Batch Titration of Calcium in Water Samples by Sequential Injection Analysis Derivative Spectrometry

N. Sánchez - Rosado, A. Morales-Rubio* and M. de la Guardia.

Department of Analytical Chemistry, Research Building, University of Valencia,
50 Dr. Moliner st.,46100 Burjassot- Valencia (Spain).

Abstract

A sequential injection analysis (SIA) titration method has been developed for the determination of calcium in water. The method is based on the aspiration of increasing volumes of sample, corresponding to different aspiration times, which were mixed with fixed volumes of a murexide solution and a sodium ethylenediamine tetraacetate alkaline solution (EDTA). After complete reaction, in a well stirred reaction vessel, the mixture was degassed and introduced into a 50 µl and 1 cm pathlength flow cell of a spectrometer, carrying out measurements in the first order derivative spectra from the 480 nm peak to the 544 nm valley. The representation of the previous data as a function of the sample aspiration time provides two different zones, which can be adjusted using linear models. The point of intersection between these lines provides an aspiration time corresponding to a calcium concentration in the sample. Results obtained are comparable with those found by manual titration and the method is free from interference of SO_4^{2-}, Cl^-, NO_3^- and K^+ at 100 mg l^{-1} concentration level, that of Mg^{2+} at 50 mg l^{-1} and that of Fe^{3+} at 10 mg l^{-1}.

Keywords: SIA, calcium determination, water analysis, titration.

1. Introduction

Automation of classical analytical methods, like titrimetric ones, could be very convenient in order to control on-line industrial processes and to avoid human errors. Additionally, the use of automated procedures involves a strong reduction of the amount of reagents used and the volume of waste generated thus providing an environmentally friendly analytical methodology [1,2].

Classical flow injection analysis (FIA) [1] sequential injection analysis (SIA) [3,4] and multicommutation and binary sampling [5,6] have been applied for the automation of titration methods. Classical FIA titration methods are carried out based on the injection of samples into a carrier stream of the titrant containing an indicator, and based on the exact titration of sample zones in both, leading and tailing of the injected volume. The peak width between the two equivalence points can be employed as the analytical variable that is proportional to the logarithm of the sample concentration. The same approach has been adapted to SIA, based on the aspiration of the sample between two volumes of the titrant and using the peak width measurements for quantification [3].

Recently, it has been proposed a strategy for SIA acid-base titration, based on the sequential aspiration of a sample zone of acid and one reagent zone of a basic titrant containing the indicator, which were let to react in a holding coil and let to disperse before to measure the color of the unneutralised base [4]. In this case the area of the SIA peak is employed as the analytical variable, which can be interpolated in a calibration curve obtained as a function of the acid concentration logarithm.

Titration procedures involving the use of binary search strategy, based on solenoid valves, has been proposed in continuous flow photometric end-point detection of HCl with NaOH [5] and in monosegmented flow potentiometric detection of acidity in liquid samples [6].

There is only a single precedent on the use of SIA for complexometric titrations based on the use of miniaturised solid-state electrochemical sensor [7]. Thus, it could be convenient the development of an automated procedure which could be based on a series of experimental points, in contrast to the main strategies proposed before for titration which uses single measurements of each sample, and could be adapted to single commercially available spectrophotometers.

Based on a previous study on the volume of reagents consume and waste generation [8] in which it was carried out a comparison between FIA, SIA and multicommutation strategies, SIA was selected in order to reduce as much as possible the amount of wastes.

2. Experimental

2.1. Apparatus and reagents

A SIA system FIALAB from Alitea (Medina, WA), equipped with a Valco peristaltic pump, a Valco E-10-220 ten ways valve and a software with a real time analogical-digital system ADA-1100, were used for the automation of complexometric titrations, having employed flexible polyvinyl chloride tubes of 1.3 mm i.d. and 0.8 mm i.d. PTFE Teflon tubes. For detection, a diode array Hewlett-Packard HP 8452A

spectrometer, from Agilent (Barcelona, Spain), equipped with a 50 μl internal volume and 1 cm pathlength flow cell, was employed. The set-up used in this study is indicated in Fig. 1.
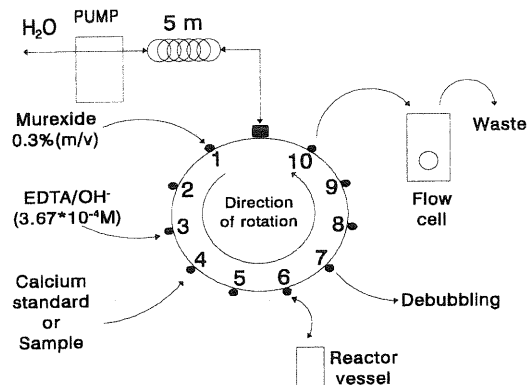

Fig. 1 SIA manifold employed for complexometric titration of calcium in waters.

CaCO$_3$ purchased from Probus (Barcelona, Spain) was employed for the preparation of the stock standard solution. The dihydrate disodium ethylenediamine tetraacetate, from Probus, was used as titrant, being employed murexide as indicator. All these reagents were of analytical grade and solutions were prepared in pure water, with a resistivity of 18.2 MΩ cm^{-1}, obtained with a Milli-Q water system from Millipore Inc. (Paris, France).

2.2. Procedure

Increasing sample volumes from 0 to 0.50 ml, corresponding to aspiration times from 0 to 10 seconds, were introduced into a stirred reaction vessel of 9.5 ml together with previously aspirated 0.48 ml murexide 0.3 % (m/v) and 0.19 ml EDTA 3.67*10^{-4} M in NaOH 0.1 M. After 5 seconds, the mixture was aspirated, degassed and introduced into the UV/vis spectrometer. Table 1 summarizes the different steps of this procedure, carried out during the titration.

2.3. Principle of measurement

Measurements were carried out in the first order derivative spectra from the 480 nm peak to the 544 nm valley. These experimental peak-valley height values were represented as a function of the sample aspiration time and it can be identified two differentiate zones. For aspiration times corresponding to a clearly small calcium concentration, as compared with that of EDTA employed, a plateau is found. On the other hand, a rising zone was found when higher than stoichiometric calcium concentrations were employed. Both of these series of data were adjusted using linear models, being obtained its point of intersection. This point provides a sample aspiration time which, taken into consideration the relationship between calcium concentration and aspiration time in the experimental conditions employed, permits the determination of the calcium concentration in the original sample.

3. Results and Discussion

3.1. Selection of wavelength for measurement

The absorbance spectra of alkaline solutions of free murexide and murexide in the presence of calcium and an excess of EDTA are shown in Fig.2. This indicates that the spectrum of the calcium-murexide complex, which provides a maximum at 510 nm, is modified by calcium complexation with EDTA, providing a shift of the absorbance maximum to 544 nm. However it is clear that both spectra are overlapped and so it could be convenient to work with the derivative spectra to be able to control the process of titration.

Fig. 3 shows the first order derivative spectra of the calcium-murexide complex and that of murexide in the presence of the calcium-EDTA complex with an excess of EDTA. From these spectra it can be seen that the distance between the peak at 480 nm and the valley at 544 nm, or alternatively that between 510 nm and 590 nm, can be used to control the calcium-murexide complex destruction by EDTA or the formation of free murexide. So, analytical signals can be represented as a function of the calcium introduced inside the system in front of EDTA present.

Table 1 Steps of the SIA-titration procedure developed for calcium determination in water

| Step	Position	Function	Time (s)	Reagent	Objective
1	10	Elution	15	Water	Cleaning
2	1	Aspiration	12	Murexide 0.3%(m/v)	Aspiration of murexide (0.48 ml)
3	3	Aspiration	3	EDTA 3.67 10^{-4}M	Aspiration of EDTA (0.19 ml)
4	4	Aspiration	0 to 10	Ca 10 mg l^{-1} or sample	Aspiration of standards or samples
5	6	Elution	35	mixture	Mixing of solution
6	6	Stop	5	mixture	Reaction
7	6	Aspiration	37	mixture	Aspiration of reaction mixture
8	7	Elution	10	mixture	Debubbling
9	10	Elution	25	mixture	Signal obtained
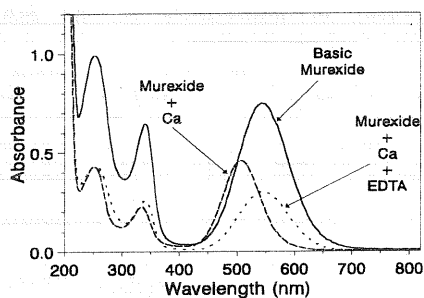
Fig. 2 Absorption spectra of a 0.2 % (m/v) murexide in 0.1 M NaOH (—), of murexide in the presence of 10 mg l^{-1} calcium and $2.45*10^{-4}$ M EDTA (---) and of murexide 0.2% (m/v) in 0.1 M NaOH with 10 mg l^{-1} calcium (- -).
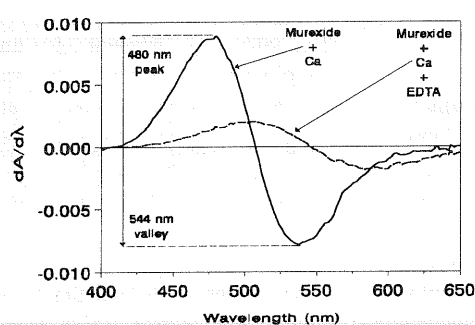

Fig.3 First order derivative spectra of a 0.2 % m/v murexide solution in the presence of 10 mg l^{-1} calcium and $2.45*10^{-4}$ M EDTA (----) and that of a 0.2 % m/v murexide in the presence of 10 mg l^{-1} calcium (- -).

3.2. Calcium- EDTA titration curves

Fig. 4 shows the titration curves obtained for a fixed quantity of 0.19 ml $3.67*10^{-4}$ M EDTA as a function of the aspiration time of a 10 mg l^{-1} calcium solution using the peak-valley measurements criteria indicated in the previous section, for calcium-murexide complex formation. As can be seen the titration graph provides a t_{Ca} intersection point of both lines corresponding to 4.9 ± 0.2. In this figure it can be seen also that the initial part of the titration curve corresponds to a plateau with a practically zero slope, after the equivalence point, increasing signals which correspond to the increase in the concentration of calcium-murexide complex. The corresponding regression lines are included in the figure.

3.3. Effect of the murexide and EDTA concentrations on calcium titration.

Murexide concentrations of 0.2 % (m/v) and 0.3 % (m/v) were assayed, also using different aspiration times, in order to do titrate calcium with $3.67*10^{-4}$ M EDTA in the presence of different indicator quantities. Using the first derivative measurement mode criterion it was evaluated the relative error found in the titration of different calcium solutions. The use of an aspiration time which is equal to or higher than 12 seconds for a 0.3 % (m/v) solution of murexide provide the best results, being selected the use of this aspiration time, which corresponds

to a value of 0.48 ml, and derivative measurements between 480 and 544 nm in order to obtain as faster as possible methodology with an appropriate accuracy.

The use of a murexide concentration of 0.2% is not enough to obtain accurate results due to the absence of a clear colorimetric titration end point.

For a fixed quantity of murexide, 0.48 ml of 0.3 % (m/v), the aspiration of increasing volumes of EDTA, at concentrations from $2.45*10^{-4}$ M to $4.90*10^{-4}$ M, provided different relative errors in the calcium determination from –26% to 5.0%.
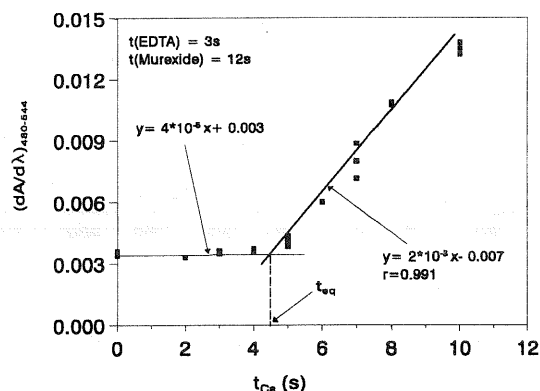

Fig. 4 Titration curves obtained for a fixed amount of 0.19 ml EDTA $3.67*10^{-4}$ M as a function of the aspiration time of a 10 mg l^{-1} calcium using derivative measurements corresponding to calcium-murexide complex formation t_{eq}: time of stoichiometric point. In each time point n=3.

In general, these errors were negative except for the use of a t_{EDTA}= 3 s (0.19 ml) of a $3.67*10^{-4}$ M EDTA, in which case small positive errors were obtained.

From the aforementioned experiments, conditions described in the experimental part were selected, using the derivative measurements between the peak at 480 nm and the valley at 544 nm to follow the titration process.

3.4. Effect of calcium on the SIA titration process

The aspiration of increasing volumes of a 10 mg l^{-1} calcium solution in the set-up of Fig. 1 together with 0.48 ml 0.3 % (m/v) murexide and 0.19 ml EDTA $3.64*10^{-4}$ M provided absorbance spectra indicated in Fig. 5A, from which derivative spectra of Fig. 5B were established.

As it can be seen, for aspiration times equal or higher than 5 seconds, which correspond to calcium volumes higher than 0.30 ml, the calcium-murexide complex start to predominate, thus indicating the end of the titration process.

Titration curves obtained for different calcium concentrations in the original sample titrated, evidenced that for calcium concentrations equal or lower than 4 mg l^{-1} the use of 0.19 ml EDTA 3.64 10^{-4} M seems to be excessively high to obtain a t_{Ca} from the point of intersection.

In fact, the evolution of titration curves provides a value of calcium aspiration time (t_{Ca}) corresponding to the equivalence point. This t_{Ca} could be transformed in a calcium concentration value using the calibration line established for the system V =

0.03+0.05t with r^2 = 0.994 for which "V" is the volume of sample aspirated in ml at "t" aspiration time in seconds. Besides, sample volume can be transformed to calcium concentration in the sample. The known EDTA amount employed, $3.673*10^{-8}$ mol of EDTA ($3.67*10^{-4}$ M x 0.19 ml), in the equivalence point, corresponds to the same number of mol of calcium and in this particular case, equivalent to 2.8 μg of calcium.
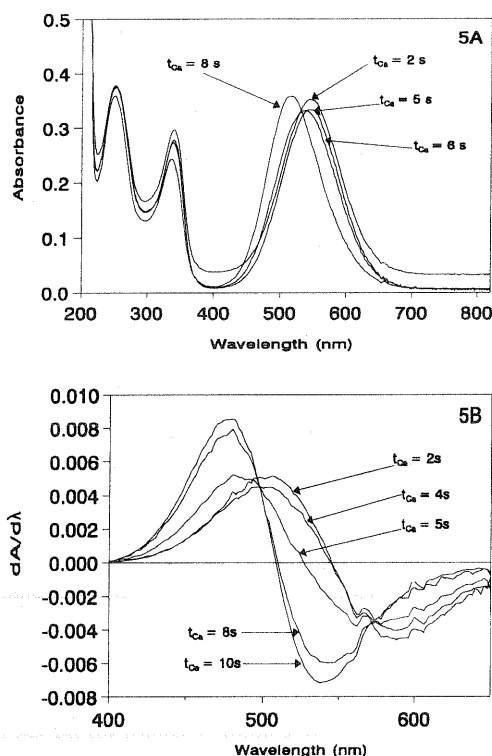

Fig. 5 Absorbance spectra (A) and first derivative absorbance spectra (B) from different aspiration times of 10 mg l^{-1} calcium solution. Experimental conditions: 0.19 ml EDTA $3.64*10^{-4}$ M in NaOH 0.1 M and 0.48 ml 0.3% (m/v) murexide solutions.

3.5. Study of interferences

For a fixed concentration of 10mg l^{-1} calcium it was evaluate the interference of increasing amounts of the main anions and cations present in natural waters, from 10 to 100 mg l^{-1}.

SO_4^{2-}, Cl^-, NO_3^- and K^+ were tolerated at concentration levels of the order of 100 mg l^{-1} but Mg^{2+} did not give a significant interference till 50 mg l^{-1}, being Fe^{3+} the highest interfering species, which provides a recovery of 91 % calcium at a concentration of 10 mg l^{-1} (see Table 2).

3.6. Analysis of natural samples

Calcium was determined by SIA titrimetry on four mineral water samples obtained from the Spanish market and data found by recommended procedure were compared with those found by a reference procedure consisting on the manual titration. Data summarized in Table 3 shows a good agreement between all the data found, thus evidencing the applicability of the method.

Table 2 Study of interferences on the SIA-titrimetric determination of calcium in waters

Interferent	Interferent concentration		
	10 mg l^{-1}	50 mg l^{-1}	100 mg l^{-1}
	%R	%R	%R
SO_4^{2-}	98.0	95.3	97.0
Cl^-	101.6	95.0	94.3
NO_3^-	101.0	97.0	101.0
K^+	98.2	103.0	100.5
Mg^{2+}	101.8	105.0	88.0
Fe^{3+}	91.3	67.6	----

Interferences were evaluated at a 10 mg l^{-1} calcium concentration. %R: Recovery percentage.

Table 3 Titrimetric determination of calcium in waters

Sample	[Ca] (mg l^{-1})		
	SIA titration	Manual titration	Label value
"Fuente Primavera"	90 ± 2	84.7 ± 0.5	86.6
"Solan de Cabras"	60 ± 2	59.1 ± 0.5	60.1
"Fuente Liviana"	68 ± 1	63.4 ± 0.5	64.9
"Font Vella"	35 ± 1	37.0 ± 0.5	40.9

4. Conclusions

The complexometric determination of calcium in waters could be automatized using a SIA system which permits to reduce drastically the amount of reagents consume, also reducing the waste generation. The sequential injection of separated solutions of murexide and EDTA drastically reduces the wastes. On the other hand, the fact that the final concentration obtained from a series of aspirated volumes of sample increases the confidence level on the calcium concentration found, as a difference of methods based on the measurement of a SIA parameter, like the peak width or peak area, corresponding to a single volume of sample. As compared with the methodology developed by Alerm and Bartrolí [7], our procedure provides a better-defined final point and allows us the use of commercially available spectrophotometric instrumentation.

References

[1] J. Ruzicka and E.H. Hansen, *Flow Injection Analysis*, 2nd.ed.Wiley N.Y, (1988).

[2] M. de la Guardia and J. Ruzicka, *The Analyst*, **120**, 17 (1995).

[3] J.F. van Staden and H. du Plessis, *Anal Comm*, **34**, 147 (1997).

[4] S. Maskula, J. Nyman and A. Ivaska, *Talanta*, **52**, 91 (2000).

[5] M. Korn, L. F.B.P. Gouveia, E. de Oliveira, B. F. Reis, *Anal. Chim. Acta*, **313**, 177 (1995).

[6] P.B. Martelli, B. F. Reis, M. Korn, J. L. F. Costa Lima, *Anal. Chim. Acta*, **387**, 165 (1999).

[7] L.Alerm and J. Bartrolí, *Anal. Chem.*, **68**, 1394 (1996).

[8] B.F. Reis, A. Morales-Rubio and M. de la Guardia, *Anal. Chim. Acta*, **392**, 265 (1999).