

Magnesium-selective test strip

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Abstract

A selective test strip based on an ion-exchange mechanism to determine magnesium is described. This optical and reversible test strip, made on a transparent polyester sheet, has a circular polymeric film of plasticised PVC that contains all of the reagents necessary to produce a response to magnesium, namely, a cation-selective neutral ionophore, 2-amino-*N,N'*-diheptyl-*N,N'*-dimethyl-butanediamide, a chromoionophore, *N,N*-diethyl-5-(octadecanoylimino)-5*H*-benzo[*a*]phenoxazine-9-amine, and potassium tetrakis (4-chlorophenyl)borate (TCPB) as a lipophilic salt, which is evaluated by absorbance measurement at 655 nm in a standard photometer. The experimental variables that influence test strip response, especially in terms of selectivity and response time, have been studied. The test strip responded linearly to magnesium between 0.009 and 160 mM in activities. The reproducibility intermembrane at a medium level of the range was 8.0%, as R.S.D., of $\log a_{\text{Mg}^{2+}}$, and 5.9% as R.S.D. intramembrane. The procedure was applied to the determination of magnesium in different types of waters (tap, well and mineral) validating the results against a reference procedure. This proposed method is quick, inexpensive, selective and sensitive and uses only conventional instrumentation.

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1. Introduction

The ability to monitor analyte concentrations in real time and real space using methods of chemical analysis called rapid methods has applications in many fields, including medical diagnostic, environmental control, industry, security and others.

These methods make it possible to detect and even determine a particular analyte of interest in situ without trained personnel or complicated sample treatment. Thus, it is possible to cut down on costs and make quick decisions when unforeseen problems arise.

One type of rapid method is the dry-chemical method, also known as test strips, which, when placed in contact with the problem, trigger a set of reactions and processes that

make identification or determination of the analyte possible. The estimation of the presence or amount of the analyte can be done visually, either using a colour scale to obtain a qualitative or semi-quantitative assay value or measuring a property, usually optical or electrochemical, by means of a bench-top instrument or a miniature device designed especially for this purpose. The particular advantages of test strips are: ease in handling, short analysis time, low cost and possibility of use with small instrumentation. Additionally, few or no liquid reagents are required and there are, therefore, no problems associated with the disposal of chemicals. Their main disadvantage is that they sometimes produce semi-quantitative conclusions due to low accuracy. However, the design of new strategies for recognition, measurement and manufacture may well improve this characteristic.

Magnesium is an alkaline earth ion that is ubiquitous both in nature and in manmade products. Its concentration

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in different aqueous systems, industrial products, wastes and consumer products, as well as in pharmaceuticals must be determined frequently. Additionally, the activity of magnesium in blood and serum is an important clinical parameter that needs to be monitored in different situations.

There are quick test procedures for the determination of magnesium, for example, Reflectoquant[®] magnesium test (Merck) for determination in milk or cheese using phthalein purple as the reagent after sample deproteinisation, pH adjustment and diffuse reflectance measurement [1]. In the case of water, the most often proposed test strips determine calcium plus magnesium (in fact, hardness, more than magnesium), which is the case with 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 calcium and/or magnesium ions 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 magnesium determination in biological fluids, such as blood or urine. The most simple are composed of a chelatometric dye such as Calmagite.RTM [2] or a cyanofornazan derivative [3], 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 an analyte to produce an optically detectable change, a pH buffer, a nonionic surfactant, and a porous spreading layer containing a spreading action controller [4].

Another type of test strip uses ionophore–chromoionophore chemistry and is comprised of a porous carrier matrix, for example filter paper, incorporated with a homogeneous hydrophobic mixture containing three principal ingredients: a magnesium ionophore such as *N,N'*-diheptyl-*N,N'*-dimethyl-1,4-butanediamide, a plasticiser and a chromoionophore that produces a detectable optical response, in this case an indonaphthol derivative, and a buffer, all in dry state. Other compounds that may be present are interferent removal chemicals or wetting compounds [5].

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 a dedicated reflectance photometer.

In this paper, we study a new test strip procedure to determine magnesium in different types of waters by a non-continuous but reversible optical test strip, which is a support with a transparent microzone that contains the chemistries needed to selectively respond quantitatively to magnesium by modifying its colour. The test strip proposed here is based on the use of a chromogenic compound that responds to the primary recognition process and works by an ion-exchange mechanism [6].

2. Experimental

2.1. Apparatus and Software

A diode array spectrophotometer from Hewlett Packard HP-8453 (Nortwalk, CT, USA) interfaced to a Pentium MMX 200 computer 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. A 44 mm high, 12 mm wide homemade cell holder made in a matte black painted iron block was used for strip absorbance measurements [7]. Other apparatus and laboratory materials consist of a laboratory-made spin-on device [8], and a Crison (Crison Instruments, Barcelona, Spain) digital pH-meter with combined glass-saturated electrode.

Software programs used for treatment of the data were: Chemstation software package supplied by HP for the acquisition and manipulation of the spectral data; 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. Hertzner and adapted by J. Garrido.

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 (2 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 and potassium stock solutions (2 M) were prepared in water from chlorides (Merck). Solutions of lower concentration were prepared by dilution with water. A pH 9.0 buffer solution 0.2 M was prepared from tris[hydroxymethyl]aminomethane (Tris) (Sigma–Aldrich Química S.A., Madrid, Spain) and HCl (Merck).

The test strips were prepared on sheets of Mylar type polyester (Goodfellow, Cambridge, UK) using the following chemicals: tributylphosphate (TBP), dioctylphthalate (DOP), tris(2-ethylhexyl)phosphate (TEHP), 2-nitrophenyloctylether (NPOE), bis(2-ethylhexyl) sebacate (DOS), poly(vinylchloride) (PVC; high molecular weight), and tetrahydrofuran (THF) all from Sigma; potassium tetrakis (4-chlorophenyl)borate (TCPB) from Fluka (Fluka, Madrid, Spain). *N,N*-Diethyl-5-(octadecanoylimino)-5*H*-benzo[*a*]phenoxazine-9-amine (lypophilised Nile blue; ETH 5294) was synthesized, purified and identified by us according to Morf et al. [9].

The magnesium-selective ionophore 2-amino-*N,N'*-diheptyl-*N,N'*-dimethyl-butanediamide, also known as *N,N'*-diheptyl-*N,N'*-dimethylaspartamide or ETH 2220, was synthesised, purified and identified by us according to Rouilly et al. [10].

2.2.1. Membrane preparation

Mixtures for the preparation of magnesium-sensitive membranes were made from a batch of 25.0 mg (27.5 wt.%) of PVC, 63.0 mg (69.2 wt.%) of TBP, 0.95 mg (1.0 wt.%) of 2-amino-*N,N'*-diheptyl-*N,N'*-dimethyl-butanediamide, 0.78 mg (0.9 wt.%) of *N,N*-diethyl-5-(octadecanoylimino)-5*H*-benzo[*a*]phenoxazine-9-amine and 1.33 mg (1.5 wt.%) of TCPB, all dissolved in 1 ml of freshly distilled THF. The single-use membranes were cast using a homemade spin-on device by placing 20 μ L of the mixture on a 14 mm \times 40 mm \times 0.5 mm thick polyester sheet. Thirty seconds after deposit, the rotation was stopped and the membrane was left in a dryer with saturated THF atmosphere for 3 min at room temperature to enable a slow evaporation of the THF. The dry 6 mm diameter red magnesium-sensitive membrane formed was calculated to have a thickness of about 7 μ m and a concentration of 29.34 mmol kg⁻¹ in ionophore, 14.67 mmol kg⁻¹ in chromoionophore and 29.43 mmol kg⁻¹ in lipophilic salt.

2.2.2. Absorbance measurements

The analytical parameter was the absorbance of the sensing area of the disposable strip measured at 655 nm against a Mylar polyester strip.

2.2.3. Procedure for samples and standards

An aliquot of an aqueous standard solution containing between 0.009 and 160 mM in magnesium activities was placed into a 50 mL volumetric flask along with 5 mL of pH 8.5 Tris buffer solution 0.2 M. Then, 10 mL of the above solution was placed in a 10 cm \times 1.5 cm polyethylene plastic tube and a disposable test strip was introduced for 2 min into the tube without shaking. Next, the membrane was pulled out of the solution, wiped to remove any solution droplets and its absorbance was measured at 655 nm against a Mylar polyester strip in the cell holder described above. All measurements were carried out at room temperature. The membranes were not conditioned before use.

In the case of water samples, 9 mL of water was introduced in a polyethylene tube together with 1 mL of pH 8.5 Tris buffer solution 0.2 M, operating then as described above.

2.2.4. Calculations

The ion activities ratio in aqueous phase is related to the equilibrium constant K_e and the effective degree of protonation α_{eff} through the response function:

$$a_{\text{Mg}^{2+}} = \frac{1}{K_e^{\text{MgL}_p^{2+}}} \left(\frac{a_{\text{H}^+} \alpha}{1 - \alpha} \right)^2 \times \frac{C_R - (1 - \alpha)C_C}{2(C_L - (p/2)(C_R - (1 - \alpha)C_C))^p} \quad (1)$$

where p is the stoichiometric ratio of ionophore/magnesium and C_L , C_C and C_R are the analytical concentrations of ionophore, chromoionophore and lipophilic anion, respec-

tively. The activities of Mg^{2+} and H^+ in the sample determine their concentrations in the test strip. Activities were calculated according to the Debye Hückel formalism [11]. The $K_e^{\text{MgL}_p^{2+}}$ value to obtain an optimal fit of the experimental data was calculated according to [12], using values in the maximum slope zone of the experimental response function, which provided more information with less error.

The degree of protonation $1 - \alpha$ of chromoionophore (Eq. (2)) was obtained using the problem absorbance from the test strip and the maximum and minimum absorbance values (A_{HC^+} and A_C) from the equilibrated test strip with 10^{-2} M HCl and 10^{-2} M NaOH, respectively.

$$1 - \alpha = \frac{[\text{HC}]}{[\text{C}]_0} = \frac{A - A_C}{A_{\text{HC}^+} - A_C} \quad (2)$$

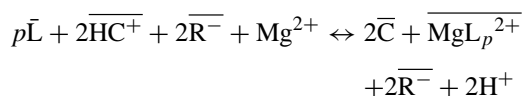
But since the chromoionophore could not be fully protonated ($1 - \alpha \cong 0.9$) at the working pH (8.5), and consequently the experimental response function began in any case at values $1 - \alpha \cong 0.9$, diminishing the interval of possible values of the analytical parameter $1 - \alpha$, we defined an effective α value, α_{eff} , in order to use a measurement which gave us the degree of protonation $1 - \alpha_{\text{eff}}$ with respect to the pH 8.5 buffer solutions. Thus, we calculated the maximum and minimum absorbance values, A_{buffer} and A_C , equilibrating strips with buffer and 10^{-2} M NaOH, substituting the absorbance value of the fully protonated membrane (HCl) with the absorbance in buffer to calculate the normalized absorbance α makes it possible to expand the response function to 1 values at low magnesium activities.

Selectivity coefficients $K_{\text{Mg},j}^{\text{opt}}$, defined as the activities quotient between the principal and interferent ion, were calculated by the separate solution method [13,14].

3. Results and discussion

The development of an optical test strip for magnesium determination requires the correct selection of reagents and a good fit to the intended application – in this case, natural waters – in terms of sensitivity and selectivity. The selected mechanism relies on a cation exchange system between a complete organic membrane of plasticised PVC containing an ionophore L and a chromoionophore C and the aqueous problem containing the analyte [15]. This system provides advantages in terms of reversibility (although this is not strictly necessary for a test strip), ample measuring range and a short response time.

In the presence of an alkaline salt of a highly lipophilic anion R^- in the membrane, the following ion-exchange equilibrium holds, if it is assumed that MgL_p^{2+} and HC^+ are the species produced:



By using the absorbance of the protonated form of chromoionophore, which is the measurable species in membrane phase, the degree of protonation $1 - \alpha_{\text{eff}}$ obtained is connected with the magnesium to proton activities ratio through the response function (Eq. (1)). Adjusting the pH with an appropriate buffer makes it possible to optically determine magnesium activity in solution.

The ionophore present in the membrane first determines the response to the magnesium. Of the different types of synthetic ionophores studied, some noncyclic diamides, especially bipodale and tripodale ionophores based on succinic and malonic acid diamides, offer very good characteristics for magnesium. The magnesium selectivity of some of those ligands is associated with the presence of one secondary amine in the diamide moiety, due to preformation of the ionophore through a resonance structure stabilized by the intramolecular hydrogen bond. The introduction of an amine as a basic hydrogen acceptor group adjacent to the diamide moiety, facilitates the displacement of the hydrogen and makes the carbonyl group easily accessible for coordination of the magnesium [16]. This is the case with the ionophore 2-amino-*N,N'*-diheptyl-*N,N'*-dimethyl-butanediamide that was designed by Simon and co-workers [10] as a neutral ionophore for ion-selective electrodes through molecular modelling. As an ISE carrier, it shows good potentiometric selectivity for alkaline earth over alkaline ions and especially for magnesium, but this ionophore has been not used for optical sensors.

3.1. Optimisation of test strip

The composition and response of the optical test strip were optimised taking into consideration: (1) factors related to the design of the selective membrane, such as proportions and components of the cocktail, and conditions used for making the membrane; and (2) factors related to the reaction between the analyte and the test strip, such as pH, contact time, and magnesium activity.

N,N-Diethyl-5-(octadecanoylimino)-5*H*-benzo[*a*]phenoxazine-9-amine was used as chromoionophore, taking into consideration its acidity characteristics and the pH requirements of the reaction and as lipophilic salt, potassium tetrakis (4-chlorophenyl)borate.

The hydrophobic environment of the sensing membrane, determined by the lipophilicity and polarity of the plasticiser, has a preponderant role in the increase of the Lewis acidity of magnesium, which enables it to coordinate with diamide carbonyls. As a plasticiser, we tested TBP, DOP, TEHP, NPOE and DOS. The sensitivity, understood to be the value of the signal for a given concentration and time, as well as the response time of the different test strips towards magnesium ion, increased with the plasticiser in the order phosphates esters > carboxylic esters > ethers, namely TBP > TEHP > DOS > DOP > NPOE. TBP was selected as plasticiser for all subsequent experiments.

The concentration of lipophilic salt controls the overall magnitude of the optical response via the electroneutrality

condition within the polymeric membrane, just as the proportion of anionic sites influences the selectivity.

The variation of the selectivity coefficient $K_{\text{Mg},j}^{\text{opt}}$ (SSM method) for alkaline and alkaline earth ions at pH 8.8 using a test strip prepared with different lipophilic anion to ionophore ratios ranging from 50% to 130% was studied for two plasticisers: TBP, which offers the best sensitivity, and NPOE, used in ISE with the same ionophore with good results [10]. The quantity of the chromoionophore used was kept constant in an amount adequate to minimise photometric error in the measurement of the absorbance. Experimental results indicate that plasticiser NPOE does not offer any selectivity to the membrane; on the contrary, membranes containing TPB exhibit maximum rejection of calcium, sodium and potassium if 100 mol% anionic sites relative to neutral carrier are added to the membrane (Fig. 1). This behaviour is different from potentiometric membranes containing the same ionophore and lipophilic salt and NPOE as plasticiser, where the maximum rejection is observed at 73% [10,17], which agrees with the formation of a 1:2 (Mg:L) complex according to the theoretical model of the selectivity-modifying influence of charged components in neutral-carrier-based membrane electrodes [18].

The values of $K_{\text{Mg},j}^{\text{opt}}$ obtained using membranes with the optimum ratio of lipophilic anion to ionophore for alkaline and alkaline earth ions, are -2.901 Ca(II); -3.310 Na(I) and -3.098 K(I), which means that the proposed method is in the order of 796 times more selective for magnesium than for calcium, 2042 times more than for sodium and 1253 times more than for potassium. This membrane exhibits sufficient magnesium selectivity against the interfering ions that were studied considering the required selectivity coefficients [13] for the determination of magnesium in natural waters ($\log K_{\text{Mg},j}^{\text{opt, req.}}$: -2.8 (Mg); -3.1 (Na); -1.9 (K)). These required selectivity coefficients were calculated based on a maximum tolerable error of 3% in the determination of magnesium by means of a test strip and using the high and low mean values of those ions in the Spanish basins [19].

To optimise the amounts of plasticiser TBP, and hence polymer PVC, we studied the response time of test strips containing different amounts ranging from 30 wt.% to 80 wt.% in TBP. For these experiments, the strip was placed on one side of a 10 mm path-length optical cell, and 5 ml of $1 \times$

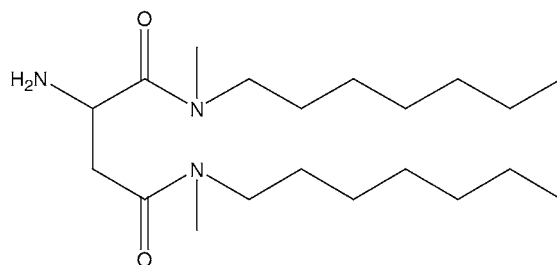


Fig. 1. Structure of ionophore 2-amino-*N,N'*-diheptyl-*N,N'*-dimethyl-butanediamide.

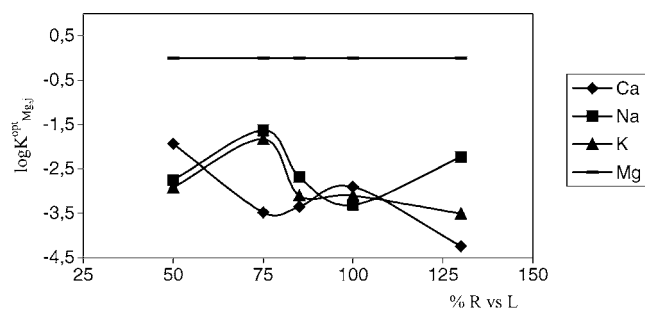


Fig. 2. Selectivity (SSM method) variation of the test strip as function of lipophilic anion/ionophore at pH 8.5 and using TBP as plasticiser.

10^{-1} M of Mg (II) solution was added. Amounts below 50% do not give off a good response. The response times to reach the equilibrium were: 1500 s for 30%, 150 s for 50%, and 100 s up to 60%. Despite the fact that the rate increased with the amount of TPB, a percentage of 70% was selected as optimal, since higher percentages worsens the physical properties; specifically, the membrane is less homogeneous and the drying time increases.

The presence of a basic amine group (pK_a 7.22) in the ionophore molecule is a drawback for the magnesium-selective electrode based on the same ionophore because heavy interference of hydrogen ions is observed [10]. This is usual with ISE in that only one kind of ion is allowed to partition between sample and membrane phases, and therefore carriers that contain an additional site binding, as the amine group in this case, show considerable protonic interference. In bulk optodes, those ionophores do not pose any problem as long as the second ion is chosen as reference.

Since the ion-exchange equilibrium depends on the pH value as shown in Eq. (1), it is possible to adjust the selectivity by modifying the pH value [13]. Only at pH values above 7.5 does the exchange reaction of H^+ by Mg^{2+} between membrane and bulk solution begin. Fig. 2 shows that selectivity towards magnesium ion is enhanced by an increase of pH and that the response level reaches a maximum at pH 8.5. As a buffer, we use pH 8.5 Tris 2×10^{-2} M solution.

The optical response of the test strip based on 2-amino- N,N' -diheptyl- N,N' -dimethyl-butanediamide ionophore to magnesium activities between 1.36×10^{-1} M and 7.91×10^{-8} M in activities (1 M and 10^{-7} M in concentrations) at

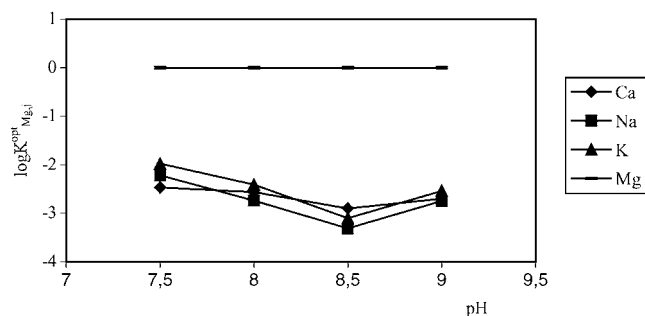


Fig. 3. Effect of pH on the selectivity.

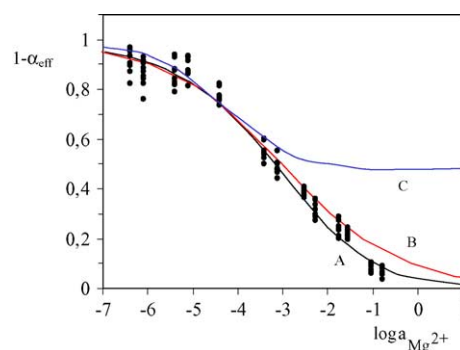


Fig. 4. The effect of stoichiometry on the response curve. Theoretical curve for (A) 2:1 (L:M); (B) 1:1; and (C) 1:2.

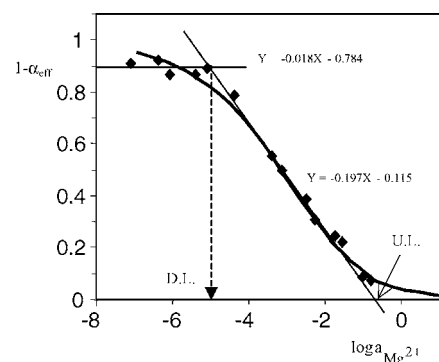


Fig. 5. Calibration plot for free magnesium activity.

pH 8.5 is shown in Fig. 3 along with the theoretical response function using Eq. (1) for the stoichiometric ratio of ionophore/magnesium, $p = 1-3$. With ions with a charge higher than 1, the effect of stoichiometry on the response curve is small and a clear distinction between different stoichiometries is difficult to make from the prior curve [20]. The effect of stoichiometry on the response curve shows a clear distinction between the stoichiometry 2:1 Mg:L and the others, 1:1 and 1:2. The distinction between 1:1 and 1:2 sto-

Table 1
Analytical Figures of Merit

Parameter	Value; S
Intercept	-0.1153; 0.0098
Slope	-0.1967; 0.0033
Probability level % (lack-of-fit test)	15.3
Linear range (mM)	0.009–160
Detection limit (mM)	0.009
Cost (€/strip)	0.0080
R.S.D. (%) ^a intramembrane (mM)	5.4
0.073 ^b	3.5
5.3 ^b	11.3
90.1 ^b	
R.S.D. (%) ^a intermembrane (mM)	8.0
0.073 ^b	14.1
5.3 ^b	
90.1 ^b	39.8

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

^b Activities.

Table 2
Determination of magnesium in different types of water using AAS as a reference method

Matrix	Test strip (mM Mg ²⁺)	S	Reference method (mM Mg ²⁺)	S	P _{val} (%)
Tap water (City of Granada, Spain)	0.477	0.085	0.445	0.011	28.3
Tap water (Otura, Granada, Spain)	1.74	0.13	1.640	0.026	12.6
Well water (Colomera, Granada, Spain)	0.88	0.18	0.876	0.082	47.0
Mineral water (Fonte Forte)	0.43	0.11	0.386	0.003	27.3
Mineral water (San Vicente)	0.367	0.055	0.352	0.001	33.6
Mineral water (Lanjarón)	0.54	0.11	0.425	0.003	10.1
Mineral water (Fuente primavera)	1.31	0.11	1.131	0.005	5.7
Mineral water (Fuente Liviana)	0.86	0.17	0.851	0.005	44.9
Mineral water (Zambra)	1.28	0.23	1.177	0.005	36.1
Mineral water (Solán de Cabras)	1.33	0.12	1.250	0.013	19.6

Three replicate samples in both cases.

ichiometries is not clear, but we assume according to molecular modelling of Rouilly et al. [10] that 1:2 octahedral complex occurs in membrane.

The fit by least-squares of the experimental points, in the linear maximum slope zone (eight different concentration levels and nine replicates of each one) of the response curves for both alkaline earths to the theoretical model indicated by Eq. (1), makes it possible for us to calculate for apparent $\log K_e^{\text{MgL}_2^{2+}}$ the value 14.11.

3.2. Analytical parameters

As a measuring range, we used the linear relationship in the middle of the sigmoidal response function defined by means of a lack-of-fit test and as the detection limit the intersection of the linear calibration function defined above and a linear function adjusted in the minimal slope zone (background) [12].

In order to determine the range and the detection limit, we prepared two series of standards; one in the maximum slope zone (five standards, nine replicates each one, each replicate being measured with the same test strip), between 9.13×10^{-2} and 3.79×10^{-4} in activities (5×10^{-1} and 5×10^{-4} M in concentration), and the other in the minimum slope zone of lower activity (five standards, nine replicates each one, again each replicate being measured with the same test strip), between 7.92×10^{-6} and 7.93×10^{-8} in activities (10^{-5} and 10^{-7} M in concentration) (Fig. 4). The linearity of both series was tested by applying a lack-of-fit test and the following linear functions were obtained: $1 - \alpha_{\text{eff}} = 0.784 - 0.018 \log a_{\text{Mg}^{2+}}$ and $1 - \alpha_{\text{eff}} = -0.115 - 0.197 \log a_{\text{Mg}^{2+}}$. The interception of both functions gave us a detection limit of 0.009 mM. The upper limit of the measuring range was obtained from the intercept of the linear calibration function with the axis of abscise; the value obtained was 260 mM. Thus, the measuring range for magnesium determination was between 0.009 and 260 mM, expressed in activities. But in practice we prefer to use the highest value tested, 160 mM (1000 mM in concentrations) as the upper limit of the measuring range.

The precision using the same test strip, expressed as relative standard deviation (R.S.D.), was obtained at three activity levels of magnesium (Fig. 5), namely 7.31×10^{-4} , 5.33×10^{-3} and 9.13×10^{-2} M in activities (1×10^{-3} M, 1×10^{-2} and 5×10^{-1} M in concentrations) and 10 replicates of each one, and had values of 5.4, 3.5 and 11.3% for $\log a_{\text{Mg}^{2+}}$. The repeatability using different strips was determined as above, using the same activity levels as before and 10 replicates of each one, and had values of 8.0, 14.1 and 39.8% for $\log a_{\text{Mg}^{2+}}$. Table 1 shows these and other analytical parameters.

3.3. Application of the test strip

The proposed test strip for magnesium was applied to actual samples of waters of diverse provenance (spring, mineral, and tap). Table 2 shows the results obtained using the proposed optical test strip with an atomic absorption procedure used as a reference method and 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 for both methods. As can be seen, the results obtained for both methods are statistically similar.

4. Conclusion

We have studied an optical test strip for magnesium determination with good performance based on a diamide ionophore developed for ISE, which measures by transmission and which offers sufficiently good repeatability and may be considered as an inexpensive alternative to obtaining analytical information in situ. The prepared membrane has sufficient selectivity for the determination of magnesium in natural waters and can be successfully applied to the determination of this ion in waters from different provenances. Only needing buffering, this procedure offers good results, with an accuracy, precision and cost that make it useful for possible routine analysis. The lifetime of the studied test strip is a half months in usual conditions when protected from light.

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References

- [1] Merck, Reflectoquant. Magnesium in Milk, <http://www.environmental-center.com/technology/merck/#merck>, 2004.
- [2] G.D. Steinman, US 5,397,710, 1995.
- [3] M.J. Smith-Lewis, J.C. Mauck, J.L. Toner, US 4,753,890, 2004.
- [4] M. Tanaka, F. Arai, K. Terashima, N. Yaginuma, US 4,966,784, 1990.
- [5] M.L. Gantzer, P.R. Hemmes, D. Wong, US 4,670,218, 1987.
- [6] U.E. Spichiger-Keller, Chemical Sensors and Biosensors for Medical and Biological Applications, Wiley-VCH, Weinheim, 1998.
- [7] L.F. Capitán-Vallvey, M.D. Fernández-Ramos, P. Alvarez de Cienfuegos, F. Santoyo-Gonzalez, Anal. Chim. Acta 481 (2003) 139.
- [8] K. Seiler, W. Simon, Anal. Chim. Acta 266 (1992) 73.
- [9] W.E. Morf, K. Seiler, B. Rusterholz, W. Simon, Anal. Chem. 62 (1990) 738.
- [10] M. Rouilly, M. Badertscher, E. Pretsch, G. Suter, W. Simon, Anal. Chem. 60 (1988) 2013.
- [11] P.C. Meier, Anal. Chim. Acta 136 (1982) 363.
- [12] L.F. Capitán-Vallvey, M.D. Fernández-Ramos, P. Alvarez de Cienfuegos, Anal. Chim. Acta 451 (2002) 231.
- [13] E. Bakker, W. Simon, Anal. Chem. 64 (1992) 1805.
- [14] M. Lerchi, E. Bakker, B. Rusterholz, W. Simon, Anal. Chem. 64 (1992) 1534.
- [15] E. Bakker, P. Buhlmann, E. Pretsch, Chem. Rev. 97 (1997) 3083.
- [16] U.E. Spichiger-Keller, Chemical Sensors and Biosensors for Medical and Biological Applications, Wiley-VCH, Weinheim, 1998.
- [17] R. Eugster, P. Gehrig, W.E. Morf, U.E. Spichiger-Keller, W. Simon, Anal. Chem. 63 (1991) 2285.
- [18] P.C. Meier, W.E. Morf, M. Laeubli, W. Simon, Anal. Chim. Acta 156 (1984) 1.
- [19] J.G. Catalan Lafuente, Química del Agua, second ed., Talleres Gráficos Alonso, Madrid, 1981.
- [20] E. Bakker, M. Willer, E. Pretsch, Anal. Chim. Acta 282 (1993) 265.