dioxane moiety to mimic the electronic effects exerted by the crown ring on the 3-aroylcoumarin nucleus [8]. This compound only reacted with magnesium perchlorate in acetonitrile, showing an interesting bathochromic shift of 46 nm upon complexation.

Taking its selectivity against magnesium into consideration, we used this coumarin as a chromoionophore for the development of an optical one-shot sensor for the determination of Mg(II) in water.

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Different one-shot sensors or test strips for Mg(II) have been described and some of them even marketed. In the case of water, the most often proposed sensor determines Mg(II) plus Ca(II) – in fact, hardness, more than magnesium – which is the case of SerimTM water hardness test strips (Serim Research Co.), EM Quant® total hardness test (Merck) or Aquadur® total hardness (Macherey-Nagel), all of which are based on a reaction between a chemical indicator in the pad of the test strip and Mg(II) and/or Ca(II) in water, which results in a colour change that is compared with a colour scale to obtain a semi-quantitative assay value.

Other test strip procedures have been proposed for Mg(II) determination in biological fluids, such as blood or urine. The most simple are composed of a chelatometric dye such as Calmagite. RTM [10] or a cyanoformazan derivative [11], a masking agent, a buffer, and a stabilizer on a bibulous material, usually filter paper, covered with a semi-permeable membrane. Another proposed magnesium test strip is an integral multilayer analytical element comprising a water impermeable light-transmissive support, a reagent layer containing a water-soluble indicator, Xylidyl blue IR, capable of reacting with the analyte, a pH buffer, a nonionic surfactant, and a porous spreading layer containing a spreading action controller [12]. Phthalein purple has been used as reagent in the Reflectoquant® magnesium test (Merck) for determination in milk or cheese based on diffuse reflectance measurements [13].

Another type of test strip uses ionophore–chromoionophore chemistry and is comprised of a porous carrier matrix, for example, filter paper, incorporated into a homogeneous hydrophobic mixture containing N,N-diheptyl-N,N-dimethyl-1,4-butanediamide as a Mg(II) ionophore next to an indonaphthol derivative acting as chromoionophore, a plasticizer, a buffer and additional reagents such as interferent removal chemicals or wetting compounds [14]. Transparent bulk membranes of the same type have been proposed also for Mg(II) [15]. In all cases, the amount of colour change is proportional to the quantity of magnesium in the sample and this can be measured by visual comparison to a standard colour chart or with dedicated reflectance or transmission photometers.

To the best of our knowledge, chromoionophore chemistry has been not used for one-shot sensors. We describe here a selective optical one-shot sensor procedure for Mg(II) based on a ketoaminocoumarin receptor that is applied to its determination in different types of waters.

2. Experimental

2.1. Apparatus and software

A Hewlett Packard HP-8453 diode array spectrophotometer (Nortwalk, CT, USA) interfaced to a Pentium MMX 200 microcomputer via a HP IB interface board and HP IB cable for spectral acquisition and subsequent manipulation of data were used to perform the absorbance measurements. As software for the acquisition and manipulation of the spectral data, a UV–visible Chemstation software package supplied by HP was used. A 44 mm high, 12 mm homemade cell holder made of a wide painted iron block was used to obtain the absorbance measurements. The diameter of the central hole of the cell holder was 5 mm and it was placed 11.5 mm from the base. The cell holder contained a 1 mm thick space for the introduction of the sensor [16]. A Varian Cary Eclipse fluorescence spectrophotometer and an Edinburgh Instruments OB 920 fluorescence lifetime spectrometer (TCSPC technique) were used for emission measurements. Other apparatus and laboratory materials were a laboratory-made spin-on device [17], and a Crison Basic 20 (Crison Instruments, Barcelona, Spain) digital pH-meter with combined glass-saturated electrode.

2.2. Reagents and materials

All chemicals used were of analytical-reagent grade and reverse-osmosis type quality water (Milli-RO 12 plus Milli-Q station from Millipore) was used throughout. Magnesium and calcium stock solutions (0.5 M) were prepared in water from dry magnesium carbonate and calcium carbonate, respectively (Merck, Darmstadt, Germany) by adding 1:1 HCl until dissolution (pH 2.2); sodium, potassium, barium, iron(III), and zinc stock solutions (0.5 M) were prepared in water from chlorides (Merck), as well as potassium sulphate, sodium hydrogen carbonate, potassium nitrate, strontium nitrate, and sodium hypochlorite stock solutions (0.5 M) (Merck). Solutions of lower concentration were prepared by dilution with water. A pH 9.0 buffer solution 0.5 M was prepared from tris(hydroxymethyl)aminomethane (Tris) (Sigma–Aldrich Química S.A., Madrid, Spain) and HCl (Merck).

The magnesium sensitive films were prepared on sheets of Mylar type polyester (Goodfellow, Cambridge, UK) using the following chemicals: tributylphosphate (TBP), tris(2-ethylhexyl)phosphate (TEHP), 2-nitrophenyloctylether (NPOE), bis(2-ethylhexyl)sebacate (DOS), dioctylphthalate (DOP), poly(vinylchloride) (PVC; high molecular weight), and tetrahydrofuran (THF) from Sigma; potassium tetrakis (4-chlorophenyl)borate and sodium tetrakis [3,5-bis(trifluoromethyl)phenyl]borate were purchased from Fluka (Fluka, Madrid, Spain). A 5% solution of D4 and D6 polyurethane hydrogels (Tyndale Plains-Hunter L.D. Lawrenceville, NJ, USA) in 90% ethanol:water mixture and Nafion (Sigma–Aldrich) were used. The chromoionophore 7-diethylamino-3-(3,4-ethylendioxybenzoyl) coumarin was synthesized, and purified by us [8], being characterized by melting point, elemental analysis, ^{1}H, ^{13}C NMR, HRMS (FAB+), and IR.

2.3. Preparation of disposable membranes

The membranes were produced on a polyester substrate using a spin-coating technique. Mixtures for the prepara-

tion of magnesium-sensitive membranes were made from a batch of 25.0 mg (32.85 wt%) of PVC, 50.0 mg (65.70 wt%) of TBP, 0.18 mg (0.24 wt%) of 7-diethylamino-3-(3,4-ethylendioxybenzoyl)coumarin, and 0.94 mg (1.24 wt%) of potassium tetrakis (4-chlorophenyl)borate, dissolved in 1 mL of freshly distilled THF. The magnesium sensitive membranes were cast by placing 20 μL of the mixture on a 14 mm × 40 mm × 0.5 mm thick polyester sheet on a home-made spin-coater [17] rotating at 120 rpm. After spinning for 30 s, the membrane was removed from the spin coater and was left in a dryer with a saturated THF atmosphere for 3 min at room temperature to enable slow evaporation of the THF. The sensing area of the resulting one-shot sensor has the following physical characteristics: solid and homogeneous Ø 6 mm circular film, transparent and yellow, well-adhered to the solid support and with a calculated thickness of about 7.0 μm. The concentration of the chromoionophore and lipophilic salt in a dry, thin membrane was calculated to be 6.24 and 24.9 mmol kg^{-1}, respectively.

2.4. Procedure and measurement set-up

Into a glass vessel containing 50 mL of an aqueous test solution with magnesium between 4.90×10^{-4} and 5.01×10^{-6} M in activities buffered with 1 mL of pH 8.0 Tris buffer solution 0.5 M, a one-shot sensor was introduced hanging from a support. The solution was then mechanically stirred for 7 min with a magnetic stirrer at 900 rpm in such a way that the flow of the solution impinged vertically on the surface of the sensing zone without turbulence. After this, the one-shot sensor was heated with a hair dryer set 10 cm above the sensor for 1 min ($\sim$100 °C). The absorbance of the sensing membrane was measured 0.75 min after being removed from the heater at 461 nm in a spectrophotometer against a Mylar polyester strip [16]. All measurements were carried out at room temperature. The membranes were not conditioned before use.

2.5. Calculations

The analytical parameter used was a normalized absorbance α defined as $(A - A_0)/(A_1 - A_0)$, where the maximum (A_0) and minimum (A_1) absorbance values corresponded to the complexed and uncomplexed forms of the chromoionophore. They were obtained from measuring the one-shot sensors both before and after reaction with an amount of Mg(II) in the saturation zone. After optimization of the membrane composition, reaction conditions and establishing the model, it was possible to use a constant value for A_0 (0.74 ± 0.050) obtained as an average of 45 different membrane measurements. The extraction constant K_e was calculated according to [18], using values in the maximum slope zone of the experimental response functions for magnesium. Activities were calculated according to the two-parameter Debye–Hückel formalism [19]. Software programs used for the treatment of the data and fitting of experimental data

to theoretical response function were: Statgraphics software package (Manugistics Inc. and Statistical Graphics Corporation, USA, 1992), ver.6.0 STSC Inc. Statistical Graphics Corporations, USA, 1993 and Graphmatica for Win 32 ver. 1:60d, 1998 edited by K. Hertzer and adapted by J. Garrido.

3. Results and discussion

A previous study on the development of photoactive probes based on coumarins as the signalling moiety [8] reported the reaction of 7-diethylamino-3-(3,4-ethylendioxybenzoyl)coumarin against Group IIA cations, especially with magnesium in acetonitrile, a reaction explained by the cooperation of chromene and aroyl carbonyl groups (log $K_s = 3.91 \pm 0.01$).

We were interested in implementing this reaction in the one-shot sensor format for the determination of magnesium in aqueous media. Consequently, we prepared different types of membranes containing the chromoionophore being studied and the chemicals needed in each case using hydrophilic polymers, such as cellulose, polyurethane hydrogels and hydrophobic polymers such as PVC, PVA, ethyl cellulose, and Nafion, discerning that the use of hydrophobic membranes gave the best results.

Preliminary observations performed on plasticized PVC films containing the coumarin in the presence of an alkaline tetraphenylborate R showed that complexation with Mg(II) caused a bathochromic shift of 40 nm in the membrane (from 421 to 461 nm) with an isosbestic point at 436 nm (Fig. 1) very similar to the 46 nm shift (from 418 to 464 nm) observed in acetonitrile solution [8]. We also observed in the membrane that the free and complexed coumarin emitted at 473 ($\lambda_{exc} = 421$) and 491 ($\lambda_{exc} = 461$) nm, respectively, the Stokes' shift being thus smaller in the complex (from 2.61×10^{-3} to 1.32×10^{-3} cm^{-1}). Fig. 2 depicts fluorescence evolution with time. That of the free coumarin diminished in favour of an increase of the complexed one, both variations sharing a first order rate constant
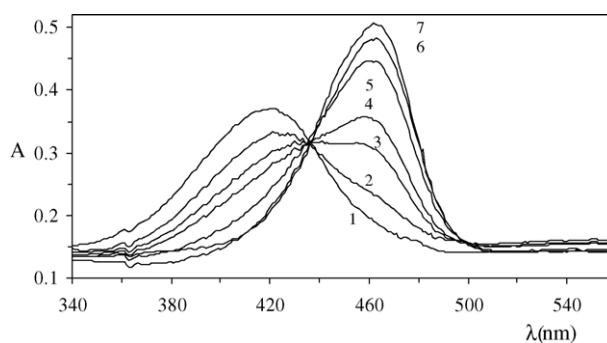

Fig. 1. Absorption spectra of one-shot sensor after reaction with different magnesium concentrations: (1) 1×10^{-5} M; (2) 3×10^{-5} M; (3) 5×10^{-5} M; (4) 7×10^{-5} M; (5) 1×10^{-4} M; (6) 4×10^{-4} M; (7) 7×10^{-4} M.
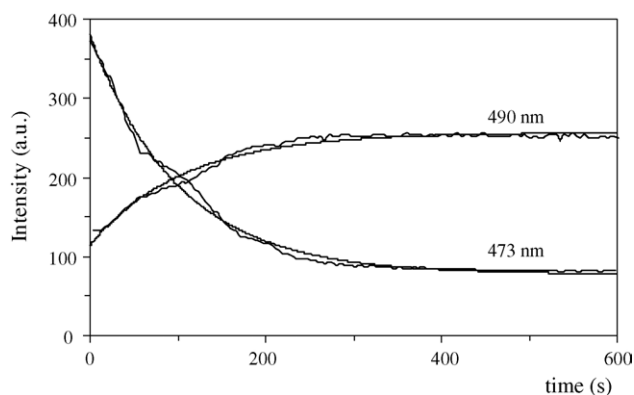
Fig. 2. Evolution of fluorescence signal of free (473 nm) and complexed coumarin (491 nm) in the membrane immediately emerged from the magnesium solution.

of $9.6 \times 10^{-3} \pm 0.4\,\mathrm{s}^{-1}$ which may correspond to Mg(II) diffusion into the viscous medium of the membrane.

After ca. 6 min emission stabilized and the overall result was a decrease of fluorescence ($\Delta \mathrm{Int} = 40\%$), as it occurred for other magnesium coumarin complexes with the same structure [20,9], although the differences could also be ascribed to the lower polarity of membrane solvent (plasticizer tributylphosphate; $\varepsilon \sim 8$ [21]).

The fluorescence lifetimes of free and complexed coumarin fitted with a biexponential decay [free coumarin: τ_1 0.52 ns (18.1%), τ_2 1.91 (81.9%), χ^2 1.123; complex: τ_1 0.91 ns (79.9%), τ_2 1.92 (20.1%), χ^2 1.084] showing that deactivation should be a relatively complicated process due to membrane heterogeneity and/or the conformational behaviour of the coumarin (vide infra) that is affected by complexation.

To finish this preliminary study we did find, to our surprise, that the extent of the reaction between the membrane and the magnesium it retained from its contact with aqueous Mg(II) solutions was limited because the subsequent heating of the film, while not submerged in the solution and after reaction, considerably increased the development of colour. This apparently unusual behaviour can be explained if one considers the conformational behaviour of the coumarin depicted in Scheme 1. Semi-empirical calculations (AM1, HyperChem) suggested that, in absence of the metal, the conformational energy minimum corresponded to an arrangement (A) where the carbonyl groups form a dihedral angle of ca. 120°. On the other hand, the large bathochromic shift observed upon complexation (40 nm) should be due to the stabilizing interaction in the excited state of the metal with the high electron density of the chromone carbonyl group transferred from the donor 7-diethylamino group [6,20]. This stabilization should be even higher in species D where the phenone and chromene carbonyl groups rest parallel to one another and co-operate in metal coordination.

We hypothesize that when the coumarin incorporates into the membrane its conformational equilibrium freezes and conformer A, less appropriate for complexation, must be the most abundant one. The initial, limited development of colour should be due to the relatively small ratio of conformer B, more suitable for complexation. Although complex D must be much more stable, the combined turning of the phenone carbonyl and phenyl groups necessary to achieve the appropriate parallel layout (B) of the carbonyl groups for Mg(II) coordination must be much more difficult in the viscous medium of the membrane (AM1 calculations predict already an activation energy of 1.5–2.0 kcal/mol in the single molecule). All evidence hints that this is the energy surpassed with the heat-
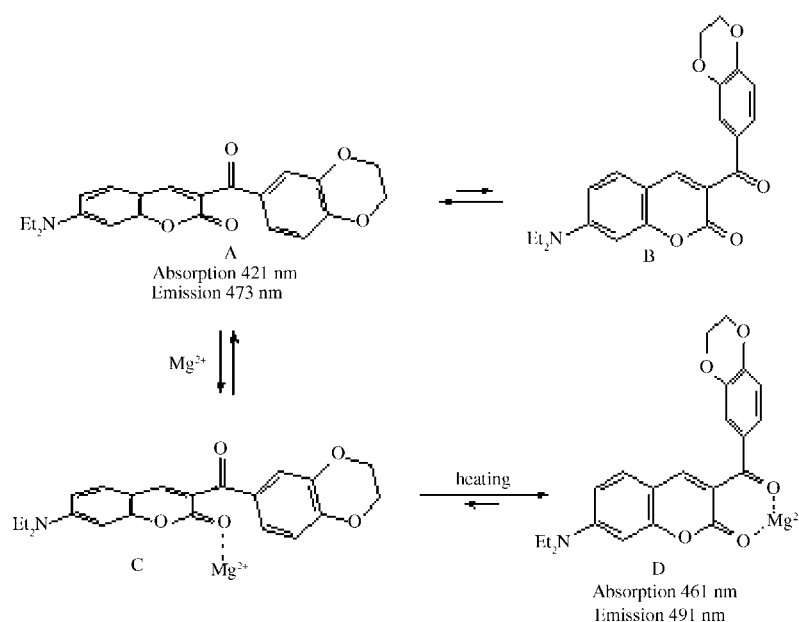

Scheme 1. Conformational behaviour of coumarin chromoionophore.

ing. Once the complex has been formed, the situation is quite stable and, thus, irreversible.

The sensing mechanism of this one-shot sensor involves a two-step process: (1) uptake of Mg(II) by ion-exchange with the ion-exchanger plasticized PVC with a limited reaction with chromoionophore L and (2) reaction of Mg(II) with coumarin concomitant to membrane heating, the whole process being irreversible. An alkaline salt of an highly lipophilic anion R^- is incorporated into the membrane to give it ion-exchange properties.

If the chromoionophore is assumed to form (1): p (M:L) complexes with magnesium, the following equilibrium holds resulting in a mass transfer of Mg(II) into the bulk of the organic membrane phase:

$$2\overline{KR} + Mg^{2+} \leftrightarrow \overline{MgR_2} + 2K^+$$

$$n\overline{L} + \overline{MgR_2} \xrightarrow{\Delta} \overline{MgL_nR_2}$$
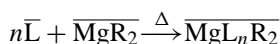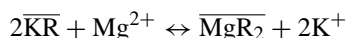
in which the over lined species are in membrane phase, while Mg(II) is in aqueous solution. The response parameter of the one-shot sensor is the protonation degree α, defined as $[C]/C_L$, measured by the absorbance of the protonated form of chromoionophore, which is the optical measurable species in membrane phase, as a normalized absorbance [22]. The α value is related to the co-extraction constant, K_e, the analytical concentrations of chromoionophore C_L and the activity of magnesium through the response function:

$$a_{Mg^{2+}} = \frac{1}{K_e} \frac{(1-\alpha)C_L}{(C_L - p(1-\alpha)C_L)^p} \tag{1}$$

Factors controlling one-shot sensor response fall into two groups: (a) those related to the design and composition of the membrane, such as proportions of components and conditions used for membrane making and (b) those related to the reaction with analyte, such as pH, contact time, heating time, and magnesium activity.

The plasticizer strongly influences the response of the membrane to magnesium, the reaction rate and selectivity. To select the plasticizer, the reaction against both magnesium and calcium was studied, finding that NPOE and DOP produced a higher response for Ca(II) than for Mg(II), DOS gave the same answer for both, TEHP exhibited a very slow response for both alkaline earth ions and, finally, TBP made it possible to discriminate between both ions. TBP was thus used as plasticizer for all subsequent experiments.

Of the different lipophilic salts tested, potassium tetrakis (4-chlorophenyl)borate provided the best results. The concentration of lipophilic salt and chromoionophore was optimized using a sequential experimental Doehlert design [23] with three levels assigned to the lipophilic salt and five to the chromoionophore. The obtained response surface (Fig. 3) did not indicate the presence of a maximum, according to Lagrange's criterion, but rather a continuous increase in the signal to concentration growth of both reagents in the membrane.
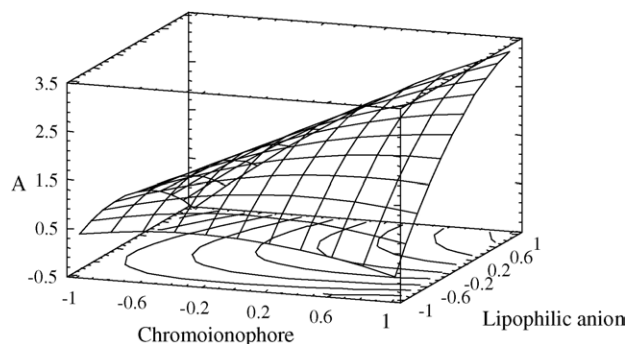

Fig. 3. Surface response for lipophilic salt and chromoionophore variation.

Notwithstanding this, the interference of Ca(II) concomitantly increased with reagent concentration, which imposes a restriction on the amount of reagent in the membrane. Thus, the optimisation of the lipophilic salt and coumarin concentration in the membrane was studied univariantly, by monitoring the calcium interference in each case. Fig. 4(1) shows the dependence of the signal on coumarin concentrations in the membrane for Mg(II) and Ca(II), illustrating the increase of Ca(II) interference with coumarin concentration. A concentration of 6.24×10^{-3} mol kg^{-1} was selected in order to minimize calcium interference at the expense of producing a poorer signal. The amount of lipophilic salt used was a 1:4 molar ratio of chromoionophore/lipophilic anion due to the observed increase in the analytical signal that was produced with lower calcium interference (Fig. 4(2)).

The percentage of plasticizer TBP in the membrane was shown to have little influence on magnesium selectivity, but a large one on the response time and physical properties of the one-shot sensor. The response time decreased up to 66% TBP, and then increased because of the worsening of the physical properties of the film (adherence, homogeneity and drying time) as shown in Fig. 4(3).

The reaction of both Mg(II) and Ca(II) with coumarin chromoionophore film is practically independent of the solution pH in the interval 6.5–9.0, as one would have anticipated considering the structure of the chromoionophore, but from pH 8.0 onwards the difference between Mg(II) and Ca(II) signals increased 15%. We selected 8.0 as the working pH and 1×10^{-2} M Tris solution as a buffer. As expected, the ionic strength of the sample influenced the one-shot sensor response. Nevertheless, experimental results showed that the signal was independent of the ionic strength, adjusted with NaCl, up to 10^{-2} M, then decreasing exponentially at higher NaCl concentrations (to 5% at 0.1 M and to 0.5% at 0.5 M), probably due to the competition of sodium with magnesium from the ionic sites in membrane. Calcium behaved identically.

It was found that the analytical signal increased with the equilibration and stirring times up to 7 min and 900 rpm, respectively, staying constant afterwards. Thus, 7 min and 900 rpm were used in the following experiments.
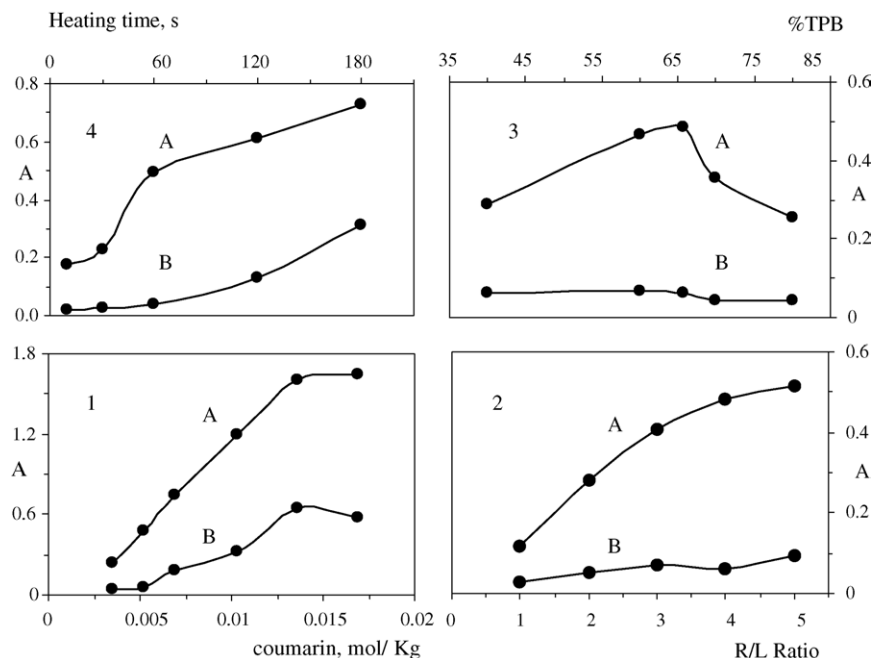
Fig. 4. Influence of several variables on one-shot sensor response: (1) chromoionophore concentration; (2) chromoionophore/lipophilic salt ratio; (3) plasticizer percentage; (4) heating time. (A) Reaction with Mg(II) (1×10^{-3} M) and (B) reaction with Ca(II) (1×10^{-3} M).

Preliminary experiments indicated that heating the membrane after contact with the solution problem greatly increased the extent of the reaction, even more than when the reaction was brought about in a warm solution. Considering different heating systems (oven, hot plate, hot air), the best results were attained with hot air coming from a conventional 1800 W hair dryer maintained 10 cm from the membrane for 1 min, thus achieving absorbance increments of 2 orders of magnitude. Higher heating times increased the calcium signal (Fig. 4(4)). From the instant the heating was ceased, the absorbance decreased reaching a constant value around 45 s later. This process was observed again with a new heating cycle.

The response of the one-shot sensor to magnesium activities was established against 20 different values between 5.4×10^{-2} and 8.7×10^{-8} (0.1 M and 10^{-7} M in concentrations) at pH 8.0 with 9 replicates of each one. Fig. 5 shows the mean experimental values along with a good adjustment of the theoretical response function calculated using Eq. (1) for the stoichiometric ratio of chromoionophore/magnesium, $p = 1$. The fitting by least-squares of the experimental points, in the linear maximum slope zone (six different concentration levels and nine replicates of each one) of the response curve for magnesium to the theoretical model indicated by Eq. (1), made it possible to calculate $\log K_e$ as 4.28 ± 0.04.

3.1. Analytical characterization and applications

To characterize the magnesium one-shot sensor we used the linear relationship in the middle of the sigmoidal response function defined by means of a lack-of-fit test as the measuring range [18]. To define the measuring range we used

three series of standards; one in the maximum slope zone (five standards, nine replicates each one, each replicate being measured with a different test strip), between 1.74×10^{-5} and 1.72×10^{-4} in activities (2×10^{-5} and 2×10^{-4} M in concentration), another in the minimum slope zone of lower activity (four standards, nine replicates each one, again each replicate being measured with a different test strip), between 8.7×10^{-8} and 2.17×10^{-6} in activities (10^{-7} and 2.5×10^{-6} M in concentration); and finally another in the minimum slope area of highest activity (six standards, nine replicates each one, again each replicate being measured with a different test strip), between 8.4×10^{-4} and 5.3×10^{-2} in activities (10^{-3} and 0.1 M in concentration). The linearity of
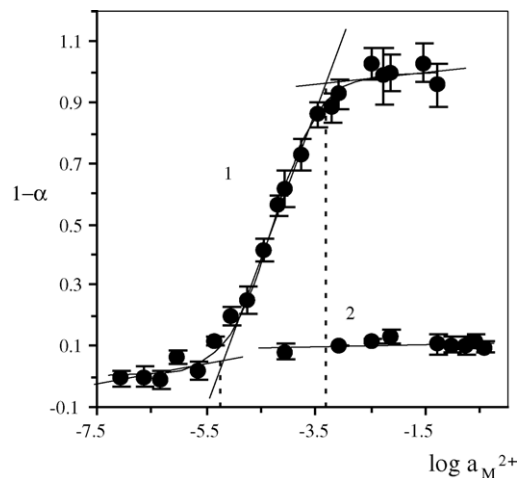

Fig. 5. Curve response of one-shot sensor: (1) against Mg(II) activity and (2) against Ca(II) activity.

each of the three series was tested by applying a lack-of-fit test and the following linear functions were obtained—(1) maximum slope: $1 - a = 0.4857 - 2.5869 \log a_{Mg^{2+}}$; (2) minimum slope in the zone of highest activity: $1 - a = 0.0195 - 1.0303 \log a_{Mg^{2+}}$; (3) minimum slope in the zone of lowest activity: $1 - a = 0.0165 - 0.1069 \log a_{Mg^{2+}}$. The interception of functions with maximum and minimum slopes in the zone of lower activity gave us a detection limit of $0.14 \, \text{mg} \, \text{L}^{-1}$ in concentration. The upper limit of the measuring range was obtained from the intercept of the linear calibration function with the linear function in the zone of higher activity, displaying a value of $14 \, \text{mg} \, \text{L}^{-1}$. Thus, the measuring range for Mg(II) determination is between 0.14 and $14 \, \text{mg} \, \text{L}^{-1}$ expressed in concentration. (5.18×10^{-6} and 4.58×10^{-4} in activities).

The precision using different one-shot sensors, and expressed as relative standard deviation (R.S.D.), was obtained at 3 activity levels of Mg(II), namely 8.69×10^{-6}, 6.07×10^{-5} and 0.34×10^{-3} in activities (1×10^{-5}, 7×10^{-5} and $4 \times 10^{-4} \, \text{M}$ in concentrations) and 10 replicates of each one, and had values of 1.1, 1.3 and 2.2% for $\log a_{Mg^{2+}}$. Table 1 shows these and other analytical parameters.

In order to check the selectivity of the one-shot sensor for the intended application to water analysis, a systematic study was conducted on the effect produced by common species in water on the determination of $1.7 \, \text{mg} \, \text{L}^{-1}$ of Mg(II). The concomitant species were tested at different concentration levels, and if interference occurred, the concentration of these species was reduced until the result was included in the interval defined by $\pm t_{(n-2;\alpha:0.05)} \cdot S_R$ (at $1.7 \, \text{mg} \, \text{L}^{-1}$). We used this interval as the reference and the maximum concentration of interfering species producing a value higher or lower to this interval was taken as the tolerance level. Table 2 shows that the obtained tolerance levels are sufficient for the analysis of magnesium in many different types of water, although the

Table 1
Analytical figures of merit

Parameter	Value (S)
Intercept	2.5869; 0.0764
Slope	0.4857; 0.0178
Probability level% (lack-of-fit test)	95.38
Linear range[a]	Up to 4.58×10^{-4}
Detection limit[a]	5.18×10^{-6}
R.S.D. (%)[b]	
8.69×10^{-6a}	1.1
6.07×10^{-5a}	1.3
0.34×10^{-3a}	2.2
Lifetime (weeks)	3

[a] Activities.
[b] R.S.D. for $\log a_{Mg^{2+}}$.

Table 2
Effect of foreign ions on the determination of $1.7 \, \text{mg} \, \text{L}^{-1}$ of Mg(II)

Foreign ions	Tolerance level (mg L^{-1})
Na(I)	162.5
K(I)	289.3
Ca(II)	5.1
Sr(II)	10.0
Ba(II)	>100
Fe(III)	>10
Zn(II)	>50
NO_3^-	>100
SO_4^{2-}	>100
ClO^-	54.4
HCO_3^-	>100

calcium interference is higher ($5.1 \, \text{mg} \, \text{L}^{-1}$) than expected considering the separate response for both alkaline-earth ions (see a calibration function for calcium in Fig. 4). This synergistic effect can be explained taking into consideration that calcium extraction by ion exchange in the membrane might be more favoured than that of magnesium. Consequently, although magnesium is complexed more favourably than cal-

Table 3
Determination of Mg(II) in different types of water using our strip and AAS as a reference method (three replicates in all cases)

Matrix	Test strip (mM Mg^{2+})	S	Reference method (mM Mg^{2+})	S	P_{val} (%)
Mineral water (Solan de Cabras)	0.8	0.09	1.0	0.02	10.7
Mineral water (Sierras de Jaén)	0.7	0.26	0.7	0.01	98.7
Mineral water (Bonaqua)	0.9	0.11	1.0	0.03	8.5
Mineral water (Lanjarón)	0.3	0.02	0.29	0.004	76.2
Horchata (Che, Puleva)	2.0	0.03	2.1	0.09	19.1
Isotonic drink (Isostar)	5.6	0.22	5.9	0.07	16.3
Tap water (City of Granada, Spain)	0.3	0.08	0.29	0.002	89.8
Tap water (La Línea, Cádiz, Spain)	0.1	0.05	0.19	0.001	5.3
Tap water (Ogíjares, Granada, Spain)	0.9	0.05	0.9	0.01	60.9
Tap water (Viznar, Granada, Spain)	0.7	0.04	0.8	0.01	5.4
Tap water (Monachil, Granada, Spain)	0.9	0.09	1.0	0.01	20.8
Tap water (Huetor Santillán, Granada, Spain)	0.8	0.10	0.9	0.01	30.2
Tap water (Carchuna, Granada, Spain)	1.6	0.17	1.6	0.01	95.3
Tap water (Armilla, Granada, Spain)	0.3	0.02	0.3	0.01	12.7
Spring water (La Peza, Granada, Spain)	1.0	0.09	1.1	0.01	8.2
Spring water (Morollón, Granada, Spain)	1.1	0.22	1.2	0.01	54.8
Well water (Otura, Granada, Spain)	2.6	0.06	2.7	0.03	6.3

cium, a high concentration of the latter led to a decrease in magnesium reaction. Despite the increase in calcium interference when it was mixed with the analyte, the tolerance level was sufficient for different applications.

To check its usefulness, the proposed one-shot sensor for water analysis was applied to different types of water (spring, mineral, and tap) and soft drinks. Table 3 shows the results obtained with the proposed optical test strip and with ASS used as a reference method. Table 3 also includes the mean values from three determinations of each sample, standard deviations of these measurements and the probability value (P_{val}) of the test used for the comparison of the measurements obtained from both methods. It may be easily seen that the results obtained from both methods are statistically similar.

The lifetime of the one-shot sensor was a mean of 3 weeks, as tested with a series of different membranes at a magnesium concentration in the middle of the range and preserved dry and protected from light and humidity.

4. Conclusion

An optical one-shot sensor for magnesium is presented that uses a coumarin-based chromoionophore implemented in a transparent membrane that works by ion exchange offering its absorbance as an easy-to-measure analytical signal.

The described one-shot sensor makes it possible to monitor magnesium for water and soft drinks, with advantages in reducing contamination, cost reduction (ca. $<$€25 g^{-1} of coumarine), and short response time. It is environmentally friendly and has an estimated lifetime of 3 weeks in usual conditions. The use of other coumarin chromoionophores that reduce temperature dependencies is now under investigation.

Acknowledgements

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