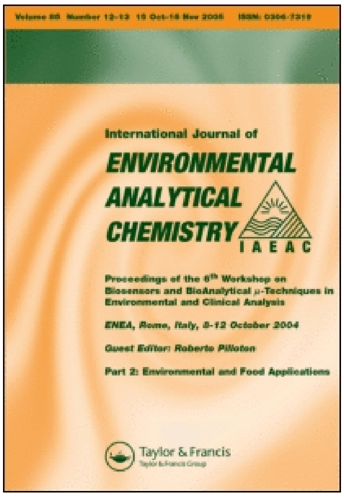

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

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To cite this Article Mas-torres, Francisca , Muñoz, Antonio , Estela, José Manuel and Cerdà, Víctor(2000) 'Simultaneous Spectrophotometric Determination of Phosphate and Silicate by a Stopped-Flow Sequential Injection Method', International Journal of Environmental Analytical Chemistry, 77: 3, 185 — 202

To link to this Article: DOI: 10.1080/03067310008032682

URL: http://dx.doi.org/10.1080/03067310008032682

Intern. J. Environ. Anal. Chem., Vol. 77(3), pp. 185-202
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SIMULTANEOUS SPECTROPHOTOMETRIC DETERMINATION OF PHOSPHATE AND SILICATE BY A STOPPED-FLOW SEQUENTIAL INJECTION METHOD

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(Received 19 November 1999; In final form 14 February 2000)

A sequential injection analysis method for the simultaneous spectrophotometric determination of phosphate and silicate has been developed. The method is based on the different reaction rates of the heteropolymolybdate formation reactions. Concentrations within the range 0.026–0.485 mmol P l^{-1} and 0.125–2.848 mmol Si l^{-1} have been determined at a frequency of 30 samples per hour. An R.S.D. of 2.1% was obtained for 0.162 mmol P l^{-1} and of 1.1% for 1.424 mmol Si l^{-1}. The method was found to be suitable for the determination of phosphate and silicate in wastewater.

Keywords: sequential injection; kinetic determination; phosphate; silicate; wastewater

INTRODUCTION

Procedures that allow the simultaneous determination of two or more components in the same injected sample are attractive for routine use on account of advantages such as a high analytical rate, efficiency and economy. The most common design of multicomponent analysis in a FI system is based on the use of several detectors connected in parallel or in series. Other less used alternatives are those based on the spectral resolution by means of multicomponent techniques and those based on the way the sample is introduced into the system. The latter possibility has given rise to the "sandwich" technique that basically con-

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sists of introducing a sample zone between two different reagent solutions[1,2]. The sample volume should be sufficiently large to obtain two clearly separated peaks corresponding to the two-sample/reagent mixing zones. In a previous work[3] a SIA method was proposed by using large sample volumes for the simultaneous spectrophotometric determination of phosphate and silicate.

Reaction-rate procedures, as the stopped-flow technique and differential kinetics, also enable to simultaneously determine different analytes without separations and without reducing the measurement sensitivity[4,5]. If two chemical reactions have significantly different half-lives, the slower reaction rate can be measured after the faster reaction has reached equilibrium. Among others the kinetic methods offer the following advantages: short analysis time, elimination of both the matrix effects (such as turbidity) which remain constant throughout time and interferences from reactions faster or slower than the analytical reaction. One of the main disadvantages of this technique regarding its application in FIA is the need to provide reproducible delay times and measurement periods. The characteristics of sequential injection analysis make it very appropriate for its application in stopped-flow procedures. In fact, several applications involving SIA technique have been found in the literature[6–9], being SIA first applied to a stopped-flow procedure by Ruzicka and Gübeli[6].

The standard methods for the determination of phosphate and silicate are both based on reaction with molybdate in acid medium, leading to the formation of heteropolymolybdates which present nearly identical absorption spectra. Hence, the presence of silicate interferes with determinations of phosphate, and vice versa. Several FIA methods have been proposed for the simultaneous determination of phosphate and silicate with on-line column separation[10–12] or by using intermittent flows[13]. The phosphomolybdate is formed in strong acid solutions ($pH<0.9$), while the silicomolybdate is usually formed in dilute acid solutions (pH between 1.0 and 1.8). Kircher and Crouch[14] performed a study on differential kinetic measurements for phosphomolybdate and silicomolybdate formation at different acidities.

In this paper the vanadomolybdate used for phosphate determination[15] was considered for kinetic determination of both phosphate (on the peak height as in normal SIA) and silicate (by means of reaction rate measurements) by SIA. In the final established conditions silicate presents a small contribution on the peak height of phosphate, and hence three calibration curves should be constructed: one corresponding to the silicate reaction rate (slope), a second corresponding to the silicate signal on the peak height and a third corresponding to phosphate (also on the peak height). Thus, phosphate is determined subtracting the silicate contribution on the peak height.

EXPERIMENTAL

Reagents

All chemical used were of analytical grade and were stored in polyethylene bottles except phosphate solutions which were stored in glass containers.

Stock standard solutions of phosphate (3.23 mmol P l^{-1}) and silicate (35.6 mmol Si l^{-1}) were prepared from KH_2PO_4 and $Na_2SiO_3.5H_2O$, respectively. Working phosphate and silicate solutions were prepared daily by suitable dilution of the stock solution. A 0.5 M ammonium molybdate stock solution and a 0.05 M vanadate stock solution were prepared from $(NH_4)_6Mo_7O_{24}.H_2O$ and NH_4VO_3, respectively. For the determination, a vanadomolybdate reagent was prepared to contain 0.08 M ammonium molybdate and $7.5x10^{-3}$ M ammonium vanadate in 0.6 M hydrochloric acid.

Apparatus

The sequential injection system used (Figure 1) is similar to that described in a previous paper[3] and was constructed from the following components: a titration autoburette Crison 738 (Alella, Spain) with adjustable dispensing rate, a electromechanically controlled 6-port valve (Rheodyne 5011), an autosampler Crison 2040 and a Hewlett-Packard HP-8452A diode array spectrophotometer equipped with a 10 mm Hellma flow-through cell (volume 18 µl). Data acquisition and device control were achieved using a PC-486 compatible computer.

All the tubing connecting the various units was made of PTFE. The holding coil (HC) was 2.55 m long and 1.97 mm i.d. All the remaining tubing was 0.86 mm i.d. The length of the reaction coil was 40 cm.

No temperature control was carried out in the experiments.

Procedure

The different ports of the valve used in this method were connected to the detector, sample, reagent and waste, respectively. The analytical procedures of the SIA system were controlled by the DARRAY* v2.16 software developed by the authors' group and the protocol sequence is listed in Table I. The vanadomolybdate reagent (100 µl) and the sample solution (300 µl) were sequentially aspirated into the holding coil, and next pushed in the forward direction to the

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* The software used in this work can be obtained on request from SCIWARE, E-mail: AEST@p01.uib.es

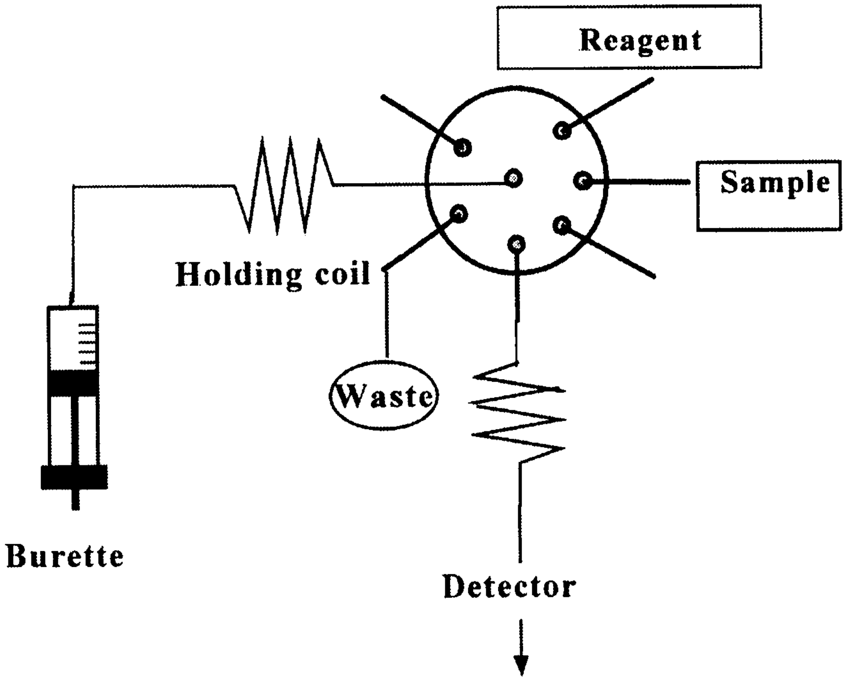

FIGURE 1 Schematic diagram of the SIA manifold used

detector. The stroke length was adjusted in order to assure that the preselected section of the interdispersed sample/reagent zone was transported into the detector. The flow was stopped for reaction rate monitoring (60 s) and finally the detection line was flushed for subsequent determinations. The total analysis time was 132 s.

The absorbance was measured at 420 nm and the baseline noise, due to refractive index changes, was corrected at 550 nm (A_{420nm}-A_{550nm}).

RESULTS AND DISCUSSION

Method optimization

Chemical parameters

When considering the simultaneous determination of phosphate and silicate making use of the different reaction rates with molybdate, a solution of molybdate in acidic medium could be used as a reagent. Nevertheless, to enhance the intensity of yellow colour of molybdophosphate the use of the molybdovanadate reagent is recommended[15], of which no references regarding its application for silicate has been found. After several preliminary experiments a molybdate-vanadate mixture was considered in this application.

TABLE I Protocol sequences of the SIA system for the simultaneous determination of phosphate and silicate developed in this study

Step	*Valve position*	*Burette (ml)*	*Time (s)*	*Description*
1	6	D 1.00	1.6	Place burette piston for subsequent steps
2	4	A 0.50	5.8	Load reagent tubing
3	6	D 1.50	2.4	Dispense to waste
4	2	A 0.50	5.8	Aspirate sample to wash the sample line
5	6	D 1.50	2.4	Dispense to waste
6	2	A 0.70	8.1	Aspirate sample to wash the sample line
7	6	D 1.70	2.7	Dispense to waste
8	2	L 3.00	9.9	Load the burette
9	4	A 0.10	1.3	Aspirate reagent
10	2	A 0.30	4.0	Aspirate sample
11	1	D 0.59	7.9	Propel to detector; acquire data
12			60.0	Stopped-flow; acquire data
13	1	D 2.03	6.7	Flush detection line; acquire data
14	1	D 1.48	4.9	
15	1	L 3.70	12.2	Load burette
16	Repeat from step 9, n-1 replicates			
17	6	D 1.00	5.9	Adjust piston position for next cycle
18	Repeat from step 4, n-1 samples			

D: dispense: A: aspirate; L: load valve position.

During the optimization of the chemical parameters the reagent and sample volumes were fixed on 200 and 100 μl, respectively, and their influence on both the peak height and the reaction kinetics was studied. Kinetic curves, for the formation of silicomolybdate at different silicate concentrations, were recorded and a saturation signal was achieved at 200 s for the entire silicate concentration range. A "delay time" is defined as the time elapsed from the injection point and the beginning of the flow stop. The delay time was fixed on 14 s, time enough to identify the maximum peak height. The stopped-flow time was fixed on 60 s during which absorbance readings were continuously taken (2 readings/s) and the slope method was applied[16]. The reaction rates were calculated according to zero-order kinetics by linear least-squares regression of the data obtained during the stopped-flow time. In each of these experiments, the intermixed zone of the sample and reagent were allowed to settle for 20 s after reaching the detector, and then data were considered for slope calculation for 42 s (Figure 2).

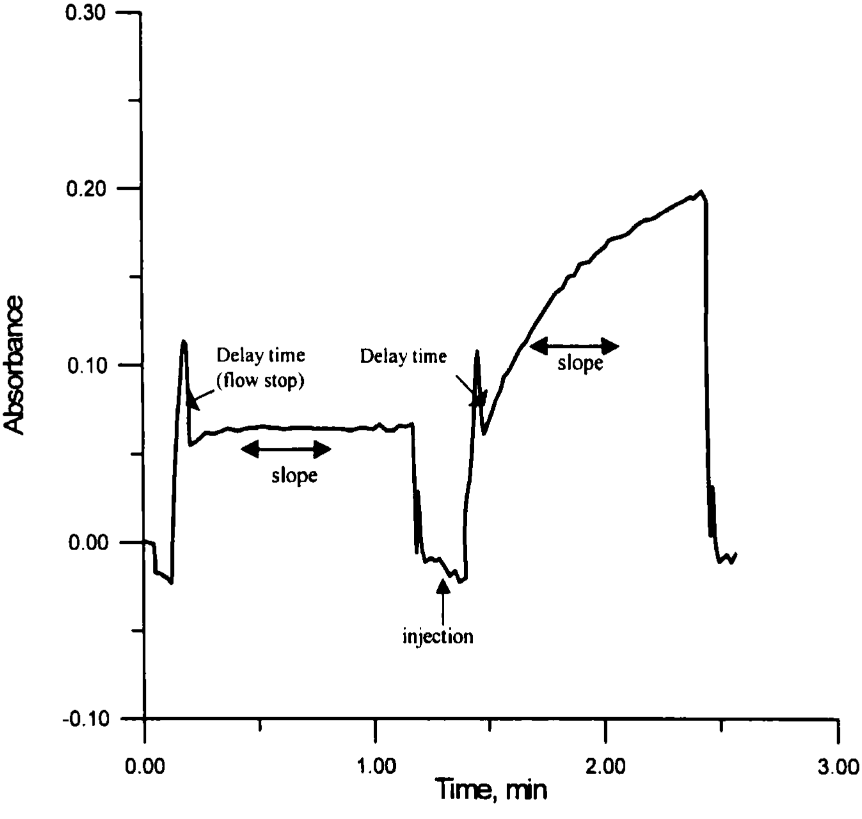

FIGURE 2 Stopped-flow response curves, obtained for 0.065 mmol P l^{-1} and 0.712 mmol Si l^{-1}. Time range of 12–36 s for slope determination is shown as slope

In all experiments the following were analyzed: a blank as a reference, a 1.424 mmol Si l^{-1} solution to study the effect on the slope and a 0.162 mmol P l^{-1} and 1.424 mmol Si l^{-1} mixture solution in order to attain the effect of phosphate both on the slope and the peak height. The peak height of silicate represented in all figures corresponds to the peak height obtained by a silicate solution by subtracting the blank. In the same way, the peak height of phosphate is obtained subtracting to the peak height of a phosphate-silicate mixture the contribution of the silicate.

Molybdate concentration: The influence of molybdate concentration within a range between 0.01 M and 0.125 M was studied with constant vanadate (0.01 M) and hydrochloric acid (0.5 M HCl) concentrations and the results are shown in Figure 3. The good overlapping of the two obtained slope curves (one with and the other without phosphate) corresponding to the stopped-flow period clearly indicate that phosphate does not affect the kinetics within all the assessed concentration ranges. The slope increases with the molybdate concentration, a maximum being obtained between 0.07–0.10 M.

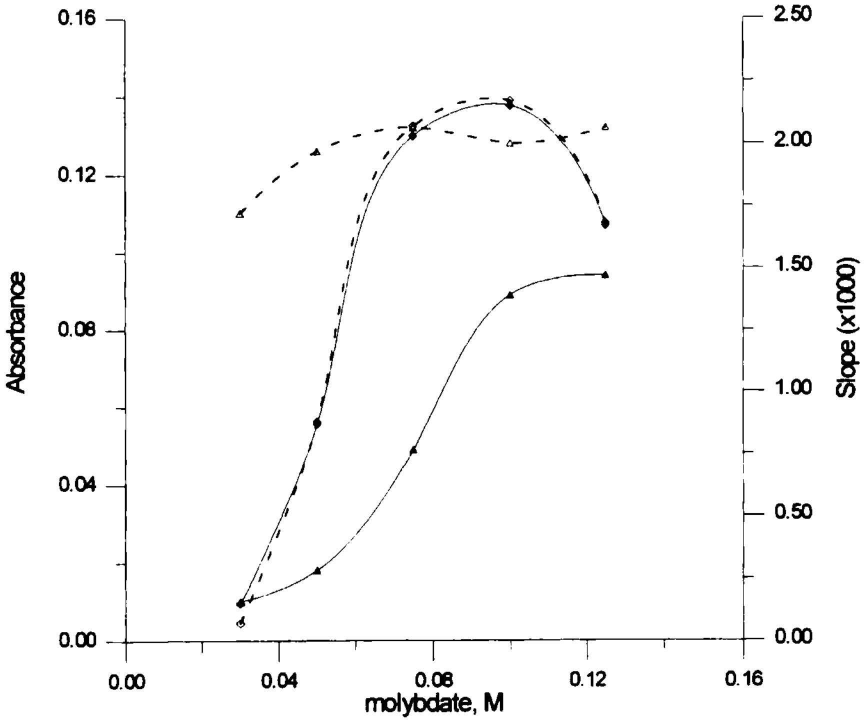

FIGURE 3 Dependence of molybdate concentration on peak height (absorbance) and slope (absorbance s^{-1}). The continuous line is referred to silicate (1.424 mmol Si l^{-1}) and the dotted line to phosphate (0.162 mmol P l^{-1}). The rhombs represent the slope and the triangles the peak height. The slope corresponding to phosphate involves a phosphate and silicate mixture solution. $[VO_3^{2-}]$=0.01 M; [HCl]=0.5 M

The phosphate signal on the peak height remains constant with the molybdate concentration for concentrations >0.04 M, whereas both the blank and silicate increase with the former concentration. The silicate contribution is practically negligible for concentrations <0.03 M. Nevertheless, since the slope for this concentration was very low a concentration of 0.08 M was then considered in order to attain sufficient sensitivity for that analyte.

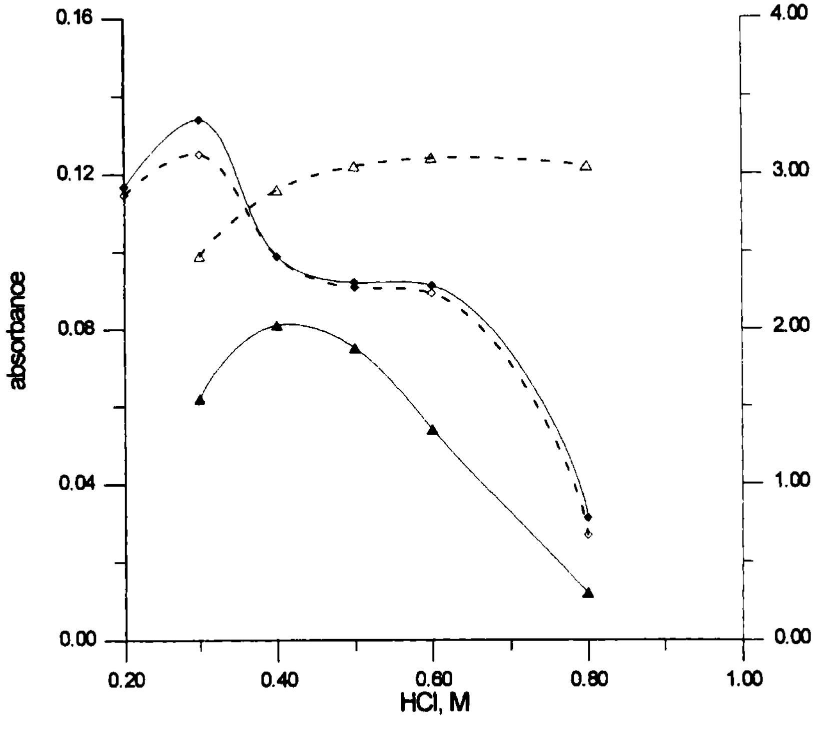

FIGURE 4 Influence of acid concentration on peak height and slope. Idem as figure 1. $[MoO_4^{-2}]$= 0.08 M

Acid concentration: For a hydrochloric acid concentration ranging between 0.2 and 0.8 M and remaining the molybdate and vanadate concentrations at 0.08 M and 0.01 M, respectively, the maximum contribution of silicate on the peak height was obtained for 0.4 M HCl (Figure 4). At the fixed molybdate concentration the phosphate signal slightly decreases for concentrations < 0.3 M and remains constant up to even 1.0 M HCl. In Figure 4 is represented the slope variation as a function of acidity. It is observed that phosphate does not influence the kinetics and the existence of an acid concentration range (0.4–0.6 M) where the slope remains constant. At higher concentrations the slope decreases and at lower concentrations it increases until reaching a maximum. A concentration of 0.5 M HCl was considered for working conditions.

Vanadate concentration: The concentration of vanadate within a range between 1 mM and 12.5 mM did not affect the reaction rate.

In Figure 5 is represented the variation of the peak height obtained with vanadate concentration. The blank linearly increases with vanadate concentration, silicate contribution on the peak height increases very weakly and the signal corresponding to phosphate considerable increases up to 5 mM VO$_3^-$; from the former concentration it continues increasing, although, in a much lower proportion. Finally, and as a compromise between the analytical signal and the blank the vanadate concentration was fixed on 10 mM.

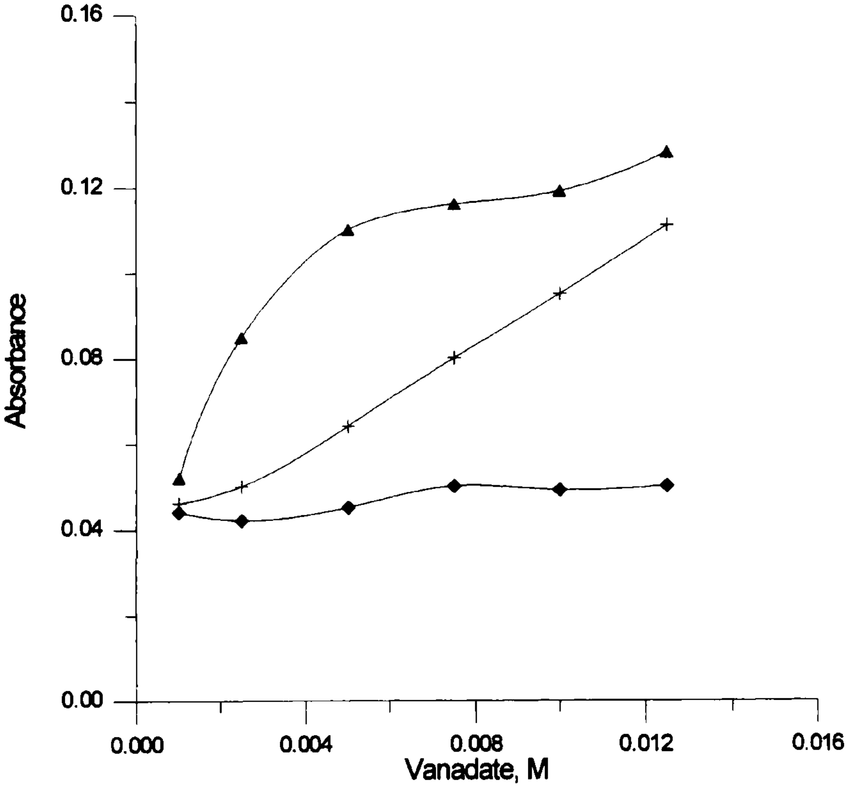

FIGURE 5 Influence of vanadate concentration on peak height. (+) blank; (♦) silicate (1.424 mmol Si l^{-1}); (▲) phosphate (0.162 mmol P l^{-1}). [MoO$_4^{-2}$]= 0.08 M; [HCl]=0.5 M

Physical parameters

In order to obtain comparative results, previous assays were carried out for each experiment with different delay times to adjust the stopped flow point in relation to the peak maximum.

Variation of the sample volume: With the previously established reagent concentrations the reagent volume remained constant at 200 µl and the sample volume was varied from 100 µl to 400 µl. The results are shown in Figure 6 where it can be observed that phosphate presents a slight maximum for volumes ranging between 200 and 300 µl and a tendency towards decreasing when the volume increases, probably due to the higher dispersion and therefore dilution of the reagent with the distance covered inside the holding coil. The silicate signal on the height peak increases with the sample volume which can be attributed to the fact that when increasing the sample volume, the pH corresponding to the reaction zone is modified, thus silicate being favoured.

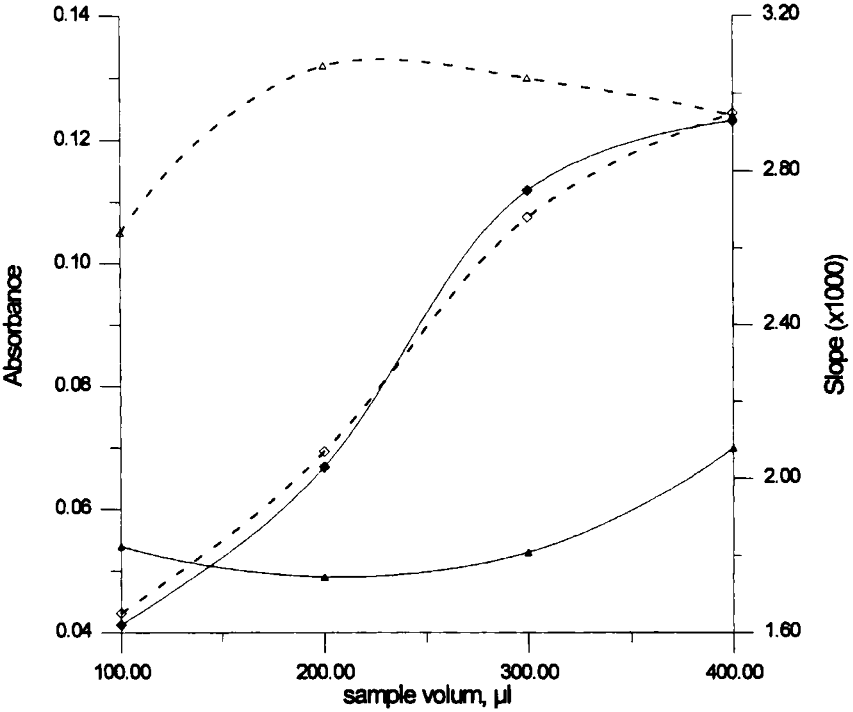

FIGURE 6 Dependence of sample volume on peak height (absorbance) and slope (absorbance s^{-1}). Idem as figure 3. $[MoO_4^{-2}]$= 0.08 M; [HCl]=0.5 M; $[VO_3^{2-}]$=0.01 M

TABLE II Effect of flow rate on peak height, slope and precision

Flow rate ml min^{-1}		*3.6*	*4.0*	*4.5*	*5.2*	*6.0*	*7.2*
Blank	Mean peak height	0.076	0.072	0.070	0.079	0.074	0.077
	% R.S.D.	(1.73)	(2.52)	(3.0)	(0.0)	(1.0)	(2.1)
1.424 mmol l^{-1} Si	Mean peak height	0.143	0.133	0.137	0.139	0.131	0.127
	% R.S D.	(2.63)	(1.26)	(2.63)	(2.22)	(1.71)	(5.0)
0.162 mmol l^{-1} P	Mean peak height	0.134	0.134	0.135	0.130	0.116	0.114
	% R.S.D.	(3.59)	(3.46)	(1.0)	(1.89)	(1.15)	(2.75)
1.424 mmol l^{-1} Si	Mean slope	0.0020	0.0019	0.0020	0.0019	0.0020	0.0020
	% R.S D.	(1.41)	(1.73)	(1.15)	(0.0)	(3.16)	(0.5)

The reaction rate of silicate increases with the sample volume between 100 and 300 μl, with a further stabilisation. A volume of 300 μl was considered in order to attain a good sensitivity for silicate with a small contribution of the former to the peak height.

Reagent volume: Once the sample volume was fixed, the reagent volume was varied from 50 to 400 μl and its effect was checked for three different molybdate concentrations: 0.05, 0.08 and 0.1 M. The slope presents a maximum at about 100 μl for the three assessed molybdate concentrations. Very small reagent volumes (50 μl) give rise to smaller height peaks if the molybdate concentration is not high enough (lower than 0.1 M), due to a reagent defect. A volume of 100 μl was considered for further experiments.

Reaction tube length: The effect of the tube length was studied for two internal diameters (0.56 and 0.86 mm i.d.). Figures 7a and 7b show different behaviours of the system according to the diameter of the tubing. With an internal diameter of 0.56 mm, contribution of silicate (Figure. 7a) to the peak height increases with the length of the reaction tube, whereas it presents a small maximum with the tube length if the internal diameter is of 0.86 mm. This behaviour could be explained in terms of dispersion effects and reaction time. When increasing the tube length the delay time is also increased and therefore the reaction of silicate is produced to a greater extent. However, if the tube diameter is sufficiently large dispersion compensates most of the obtained product.

Kinetics of silicate is less affected by the reaction tube length, specially for 0.56 mm i.d., although it seems to diminish for lengths >1.5 m and 0.86 mm i.d., due to the dilution of the reagents.

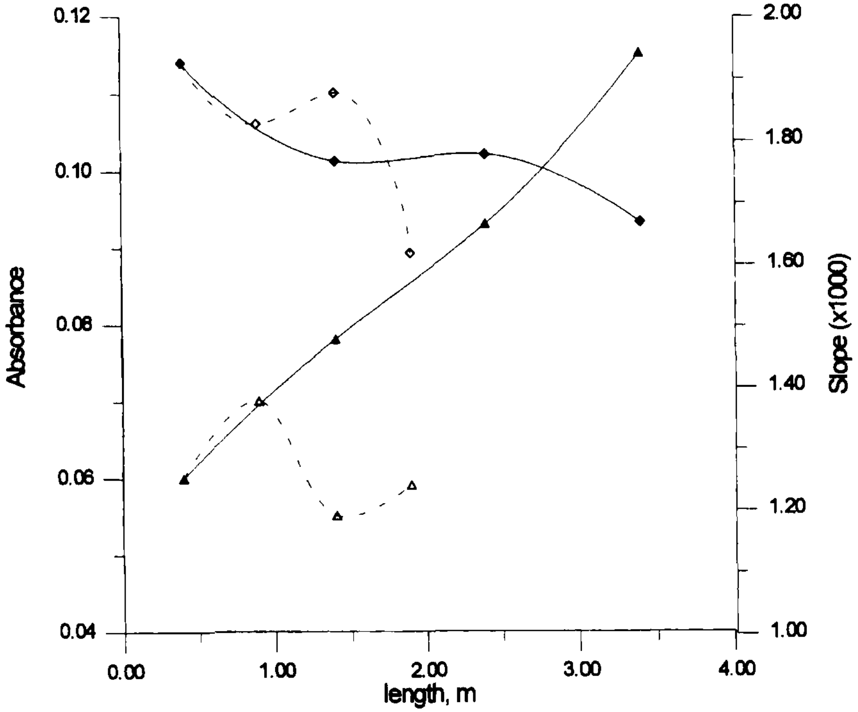

FIGURE 7A Influence of the tube length on silicate response. The continuous line corresponds to the 0.56 mm i.d. tube and the dotted line (open symbols) to the 0.86 mm i.d. tube. The rhombs represent the slope and the triangles the peak height

The phosphate signal (Figure 7b) remains almost constant from 1.5 m of length for the smallest diameter and considerably diminishes with tube length when the diameter is 0.86 mm, which implies a much higher dispersion.

Finally, and considering as selection criteria the less contribution possible of silicate to the peak height of phosphate, maximum phosphate signal and maximum silicate reaction rate, the reaction coil was kept as short as physically possible given by the distance between the flow cell and the selection valve (40 cm).

Flow rate: In Table II are summarised the results obtained when simultaneously varying the aspiration and propulsion rates from 3.6 ml min^{-1} to 7.2 ml min^{-1}. Contribution of silicate to the peak height diminished with the flow rate, especially from 6.0 ml min^{-1}, whereas the value of the slope is not affected by this variable. The signal corresponding to phosphate is also subjected to a

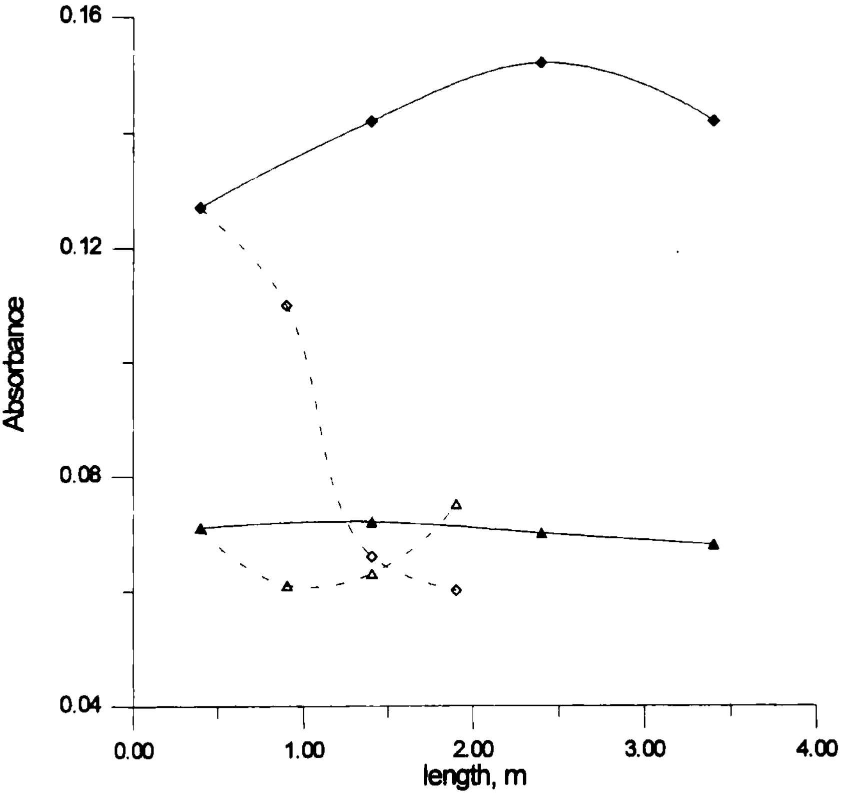

FIGURE 7B Influence of the tube length on phosphate and blank responses. The continuous line corresponds to the 0.56 mm i.d. tube and the dotted line to the 0.86 mm i.d. Phosphate is represented by rhombs and the blank by triangles

decrease for high flow rates (> 5.5 ml min^{-1}). The flow has been fixed on 4.5 ml min^{-1}.

Delay time: A range of delay time values was considered and a series of curves with increasing delay time was recorded (Table III). Delay times of 7.6–7.9 s yield the highest values of peak height, whereas the reaction rate continually decreased with increasing the delay time.

Method evaluation

The SIA method proposed in this paper was evaluated with regard to response linearity, accuracy, precision and interferences.

TABLE III Reproducibility of the measurements of peak height and reaction rates

	Silicate				*Phosphate*	
delay time, s	*reaction rate*	*% RSD*	*Peak height*	*% RSD*	*Peak height*	*% RSD*
7.2	0.0055	5.0	0.143	2.7	0.183	1.0
7.3	0.0051	2.3	0.144	2.2	0.187	1.0
7.6	0.0046	3.3	0.146	0.9	0.193	1.5
7.9	0.0041	1.9	0.148	2.7	0.192	1.2
8.1	0.0036	5.2	0.147	2.3	0.191	1.1
8.4	0 0032	4.0	0.147	1.4	0.189	1.4

N= 5

Linearity

The linearity of the proposed SIA system for the simultaneous determination of phosphate and silicate was evaluated under the established conditions. The calibration graph is linear for phosphate concentrations up to 0.485 mmol P l^{-1} according to the following equation:

$A_{\text{peak height}} = 0.0926\ (\pm 0.0068) + 0.8052\ (\pm 0.0341)[\text{mmol P } l^{-1}];\ r^2 = 0.9986\ (\pm 0.0009),\ n=6,$

and the calibration equation of silicate up to 2.85 mmol Si l^{-1}according the peak height was:

$A_{\text{peak height}} = 0.0913\ (\pm 0.0089) + 0.0562(\pm 0.0171)[\text{mmol Si } l^{-1}];\ r^2 = 0.9965(\pm 0.0024);\ n=5$

The fixed-time and slope methods were applied to the kinetic determination of silicate. In Table IV are summarised % RSD (relative standard deviation), the calibration equation and correlation coefficient (r^2) for the fixed-time and slope method, respectively.

The calibration curves obtained from the fixed time method are linear up to 3.56 mmol Si l^{-1}, the maximum assessed concentration, whereas with the slope method curves divert from linearity from 2.85 mmol Si $l^{-1}$for all segments of the kinetic curve considered. Times < 11 s (after the flow stop) give rise to a higher dispersion of the results due to the fact that after delaying the autoburette it takes the liquid several seconds to get rearranged in the flow cell, which is in agreement with that observed by other authors[10,17]. Calculation of the slope between 12 and 36 s was found to be suitable for taking measurements since at higher times approach to the saturation zone of the kinetic curves takes place.

TABLE IV %RSD and calibration equations obtained at different fixed times and different time interval considering silicate concentrations ranging between 0 and 2.848 mmol Si l^{-1}

Fixed-times, s	*Calibration equation*	r^2	*RSD % (1.424 mmol Si l^{-1})*	*RSD% (1.424 mmol Si l^{-1} in 1.424 mmo Si l^{-1} + 0.162 mmol P l^{-1})*
4	$A = 0.041 + 0.0506^{*}[Si]$	0.9940	2.58	1.68
6	$A = 0.043 + 0.0618^{*}[Si]$	0.9945	2.21	2.24
10	$A = 0.047 + 0.0786^{*}[Si]$	0.9950	1.69	1.73
15	$A = 0.050 + 0.0983^{*}[Si]$	0.9943	1.78	1.00
20	$A = 0.053 + 0.1152^{*}[Si]$	0.9940	1.14	0.95
25	$A = 0.056 + 0.1264^{*}[Si]$	0.9933	1.12	0.98
30	$A = 0.057 + 0.1376^{*}[Si]$	0.9932	1.16	0.73
Slope, s				
4–20	$S = 0.0452 + 0.2415^{*}[Si]$	0.9924	1.93	2.98
4–30	$S = 0.033 + 0.2050^{*}[Si]$	0.9954	1.78	1.70
12–24	$S = 0.0176 + 0.1966^{*}[Si]$	0.9993	1.81	4.84
12–36	$S = 0.021 + 0.1545^{*}[Si]$	0.9970	0.94	1.63

The detection limit ($3\sigma_{\text{blank}}$) was calculated to be 7.4 µmol P l^{-1} and 37.38 µmol Si l^{-1}. The analysis rate varies, depending on the criterion chosen for silicate determination, from 29 to 34 samples per hour.

Precision

The precision of the method was determined by 10 repetitive measurements of three solutions of 0.162 mmol P l^{-1}, 1.424 mmol Si l^{-1} and a mixture of 0.162 mmol P l^{-1} and 1.424 mmol Si l^{-1}. The % RSD on the peak height was 1.8%, 2.4% and 2.1% for phosphate, silicate and phosphate-silicate, respectively.

The results for the kinetic determination of silicate are listed in Table IV.

Accuracy

The accuracy of the proposed method was evaluated by analysing several standard mixtures of different phosphate and silicate concentrations. The results as shown in Tables V and VI revealed a good agreement. Besides, real wastewater samples were analysed with the SIA system and the accuracy of the method was evaluated by comparing the results with those obtained by using a standard method[15].

TABLE V Simultaneous determination of phosphate and silicate

Concns of mixtures considered		*concns of mixtures found*						
mmol P l^{-1}	*mmol Si* l^{-1}	*n*	*mmol P* l^{-1}	*% E*	*% RSD*	*mmol Si* l^{-1}	*% E*	*% RSD*
0.032	0.356	11	0.038	19	11	0.345	–3	8.4
0.032	1.068	9	0.036	9.7	8.3	1.113	4.2	3.5
0.032	1.780	10	0.033	0.5	22.9	1.790	0.5	1.8
0.065	0.356	11	0.070	9.0	7.6	0.345	–3	6.5
0.065	0.712	3	0.066	2.2	5.2	0.721	1.3	2.6
0.065	1.068	4	0.073	13.4	6.3	1.104	3.4	4.5
0.065	1.780	9	0.059	–8.6	10.2	1.770	–0.6	2.0
0.161	0.356	4	0.179	10.9	3.7	0.314	–11.7	9.1
0.161	0.712	3	0.164	1.8	11.3	0.727	2.2	2.9
0.161	1.780	4	0.144	–10.7	10.3	1.758	–1.3	1.7
0.258	0.356	11	0.265	2.5	7.8	0.321	–9.8	11.2
0.258	1.068	8	0.255	–1.8	8.6	1.098	2.8	4.4
0.258	1.780	11	0.240	–7.0	11.3	1.746	–1.9	2.2
0.323	0.356	5	0.337	4.3	5.3	0.324	–9.0	8.3
0.323	1.068	4	0.314	–2.8	3.9	1.095	2.5	1.4
0.323	1.780	5	0.300	–7.0	5.9	1.749	–1.8	2.6
0.387	0.356	4	0.392	1.3	1.9	0.307	–13.9	10.0
0.387	1.068	3	0.353	–9.0	2.6	1.082	1.3	1.7
0.387	1.780	4	0.335	–13.5	2.9	1.740	–2.3	2.6

High phosphate concentrations (> 0.323 mmol P l^{-1}) show a small negative slope due to consumption of the molybdate reagent. This consumption of the molybdate causes a decrease in the silicomolybdate formation rate and consequently a negative error in silicate determination (especially for low concentration). High silicate concentrations (>1.78 mmol Si l^{-1}) cause similar negative effect over phosphate determination.

TABLE VI Comparison of the results for samples determined by the SIA system and standard methods

Sample	*SIA mmol $P\,l^{-1}$*	*% RSD*	*Batch mmol $P\,l^{-1}$*	*SIA mmol $Si\,l^{-1}$*	*% RSD*	*Batch mmol $Si\,l^{-1}$*
Tap water	< D.L.		0.003	0.135	7.1	0.111
E1 output[a]	0.221	6.7	0.209	0.207	6.2	0.190
E1 input[a]	0.175		0.145	0.235		0.229
E2 output[a]	0.162	6.0	0.142	0.292	1.9	0.265
E2 input[a]	0.294	6.4	0.271	0.265	6.1	0.288
ST[a]	0.160	5.8	0.151	0.285	7.8	0.263
Primary settled[a]	0.201	10.4	0.188	0.325	3.6	0.315

a. Waste water samples. ST= Tertiary treatment.

Interferences

Acidity, ionic strength (as sodium chloride), fluoride, arsenic, chrome, sulphide and iron may be possible interferences in the proposed method and were therefore evaluated. The pH of the sample did not interfere in the range between 1.4 and 11.2. Ionic strength, arsenic, chrome, iron and sulphide interfered positively in the silicate determination at concentrations higher than 0.4 M, 0.13 mM, 1 mM, 0.5 mM and 0.16 mM respectively. Fluoride interfered negatively at concentrations higher than 16 mM. Phosphate determination was subjected to more interferences than silicate; arsenic, fluoride and sulphide interfered negatively at concentrations higher than 0.033, 5.26 and 0.063 mM, respectively. Chrome and iron interfered positively at 1 and 0.5 mM and the ionic strength at concentrations higher than 0.2 M.

CONCLUSIONS

A SIA stopped-flow method has been applied to the simultaneous determination of phosphate and silicate in wastewater. Phosphate determination compels to carry out the stopped-flow after reaching the peak maximum (which implies a loss of sensitivity) and at a sufficient distance from the former to attain an easy detection.

This method is simpler and less time-consuming than the previous SIA work based on the use of large sample volumes[3]. Moreover, whereas the detection limits are similar in both methods, the linear range concentration is wider in the present method, especially for silicate determination.

Besides, if the method is compared with the first simultaneous reaction-rate determination of phosphate and silicate[14] it can be concluded that for a similar analysis time, in the present work it was observed that the application range for silicate determination is wider and the range for phosphate has been narrowed. The conditions of the reagent can be modified if allowed by the range of the analyte concentrations, the simplest parameter being the acid concentration. Diminishing the silicate signal on the peak height, only two calibration curves would be necessary and each species would be directly determined on one of them: silicate on the kinetic curve and phosphate on the peak. This can be especially applied in the case of sufficiently high silicate concentrations.

Acknowledgements

The authors wish to express their gratitude to the CICyT (Spanish Council for Research in Science and Technology) for financial support received for the performance of this work as part of the projects AMB97–0537 and AMB99-0263.

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