Simultaneous determination of inorganic anions, calcium and magnesium by suppressed ion chromatography

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Abstract

Suppressed conductimetric detection ion chromatography (IC) was investigated for the separation and detection of common inorganic anions, calcium and magnesium by anion-exchange chromatography using a sodium carbonate–EDTA mobile phase. The formation of anionic Ca^{2+}–EDTA and Mg^{2+}–EDTA complexes allowed its separation from other inorganic anions opening the way for their simultaneous determination in a single chromatographic run. The effect of the pH, carbonate and EDTA concentrations in the eluent and the previous addition of EDTA to the samples has been studied. The optimised experimental conditions were applied to the determination of Ca^{2+} and Mg^{2+} in mineral waters with results in agreement with alternative ICP-MS methodologies.
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1. Introduction

Since its introduction in 1975 by Small et al. [1], ion chromatography (IC) has emerged as a very powerful method for analysis of anions and cations in a variety of environmental samples, especially aqueous solutions [2,3]. IC offers a number of advantages over alternative analytical methods in terms of speed, sensitivity, selectivity, simultaneous determination ability, stability and reliability [2]. However, anions and cations cannot be separated simultaneously in the same column in a conventional ion chromatographic system. In fact, one of the most effective developments in ion chromatography has been the introduction of procedures that allow the simultaneous separation of metal cations and simple inorganic anions [4,5]. These methodologies include both suppressed and non-suppressed techniques.

Early attempts involved dual anion and cation columns with a single conductivity detector and manual switching of the eluent flow [6,7]. More sophisticated techniques involve the use of single and dual detection systems [2], two-anion plus cation-exchange columns connected in series with two detectors and an eluent compatible with both [8–11] and also anion- and cation-exchange columns in series with a column-switching technique [12,13]. Alternative methods developed involved mixed bed ion-exchange columns packed with both anion- and cation-exchange resins, mainly containing alumina and silica [14]. More recently, single weakly acidic cation-exchange columns have been used to separate cations by ion-exchange and anions by ion exclusion [15]. A method using a single octadecyl silica column coated with a zwitterionic stationary phase has been also proposed [16].

On the other hand, attention in the literature has been focused on methods based on single-column ion chromatography with chelating agents as eluents. Aminopolycarboxylic acids (EDTA, DCTA, etc.) or benzenepolycarboxylates (phthalate, trimellitate, etc.) are commonly employed as eluent ions, in both non-suppressed and suppressed ion chromatography [17–27]. Highly charged, strongly complexing anions react with most divalent and trivalent metal cations producing singly or doubly negative charged complexes, allowing the simultaneous separation of metal cations and inorganic anions.

Detection that involves indirect UV photometric detection in non-suppressed systems has received particular attention in the literature. This is due mainly to the simplicity and high sensitivity achieved and the strong UV absorption of these chelating eluents. In this way, several authors studied

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the separation of anions and alkaline earth metal ions by using EDTA or DCTA as eluent with UV and conductivity detectors in series [17,18]. A method with DCTA as eluent was employed to achieve the separation of inorganic anions and divalent and trivalent metal cations in drinking waters [19]. In this sense, the simultaneous separation of inorganic and some organic anions and alkaline earth metal cations was studied with different aminopolycarboxylic acids as eluents [20]. Benzenepolycarboxylates or benzenepolycarboxylates–aminopolycarboxylic acid mixtures, mainly with EDTA, are widely used as eluents for the simultaneous determination of inorganic anions and cations by non-suppressed ion chromatography with indirect photometric detection [21–23].

In contrast with indirect photometric UV detection, conductivity detection is less common in the literature, due mainly to the small differences in the conductivity between inorganic anions and chelating agents. In this sense, Yamamoto et al. [25] reported the separation of inorganic anions and Ca and Mg cations on an anion-exchange column with EDTA as eluent and conductivity detection. Using EDTA as eluent, magnesium and calcium chelate anions were eluted as negative peaks. This behaviour might be caused by the lower conductivity of the chelate anion relative to that of the EDTA eluent anion.

More recently, Ohta and Tanaka [26] carried out the simultaneous determination of common inorganic anions and divalent cations by suppressed conductimetric detection using pyromellitate as eluent. A cation-exchange membrane suppressor in the H^+ form was employed after anion-exchange separation and therefore the analytes are detected as an increase of the concentration of H^+ or the pyromellitic acid in the eluent.

Attention has also been devoted to describe and predict the chromatographic behaviour of metal–EDTA complexes. Retention models have been developed by Hajós et al. [27] to study the retention of complexes by anion-exchange chromatography. Suppressed conductivity detection with carbonate eluent and EDTA as complexing agent in the sample provided detection limits about one order of magnitude better than in a non-suppressed system with EDTA as eluent. In this sense, the simultaneous determination of inorganic anions (BrO_3^-, SeO_4^{2-}, CrO_4^{2-}, etc.) and metal ions (Pb^{2+}, Cd^{2+}, Ni^{2+}, etc.) pre-complexed by EDTA by suppressed ion chromatography has been studied quite recently by Bruzzoniti et al. [28]. In their paper, the authors describe a method in which transition metals can be separated from common anions by anion-exchange chromatography and detected by conductivity at ppb levels.

The use of EDTA to form anionic complexes which can be separated from other common anions is further studied in this paper. However, our focus is different from that of Bruzzoniti et al. [28] in the sense that we tried to develop and validate a method which could be used by testing laboratories under realistic conditions. The simultaneous determination of Ca^{2+} and Mg^{2+} and other common anions by suppressed ion chromatography is evaluated, optimised and validated in this paper.

2. Experimental

2.1. Apparatus

A Dionex model DX-120 ion chromatograph (Sunnyvale, CA, USA), equipped with a 75 μl sample loop was employed along with a Dionex PeakNet chromatography workstation for instrument control as well as data acquisition and processing in conductivity detection. A Dionex Ion Pac AG 9-HC (4 mm × 50 mm i.d.) guard column and Dionex Ion Pac AS 9-HC (4 mm × 250 mm i.d.) separation column were used. The eluent consisted of 8 mM Na_2CO_3 (or 10 mM) plus 0.02 mM EDTA (1 ml min^{-1}). A Dionex ASRS-ULTRA (4 mm) anion self-regenerating suppressor (100 mA; external water source mode) was used for conductivity suppression before detection by a Dionex CDM-3 conductivity cell.

In addition, an inductively coupled plasma mass spectrometer (ICP-MS) model HP-4500 (Agilent, Yokogawa Analytical Systems, Kyoto, Japan) was connected after the conductivity detector of the IC system using a 50 cm long peek tubing (Dionex). The isotopes selected were *m/z* 25 and 44 for magnesium and calcium detection, respectively. Instrumental operating conditions, both for separation and specific alkaline earth metal detection, are summarised in Table 1.

2.2. Reagents

Eluents were prepared by using analytical grade Na_2CO_3, $NaHCO_3$ (Merck, Darmstadt, Germany) and EDTA

Table 1
Instrumental operating conditions

Parameter	Value
Chromatographic parameters	
Chromatograph	Dionex DX 120
Separator column	Dionex Ion Pac AS 9-HC (250 mm × 4 mm i.d.)
Guard column	Dionex Ion Pac AG 9-HC (50 mm × 4 mm i.d.)
Eluent	10 mM Na_2CO_3 + 0.02 mM EDTA
Eluent flow rate	1 ml min^{-1}
Sample loop	75 μl
Detection	Suppressed conductivity
Suppressor	ASRS-ULTRA (4 mm)
Regenerant	Distilled water (7 ml min^{-1})
Current	100 mA
ICP-MS parameters	
Instrument	HP-4500
Rf power	1300 W
Argon nebuliser gas flow rate	1 l min^{-1}
Isotopes monitored	^{25}Mg, ^{44}Ca
Integration time	0.3 s per isotope

(ethylenediaminetetraacetic acid disodium salt dihydrate) (Fluka, Buchs, Switzerland). An EDTA concentrated stock solution (40 mM) was prepared for the mobile phase. Eluents were filtered and degassed with helium to remove particles and dissolved gases. All inorganic salts used for anions standard solutions were sodium salts of analytical reagent grade (Merck) except bromate and phosphate, which were potassium salts. Stock solutions of each anion (1000 mg l^{-1}) were prepared by dissolving the pure salts in deionised water (resistivity 18.2 MΩ cm^{-1}) obtained from Milli-Q water purification system (Millipore, Milford, USA).

In order to avoid the use of interferent inorganic anions, $CaCO_3$ and $MgCO_3$ (Merck) were selected as inorganic salts for calcium and magnesium standards. Due to its low solubility in water, stock standard solutions (1000 mg l^{-1}) were prepared by dissolving such salts in a solution containing 0.1 M EDTA in 0.15 M NaOH (pH 10; Merck). In real samples, calcium and magnesium ions were either not treated at all or pre-complexed with 5 mM EDTA (pH 10) in order to ensure total cation complexation with a suitable excess of EDTA.

3. Results and discussion

3.1. Detection mechanism

As a chelating agent, EDTA can form chelates with alkaline earth metal ions at relatively high pH which could be separated from others anions on anion-exchange columns. However, pure EDTA eluents are not suitable for suppressed ion chromatography due to the high conductivity of the mobile phase after the suppressor column. This should be translated in a low sensitivity of the conventional conductivity detection for the EDTA complexes. Preliminary studies were carried out in order to test the suitability of EDTA as complexing agent and using a conventional carbonate/bicarbonate eluent and injecting standards of Ca^{2+}–EDTA and Mg^{2+}–EDTA prepared at pH 10. Both conductivity detection and selective ICP-MS detection were evaluated. For this purpose, the exit of the conductivity detector of the ion chromatograph was coupled on-line to an HP-4500 ICP-MS. Due to its high sensitivity and selectivity, ICP-MS have been previously employed as an alternative anion detector [29,30]. Fig. 1 compares the chromatograms obtained for Ca^{2+}–EDTA and Mg^{2+}–EDTA complexes by conductivity and ICP-MS detection with (a) or without (b) membrane suppressor under the above reported conditions. As can be observed, two peaks corresponding to Ca^{2+}–EDTA and Mg^{2+}–EDTA complexes were detected by conductivity detection in suppressed IC. However, under these conditions the analytes were not observed by ICP-MS detection. Conversely, Ca^{2+}–EDTA and Mg^{2+}–EDTA complexes were detected by ICP-MS when the suppressor column was bypassed as shown in Fig. 1b for direct ICP-MS detection.
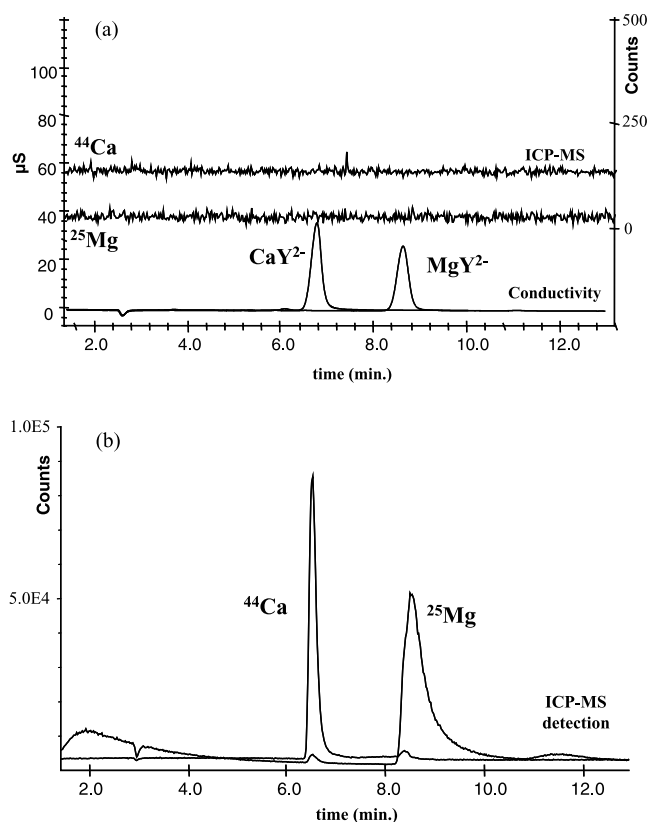

Fig. 1. (a) Chromatograms obtained for Ca–EDTA and Mg–EDTA complexes by conductivity and ICP-MS detection with membrane suppressor. (b) ICP-MS detection without membrane suppressor (isotopes: ^{44}Ca and ^{25}Mg). Eluent: 8 mM Na_2CO_3, 3.7 mM $NaHCO_3$, 0.02 mM EDTA.

These experimental results indicate that both calcium and magnesium ions from the EDTA complexes were eliminated in the suppressor column. This behaviour could be derived from the fact that when carbonate eluent is introduced into the membrane suppressor, carbonate is converted to CO_2 and H_2O and the pH of the eluent decreases to around 3. Thus, Ca^{2+}–EDTA and Mg^{2+}–EDTA complexes reaching the suppressor membrane are destroyed and so free Ca^{2+} and Mg^{2+} ions are eventually removed by the suppressor column. However, due to the partial dissociation of "freed" EDTA in the eluent at the acidic suppression pH used, the two divalent cations are detected conductimetrically as an increase of the concentration of H^+ in the eluent. As a result, high and positive conductimetric detector response is obtained similar to that of other common anions.

Calibration standards were prepared by dilution of the stock standards of calcium and magnesium (1000 mg l^{-1}) in different volumes of a 0.1 M EDTA in 0.15 M NaOH buffer solution to ensure a pH around 10 in the samples. Different EDTA concentrations were evaluated and the results showed that when the concentrations of EDTA in the standards were above 10 mM, changes in Ca and Mg retention times were observed when increasing the concentration of metal. This could be due to overloading the column with free EDTA which blocked anion-exchange sites
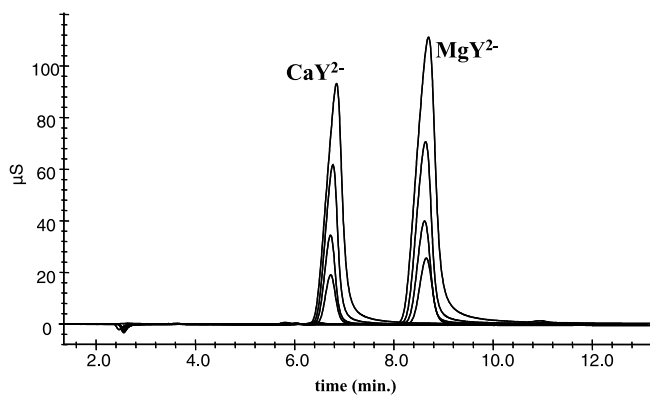
Fig. 2. Chromatograms obtained for different Ca and Mg concentrations. Calibration standards: 0, 5, 10, 20 and 40 ppm Ca and Mg in 5 mM EDTA at pH 10 (7.5 mM NaOH). Eluent: 8 mM Na_2CO_3, 0.02 mM EDTA.
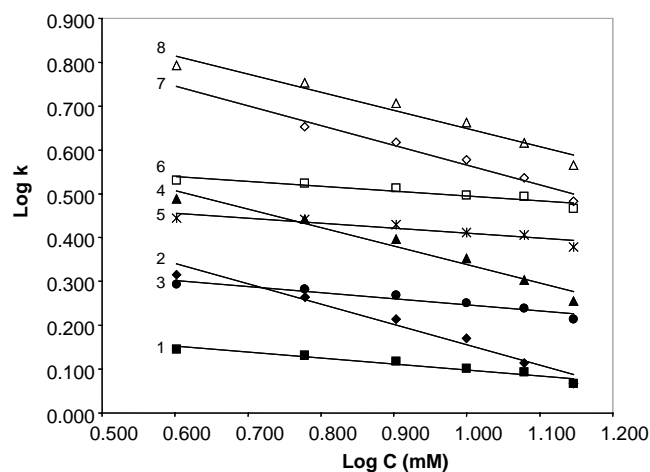

Fig. 3. Relationship between the logarithm of the retention factor (k) and the logarithm of the concentration of carbonate: (1) Cl^-; (2) CaY^{2-}; (3) NO_2^-; (4) MgY^{2-}; (5) Br^-; (6) NO_3^-; (7) HPO_4^{2-}; (8) SO_4^{2-} (0.02 mM EDTA).

in the column. This problem was eliminated by reducing the concentration of EDTA in the samples. For example, Fig. 2 shows the chromatograms obtained for the calibration standards of Ca and Mg when the standards were prepared in 5 mM EDTA and 7.5 mM NaOH. Under these conditions, no important retention times changes of calcium and magnesium complexes were observed, even for higher metal concentration levels. These conditions were selected for further studies in the optimisation of the separation from other anions.

3.2. Optimisation of the chromatographic separation

In order to separate simultaneously common inorganic anions plus calcium and magnesium, the effect of the concentration of carbonate in the eluent on the retention behaviour was investigated. The retention times of ten inorganic anions and the Ca^{2+}–EDTA and Mg^{2+}–EDTA complexes were studied at six different carbonate concentrations (4, 6, 8, 10, 12 and 14 mM) and a pH of 10.3 with no bicarbonate addition to the mobile phase. Fig. 3 shows the variation of the logarithm of the retention factor ($\log k$) for eight different analytes as a function of the logarithm of carbonate concentration in the mobile phase while keeping the EDTA concentration constant at 0.02 mM. It can be seen that the relationship between $\log k$ and $\log([CO_3^{2-}])$, in mM, was linear as expected. As shown in Fig. 3, the k values decreased when the carbonate concentration is increased and a more significant decrease in the retention is observed for divalent anions. Experimental values of the slope of the linear trend for calcium and magnesium signals was similar to the divalent anions (SO_4^{2-}, HPO_4^{2-}) and about twice that for monovalent anions, according to the expected anion-exchange mechanism. These results confirm that both Ca^{2+}–EDTA and Mg^{2+}–EDTA complexes were separated in the anion-exchange column as divalent anionic complexes. Optimum carbonate concentration selected was 8 mM Na_2CO_3, providing a good separation at reasonable elution times.

Separations were also performed at four different EDTA concentrations, 0, 0.02, 0.05 and 0.1 mM, with the carbonate concentration in the eluent fixed at 8 mM. When EDTA was not present in the eluent, the peak shape of Mg^{2+}–EDTA degraded and changes in the retention times of the analytes were observed. When using 0.02 mM EDTA and after successive injections, the symmetric peak shape was recovered and a decrease in the width of Ca^{2+}–EDTA and Mg^{2+}–EDTA peaks observed. This behaviour could originate from the competence between the excess of non-complexed EDTA in the samples and the carbonate anions of the eluent for the anion-exchange sites. These results strongly suggest that EDTA present in the eluent may act both as eluting and complexing agent. When higher concentrations of EDTA in the eluent were used (0.05 and 0.1 mM) fast column equilibration was observed, especially for doubly charged anions but retention times of the analytes decreased dramatically and a loss of resolution occurred. In addition, a significant increase of the background conductance was observed when 0.1 mM EDTA was present in the eluent, bringing about a decreased sensitivity of the conductivity detection. A concentration of EDTA in the eluent of 0.02 mM was selected as the best compromise between column equilibration time, suitable separation among the analytes studied and sensitivity.

The effect of the pH of the eluent on the chromatographic behaviour was evaluated in the range 9.5–10.5 by adding either HCl or NaOH to the mobile phase. Separations were performed by keeping the total carbonate concentration constant at 8 mM and the concentration of EDTA fixed at 0.02 mM. When the eluent pH was decreased to pH 9.5, peak broadening of calcium and magnesium complexes was observed. This behaviour was especially noticeable for the Mg^{2+}–EDTA complex. This is probably due to the loss of stability of the Ca^{2+}–EDTA and Mg^{2+}–EDTA complexes when decreasing the pH, especially for the lowest forma-

tion constant complex Mg^{2+}–EDTA. On the other hand, no change in the peak width of the other inorganic anions was observed. From the above results, it was concluded that the optimum eluent conditions were 8 mM sodium carbonate–0.02 mM EDTA, which provided a pH of 10.3, when the samples contained 5 mM EDTA to form the anionic Ca^{2+} and Mg^{2+} complexes.

3.3. Effect of the previous EDTA addition in real samples

In order to further reduce contamination risks and simplify the method, the elimination of the pre-complexation step with EDTA in real samples was studied. Initial experiments showed that when none or very low concentration of EDTA was present in the samples re-equilibration of the ion-exchange column was required as the retention times of the analytes increased after successive injections. Optimum and constant separation conditions were achieved by increasing the carbonate concentration in the eluent to 10 mM while keeping the EDTA concentration at 0.02 mM. The chromatographic behaviour observed indicated that, in the absence of EDTA in the samples, Ca^{2+} and Mg^{2+} complexes were readily formed in the chromatographic column, with EDTA acting as both complexing and eluting anion.

The final separation obtained under these conditions is shown in Fig. 4. As can be observed, adequate resolution between Ca and Mg and the rest of anions was obtained. It was also observed that the small excess of EDTA present in the calcium and magnesium calibration standards did not significantly affect the column equilibration conditions or retention times. So, in order to simplify sample preparation, no pre-complexation of calcium and magnesium was finally selected for the analysis of real samples.

3.4. Analytical performance characteristics

Table 2 shows the compared analytical performance characteristics observed for common inorganic anions plus
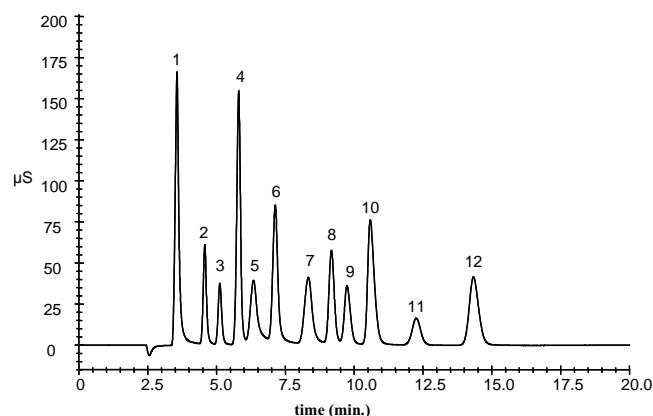

Fig. 4. Chromatograms obtained for a drinking water spiked with inorganic anions (without pre-complexation step) using a 10 mM Na_2CO_3 and 0.02 mM EDTA eluent: (1) F^-; (2) ClO_2^-; (3) BrO_3^-; (4) Cl^-; (5) CaY^{2-}; (6) NO_2^-; (7) MgY^{2-}; (8) Br^-; (9) ClO_3^-; (10) NO_3^-; (11) HPO_4^{2-}; (12) SO_4^{2-}.

Ca^{2+}–EDTA and Mg^{2+}–EDTA complexes. Calibration graphs were obtained by plotting peak area against the concentration of the corresponding anion studied. Linear calibration graphs were obtained over the concentration ranges tested up to 100 ppm for chloride, chlorate, nitrate and sulphate. Excellent linearity was obtained for both EDTA complexes up to 80 ppm (as metal) and for concentrations above 80 ppm, especially for the magnesium complex, excessive peak broadening was observed. For fluoride, chlorite, bromate, nitrite, bromide and phosphate, a good linearity was found up to the maximum concentration level assayed (Table 2). Detection limits (LODs) were evaluated as three times the standard deviation of the background signal using a 75 µl injection loop. The results obtained show the excellent detectability found for both calcium and magnesium species, similar to that of common inorganic anions (Table 2).

Peak widths (at 50% of peak height) and retention times obtained for the inorganic anions and divalent cations are

Table 2
Analytical performance characteristics

	Retention time (min)	Peak width (min, 50% height)	Linear range tested (mg l^{-1})	r^2 ($n = 10$)	LOD (mg l^{-1})	Precision (R.S.D., %, $n = 5$)
Fluoride	3.55	0.15	0–20	0.9994	0.008	0.7[a]
Chlorite	4.56	0.14	0–20	0.9980	0.01	0.5[a]
Bromate	5.12	0.14	0–2	0.9993	0.03	3[a]
Chloride	5.79	0.14	0–100	0.9986	0.006	1[b]
Calcium	6.35	0.27	0–80	0.9992	0.015	0.1[b]
Nitrite	7.12	0.21	0–20	0.9997	0.02	2[a]
Magnesium	8.32	0.31	0–80	0.9985	0.02	0.3[b]
Bromide	9.17	0.22	0–1	0.9987	0.04	2[a]
Chlorate	9.73	0.25	0–100	0.9975	0.007	2[a]
Nitrate	10.59	0.27	0–100	0.9974	0.006	0.2[b]
Phosphate	12.24	0.35	0–20	0.9996	0.03	0.4[b]
Sulphate	14.32	0.38	0–100	0.9976	0.01	0.1[b]

[a] At 1 mg l^{-1} level.
[b] At 20 mg l^{-1} level.

also given in Table 2. As can be observed, peak widths increased with analyte retention, except for the EDTA complexes. As shown in Table 2, higher peak widths were observed for calcium and magnesium complexes as compared with inorganic anions of similar elution time. This could be due to partial decomposition of the complexes during separation or to a broadening effect in the suppressor column where the complex is destroyed.

In order to test the reproducibility, five replicates from a standard solution containing a mixture of such anions, at different concentration levels, were injected. The results obtained, in terms of R.S.D. (%) of peak area, can be also observed in Table 2. For anions studied at low concentration levels (1 ppm), R.S.D. were found to be around 2% (except for fluoride and chlorite which provided precisions below 1%). At higher concentrations (20 ppm), the anions studied showed a noticeable decrease in their R.S.D. reaching the range of 0.1–1%. In this sense, excellent reproducibilities were found for both Ca^{2+} and Mg^{2+} as EDTA complexes.

3.5. Analysis of real samples

In order to demonstrate the suitability of the proposed method for the simultaneous determination of inorganic anions, calcium and magnesium by conventional suppressed IC, different water samples were analysed by two alternative methods: IC and direct ICP-MS with conventional nebulisation. All samples were analysed after filtration with a 0.45 μm membrane filter, and both pre-complexation with EDTA and no previous EDTA treatment were evaluated by ion chromatography. Fig. 5 shows the chromatograms obtained for three different mineral water samples by suppressed conductivity detection ion chromatography with no EDTA pre-complexation. The peak resolution among inorganic anions and divalent cations was quite satisfactory even for the very close Cl^- and CaY^{2-} peaks.

Fig. 6 represents the analytical results obtained for calcium and magnesium ions in nine different drinking wa-

Fig. 6. Comparisons of ion chromatography and ICP-MS for the determination of Ca and Mg in drinking water samples. No pre-complexation with EDTA performed.

ter samples both by suppressed IC and ICP-MS detection. The uncertainly ranges indicated in the figure for ICP-MS correspond to two standard deviations for $n = 3$ samples. For IC, the uncertainties were, in general, smaller than the size of the points. The experimental results indicate a good agreement between both analytical methods for all samples. In most cases, conductivity detection provided better precisions than ICP-MS detection due to its stable background conductivity, which allowed reproducible peak integration even at low concentration levels.

In the same way, conductivity measurements, obtained both with and without the addition of EDTA to the samples, showed an excellent agreement. These results confirm that prior complexation of real samples with EDTA is unnecessary.

4. Conclusions

A method for the simultaneous determination of common inorganic anions, Ca^{2+} and Mg^{2+} by suppressed anion-exchange chromatography with conductivity detection has been developed. Alkaline earth metal ions are separated from inorganic anions as anionic EDTA complexes, so metal–EDTA complexes are detected conductimetrically after their conversion to free EDTA in the suppressor column. The effect of the carbonate concentration, EDTA and pH of the eluent were studied in order to obtain the best separation conditions. Experimental results confirmed that both Ca^{2+}–EDTA and Mg^{2+}–EDTA complexes are mainly separated in a pure anion-exchange process as divalent
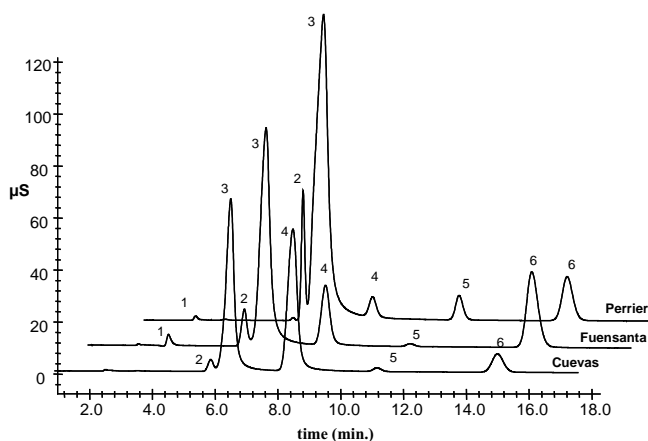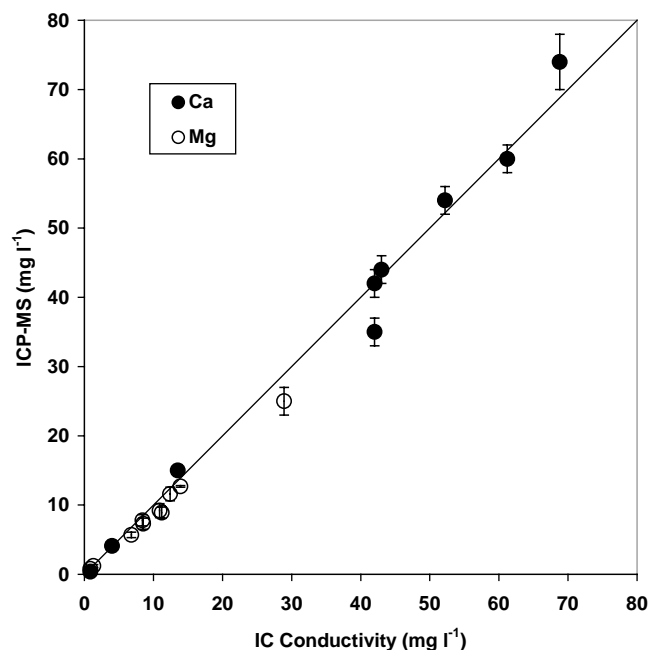

Fig. 5. Chromatograms obtained for three different mineral water samples by suppressed conductivity detection (shifted for clarity): (1) F^-; (2) Cl^-; (3) CaY^{2-}; (4) MgY^{2-}; (5) NO_3^-; (6) SO_4^{2-}.

anionic complexes. Moreover, the kinetics of formation are fast enough and so the use of a pre-complexation step with EDTA in real samples is unnecessary.

The method described offered good sensitivity and reproducibility for Ca and Mg determinations. Detection limits at ppb levels and precisions, better than 1%, were similar to those found for common inorganic anions. However, linearity observed was shorter than for other inorganic anions and peak widths were broader than inorganic anions with similar elution characteristics. The method has been applied to the determination of calcium and magnesium in real water samples. For validation purposes, the experimental results were compared with those obtained by conventional ICP-MS. A good agreement between both analytical methods has been observed both with and without the addition of EDTA to the samples.

Acknowledgements

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