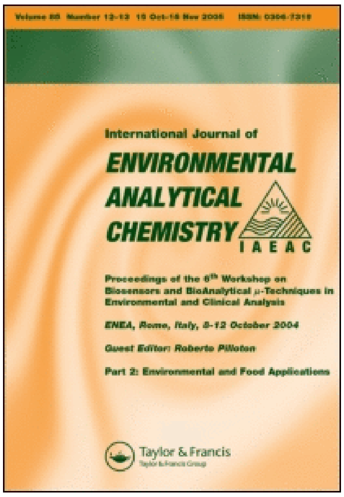

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Automatic Simultaneous Determination of Calcium and Magnesium in Waters by Flow Injection Analysis Using a Photodiode Array Detector and Multicomponent Analysis

A. Cladera[a]; E. Gómez[a]; J. M. Estela[a]; V. Cerdà[a]; A. Alvarez Ossorio[b]; F. Rincón[b]; F. Salvà[b]
[a] Departamento de Química, Facultad de Ciencias, Universidad de las Islas Baleares, Palma de Mallorca, Spain [b] Colegio de Formación Profesional «San José Obrero», Palma de Mallorca, Spain

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AUTOMATIC SIMULTANEOUS DETERMINATION OF CALCIUM AND MAGNESIUM IN WATERS BY FLOW INJECTION ANALYSIS USING A PHOTODIODE ARRAY DETECTOR AND MULTICOMPONENT ANALYSIS

A. CLADERA, E. GÓMEZ, J. M. ESTELA and V. CERDÀ

Departamento de Química, Facultad de Ciencias, Universidad de las Islas Baleares, E-07071 Palma de Mallorca, Spain.

A. ALVAREZ OSSORIO, F. RINCÓN and F. SALVÀ

Colegio de Formación Profesional «San José Obrero», Palma de Mallorca, Spain.

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A new method for the simultaneous determination of calcium and magnesium by flow injection analysis (FIA) using a photometric diode array (PDA) detector and based on the reaction of the two ions with 4-(pyridyl-2-azo)resorcinol (PAR) and the use of multicomponent analysis was developed. The process was controlled via an IBM PC microcomputer running the program DARRAY for instrumental control and data acquisition and processing. The proposed method features a linear determination range of 1–10 mg/L Ca and 1–20 mg/L Mg and a throughput of 70 samples/h, and is only interfered with by Zn(II) and Cu(II), which can also be determined simultaneously with these alkaline earths to avoid their interference.

KEY WORDS: Multicomponent Analysis, FIA, Calcium, Magnesium, Water.

INTRODUCTION

Flow injection analysis has proved to be a versatile and rather useful technique for the determination of a wide variety of analytes by simply adapting existing batch methods. The advent of fast-scan photometric detectors and computers that allow the application of multivariate methods have fostered the development of straightforward FIA systems for the simultaneous determination of several analytes. The analytical potential of FIA–PDA systems was recently analyzed by Fell.[1] One such system was used by Lázaro *et al.*[2] for the simultaneous determinatiojn of Fe(II) and Cu(II) using neocuproin and 1,10-phenanthroline as specific chromogenic reagents and taking absorbance readings at the absorption maxima of the complexes formed. A different procedure was developed by Blanco *et al.* for the simultaneous determination of Fe(II) and Fe(III) with a mixture of 1,10-phenanthroline and sulphosalicylic acid,[3] that of four components in pharmaceutical preparations[4] and that of calcium and magnesium with Arsenazo III as chromogenic reagent.[5] The method in question relies on recording the complete spectrum of the samples and using multivariate analysis to resolve the mixtures. The use of many more wavelengths than analytes to be determined allows the resolution of mixtures with extensively overlapped spectra. Nevertheless, Blanco *et al.*[5] needed a dual system injection to overcome the wide overlapping between Arsenazo III and their Ca-Mg complexes, using the reagent spectrum as a third component. By this method, these authors achieved a linear range of 0.2–1.5 μg/mL Ca and 0.1–1.0 μg/mL Mg, with an analysis rate of 50 h^{-1}. Other non-simultaneous FIA methods used non commercial reagents[6] or obtained poor sensitivity[7], both with a low sampling rate.

4-(Pyridyl-2-azo)resorcinol (PAR) is a chromogenic reagent of wide use for the photometric determination of a large number of metal ions, both directly[8] and indirectly (with post-column derivatization and application of various chromatographic techniques[9–13]. In this paper we develop a new method for the simultaneous determination of calcium and magnesium using PAR as chromogenic system, an automatic FIA–PDA configuration and multivariate analysis of spectra.

EXPERIMENTAL

Reagents

The reagents used, all of which were RA grade, included the following:

—A 5.75×10^{-4} M PAR solution prepared from the monosodium monohydrated salt (Merck) and stored in a dark polyethylene flask that was spectrophotometrically stable for at least one week.

—A 0.2 M tris(hydroxymethyl)aminomethane (Tris) buffer of pH 9.6, adjusted with HCl.

—A 1000 mg/L Ca(II) standard prepared from $CaCO_3$.

—A 1000 mg/L Mg(II) standard made from $MgCl_2 \cdot 6H_2O$ and standardized titrimetrically with EDTA using Eriochrome Black T as indicator.

Apparatus

Figure 1 depicts the instrumental set-up used for the automatic determinations. It is composed of the following elements:

—A PC-compatible computer for instrumental control and data acquisition and processing furnished with an HP-IB interface and a PC 8255 I/O card from Flytech Technology Co. Ltd.

—A customized valve-based mechanical actuator controlled by the computer via the PC 8255 card.

—A Hewlett–Packard HP 8452A diode array spectrophotometer furnished with a flow-cell of 1 cm lightpath and 18 μL void volume, and linked to the computer via its HP-IB interface.

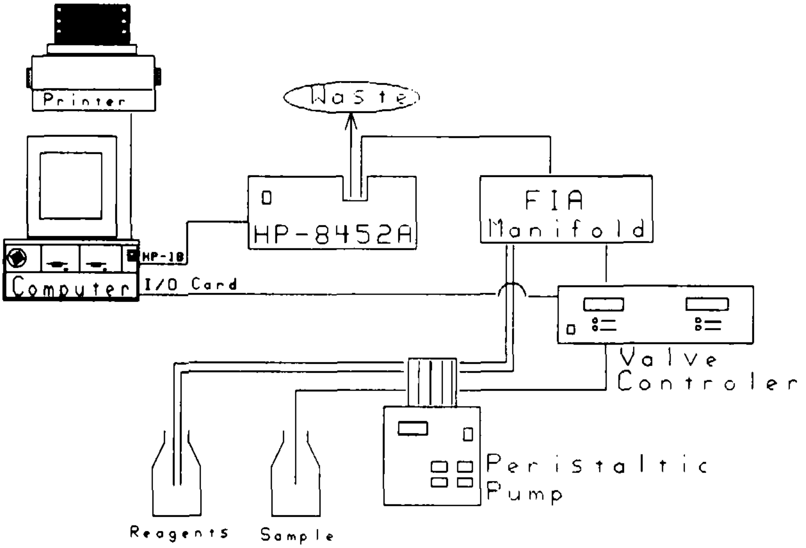

Figure 1 Instrumental set-up used for the automatic simultaneous determination of Ca and Mg.

—A FIA manifold (Figure 2) consisting of a Gilson Minipuls-3 8-line peristaltic pump, a Rheodyne 50 injection valve governed via the mechanical actuator and PTFE tubing (0.5 mm ID) as injection loop and reactors.

Software

The procedure was based on the use of two computer programs, *viz.* DARRAY and MULTIC.[14] DARRAY is a general program developed by the authors for use of the HP 8452A spectrophotometer as detector in FIA and HPLC methods. It was

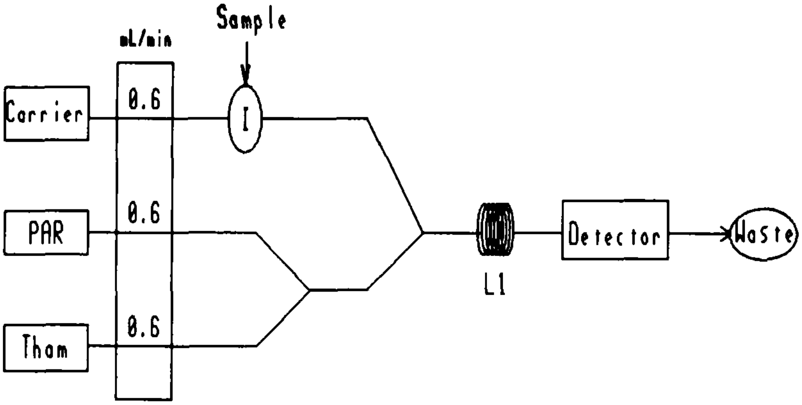

Figure 2 FIA manifold used. Carrier = distilled H_2O; [PAR] = 5.75×10^{-4} M; [Tris] = 0.2 M, pH 0.6; L_1 = 0.5 m.

originally written in QuickBASIC and subsequently compiled and linked to the handling subroutines of the HP-IB interface supplied by the manufacturer. Among others, it allows automatic control of sample injections, acquisition of the sample FIA recording and the spectra at each point along it, editing of such a recording, peak identification and quantification, spectrum processing, *etc.* In the experimental acquisition, the program generates two files for storage of the FIA recording data (variation of the absorbance at a preset wavelength with time) and the spectrum at each point along the recording, respectively. The latter file is a random-access file in which spectra are stored in binary form to save disk space. In this way, the user can rapidly retrieve the spectrum corresponding to any point along the FIA recording and, by means of an editing subroutine included in the program, generate new recordings by changing the measurement wavelength and saving the spectrum corresponding to a given point of the recording in a file format compatible with the program MULTIC. Another subroute allows these spectrum files to be retrieved and operated between them or with constant values, which permits the obtainment of averaged and standardized spectra rapidly and conveniently.

The program MULTIC was used to resolve the mixtures, which entails inputing the spectrum of one standard of each analyte to be determined and its concentration in the standard. From these data, the program calculates the absortivity of each component at each spectral wavelength, a_{ij}. Then, the program requests input of the sample spectrum and applies a multiple linear regression algorithm based on the equation system $A_j = \sum_{i=1}^{N} a_{ij}c_i$, in order to obtain the c_i values resulting in the minimum difference between the resulting combined spectrum and that of the sample. A_j is the sample absorbance at wavelength j, a_{ij} the absortivity of component i at wavelength j and c_i the concentration of component i.

Procedure

Recording of spectra The procedure is started by inserting the reagents into the FIA manifold (Figure 2) and allowing it to stabilize. Then, the reagent spectrum is recorded and stored for subtraction from every subsequent readout. Data acquisition is performed by obtaining the corresponding difference spectra over the wavelength range 470–650 nm and the FIA recording corresponding to the 510-nm readout. The elapsed time between spectra recording used was 1.0 s with an integration time of 0.2 s. Once the FIA recording has been obtained on 105-μL injections of the successive samples, the spectra corresponding to the peak maxima are stored for later processing. The sample throughput is 70 h^{-1}.

Calibration Calibration is performed by obtaining the FIA recordings of four Ca(II) standards of concentrations between 1 and 10 mg/L and as many Mg(II) standards in the range of 1–20 mg/L. Triplicate injections of each standard is made. Then, the spectra obtained are averaged and standardized by first calculating the average spectrum at each concentration and then dividing it by the corresponding concentration and finally averaging the resulting standardized spectra. The final result is a spectrum for Ca and another for Mg standardized at a 1 mg/L concentration of the corresponding ion, which constitute the standard spectra requested by MULTIC.

Sample analysis The different samples, the Ca and Mg concentrations of which must lie within the calibration ranges, are injected into the manifold and the spectra thus obtained are input into MULTIC, which delivers the corresponding calculated concentrations.

Analysis of samples containing Zn(II) and/or Cu(II) concentrations above 0.1 mg/L The experimental procedure to be applied in this case is identical to that described above except that the number of components to be handled is four (Ca, Mg, Cu and Zn) rather than two. Thus, in the calibration step the Cu and Zn standardized spectra are obtained in the same way as those of Ca and Mg, but using standards of concentrations between 0.1 and 1 mg/L. After the pertinent calculations, MULTIC delivers the concentrations of the four components analysed.

RESULTS AND DISCUSSION

Absorption spectra of the reagent and complexes

Figure 3 shows the absorption spectra of PAR and its Ca, Mg, Cu and Zn complexes. These were obtained from the peaks yielded by injections of standards according to the above-described procedure. As can be seen, they are extensively overlapped throughout the wavelength range studied; however, they feature some differences that in principle allow their resolution by multivariate analysis.

Optimization of variables

The optimal working conditions were determined by the univariate method. The first variables to be investigated were the pH and nature of the buffer used. The Ca and Mg complexes of PAR are formed best in an alkaline medium. Initially we assayed different compositions of the buffer solution and found ammonia media to result in unstable absorptions. However, Tris solutions proved to be suitable for use as pH buffers. Then, the effect of the pH of the Tris buffer was studied over the range 9–12. The absorbance of the complexes was found not to vary with pH between 9 and 11, above which it increased markedly, as did those of the reagents themselves, which resulted in unstable baselines and poor reproducibility and precision in obtaining the sample spectra. Thus, we selected pH 9.6 in all subsequent experiments.

The absorption of the complexes was found to increase with increasing PAR concentration. However, the background absorption was also increased as a result, which gave rise to the same shortcomings as did pH values higher than 11. Thus, the chosen PAR concentration (5.75×10^{-4} M) was a compromise ensuring a signal-to-noise ratio as high as possible.

Neither the temperature nor the reactor length used appeared to influence the

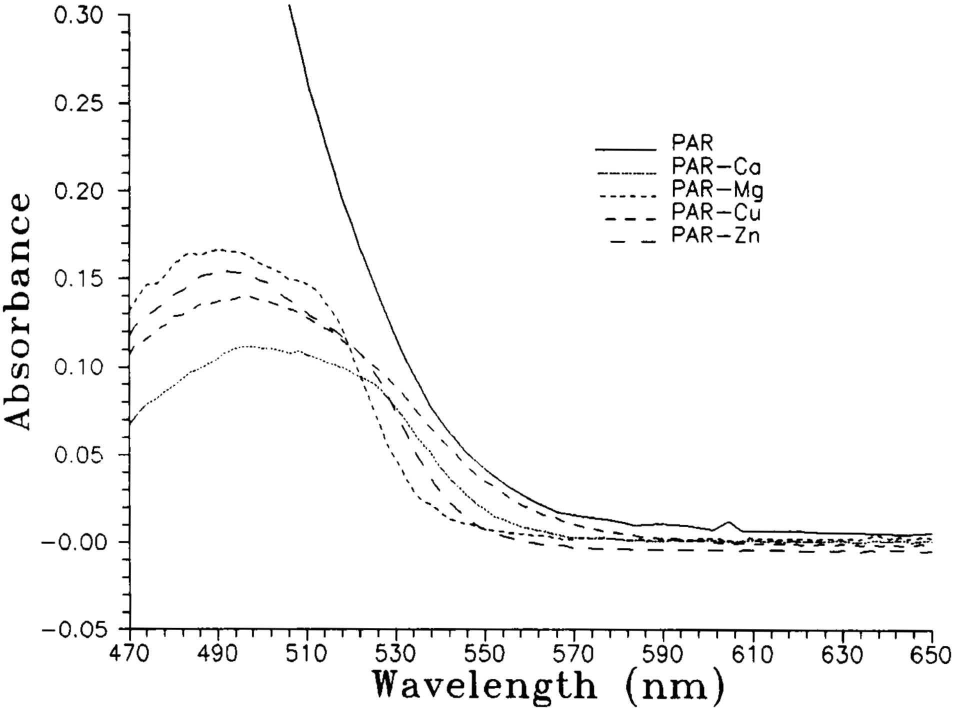

Figure 3 Absorption spectra of PAR (5.75×10^{-4} M) and its Ca (10 mg/L), Mg (10 mg/L), Cu (0.5 mg/L) and Zn (0.5 mg/L) complexes.

absorbance readings, which led us to work at room temperature and use a reaction tube as short as possible in order to achieve the highest sample throughput.

The linear response ranges of the two ions were determined by using injections of individual Ca and Mg standards containing 1–30 mg/L of either ion and measuring the height of the FIA peaks thus obtained. Responses were linear over the range 1–10 and 1–20 mg/L for Ca and Mg, respectively, the equations of the corresponding straight lines being

$$H(AU) = 3.7 \times 10^{-3} + 1.01 \times 10^{-2}[Ca](mg/L) \qquad (r = 0.9990)$$

$$H(AU) = 5.2 \times 10^{-3} + 1.53 \times 10^{-2}[Mg](mg/L) \qquad (r = 0.9996)$$

These equations were obtained from 3 injections of each standard. The standard relative deviation was 1% for Ca (5 mg/L) and 0.7% for Mg (10 mg/L). Figure 4 illustrates the FIA recording used to obtain the calibration curves.

Simultaneous determination of Ca and Mg

By using the above-described optimal conditions and experimental procedure, we determined Ca and Mg simultaneously in synthetic samples containing Ca and Mg

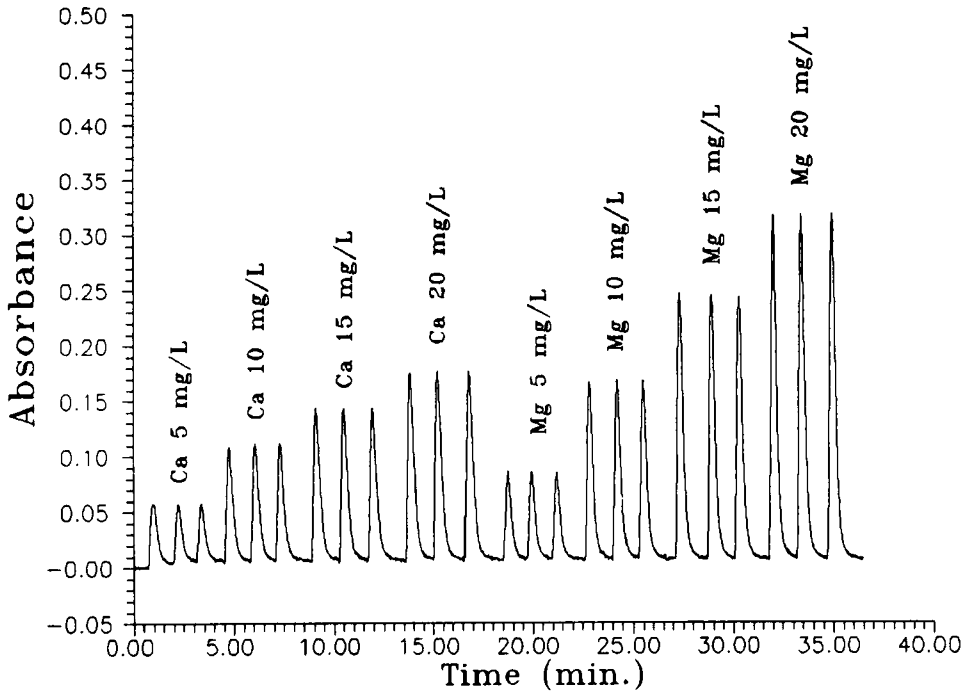

Figure 4 FIA recording obtained by injection of Ca and Mg standards of concentrations over the range 1-20 mg/L. V_i = 105 μL.

in different proportions. The results obtained are listed in Table 1. As can be seen, the concentrations found are consistent with those actually added. The worst results were obtained at concentrations of the two ions close to the limits of their linear ranges.

Effect of interferences

The absortivities of most of the complexes formed by PAR and metal ions are much higher than those of its Ca and Mg complexes. Therefore, they must seriously interfere with the determination of the two alkaline earths by the proposed procedure. However, since Ca and Mg occur as major elements in waters while the aforementioned metals are present at trace levels, a simple dilution of the sample to bring its Ca and Mg concentrations into the linear determination ranges should normally suffice to overcome most interferences.

In order to check the above assumption, we studied the potential interferences of ions usually occurring in waters at the maximum tolerated levels in drinking water permitted by Spanish regulation. For this purpose, we prepared a synthetic sample containing 100 mg/L Ca^{2+}, 20 mg/L Mg^{2+}, 355 mg/L Cl^-, 400 mg/L SO_4^{2-}, 50 mg/L NO_3^-, 6.4 mg/L PO_4^{3-}, 0.2 mg/L Al^{3+}, 5 μg/L Cd^{2+}, 0.2 mg/L Fe^{3+}, 50 μg/L Mn^{2+},

Table 1 Results and standard deviations (in parenthesis) for five consecutive injections obtained in the simultaneous determination of Ca and Mg in synthetic samples.

Added		*Found*	
[Ca] (mg/L)	*[Mg] (mg/L)*	*[Ca] (mg/L)*	*[Mg] (mg/L)*
10	0	9.7 (0.4)	0.04 (0.03)
0	10	0.0 (0.6)	9.8 (0.4)
1	4	1.37 (0.08)	4.15 (0.03)
1	8	1.3 (0.1)	8.2 (0.2)
1	14	0.8 (0.1)	14.1 (0.1)
4	4	3.9 (0.1)	3.77 (0.07)
4	8	3.87 (0.09)	7.50 (0.08)
4	14	3.3 (0.1)	13.23 (0.08)
8	4	7.7 (0.2)	4.0 (0.1)
8	8	7.4 (0.2)	7.2 (0.1)
8	14	6.79 (0.08)	12.34 (0.06)

50 μg/L Cr^{3+}, 50 μg/L Ni^{2+}, 50 μg/L Pb^{2+} and 1 μg/L Hg^{2+}. The sample contained no Cu^{2+} or Zn^{2+}, the maximum legally allowed concentrations of which are 1.5 and 5 mg/L, respectively, and thus too high for the interference to be overcome by dilution. The sample was diluted by a factor of 10 to bring its Ca and Mg concentrations into the linear ranges and analyzed as described above. The Ca and Mg concentrations obtained were 93.4 ± 1.0 and 19.6 ± 1.0 mg/L, respectively, which can be considered as acceptable.

When samples containing Cu^{2+} and Zn^{2+} at the above indicated concentrations were added, high interferences were observed. In fact, the maximum tolerated concentrations of these ions, by the proposed method, were found to be 1 mg/L. As these concentrations are below the maximum levels permitted by Spanish laws, we investigated a way to remove their interference in order to make the method applicable to drinking water. We assayed the use of KCN as masking agent for Cu and Zn, which resulted in a slightly better tolerance of the method to both ions, but

Table 2 Results and standard deviations (in parenthesis) for five consecutive injections obtained in the simultaneous determinations of Ca, Mg, Zn and Cu in synthetic samples.

Added (mg/L)				*Found (mg/L)*			
Ca	*Mg*	*Cu*	*Zn*	*Ca*	*Mg*	*Cu*	*Zn*
10	2	0.5	0.5	12.5 (0.2)	2.4 (0.1)	0.49 (0.002)	0.46 (0.01)
4	4	0.2	0.7	4.1 (0.3)	3.8 (0.4)	0.18 (0.001)	0.77 (0.01)
4	8	0.2	0.2	4.4 (0.5)	7.4 (0.1)	0.21 (0.007)	0.22 (0.001)
8	2	0.5	0.2	8.3 (0.7)	1.7 (0.1)	0.52 (0.004)	0.18 (0.02)
8	2	0	0.5	7.85 (0.05)	1.49 (0.05)	0	0.60 (0.006)
8	2	0.5	0	7.8 (0.5)	1.6 (0.3)	0.53 (0.03)	0

Table 3 Determination of the Ca and Mg contents of real samples by the proposed method and reference (EDTA titration) method. Standard deviations (in parenthesis were calculated from five replicates.

Type of water	*Proposed method*		*Reference method*	
	[Ca] (mg/L)	*[Mg] (mg/L)*	*[Ca] (mg/L)*	*[Mg] (mg/L)*
Tap (Palma de Mallorca)				
Zone 1	135 (3)	22 (1)	135 (1)	25 (2)
Zone 2	114 (2)	22.1 (0.8)	110 (1)	23 (2)
Mineral				
Zone 1 (Gerona)	23.1 (0.4)	4.6 (0.1)	21.1 (0.1)	3.5 (0.2)
Zone 2 (Mallorca)	85 (2)	33 (1)	88 (1)	31 (1)

still at concentrations below the legal limits. Thus, we considered the possibility of determining the two ions as additional components of the sample, *i.e.* of simultaneously determining Ca, Mg, Cu and Zn. Table 2 lists the results obtained in the analysis of several synthetic samples containing the four ions. As can be seen, the concentrations determined are consistent with those added to the sample.

Analysis of real samples

The proposed method was applied to the analysis of one sample each of mineral and tap water for Ca and Mg, which were also determined by titration with EDTA for comparison. As can be seen from Table 3, the results provided by the proposed method were quite consistent with those obtained titrimetrically, which testifies its applicability to real samples.

CONCLUSIONS

The new method developed for the simultaneous determination of Ca and Mg was applied to the analysis of the two alkaline earths in real water samples. The method is interfered with by no trace metals at the concentrations allowed by legislation for domestic water; in fact, the only serious interferents, Cu and Zn, can be determined simultaneously with the analytes. The use of rather a straightforward automatic FIA configuration allows analyses to be performed quite conveniently at a high rate. The proposed method improves the other existing simultaneous alternative[5] in the need for no dual injection system, the wider linear ranges it provides, its higher sapling rate and its applicability to various types of waters. Although the new proposed method features somewhat lower detection limits than[5], their values are more than sufficient to determine Ca and Mg in waters, since these elements usually are present in high concentrations.

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