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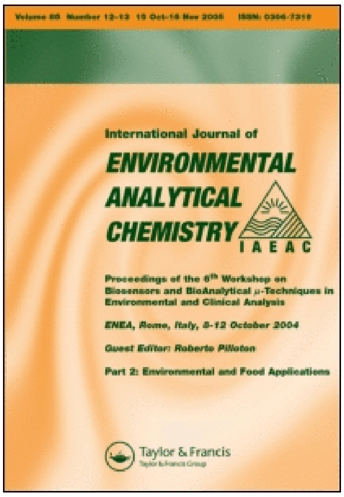

International Journal of Environmental Analytical Chemistry

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 Más, F. , Estela, J. M. and Cerdá, V.(1991) 'Simultaneous Spectrophotometric Determination of Silicate and Phosphate by Flow Injection Analysis', International Journal of Environmental Analytical Chemistry, 43: 2, 71 — 78

To link to this Article: DOI: 10.1080/03067319108026967

URL: http://dx.doi.org/10.1080/03067319108026967

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Intern. J. Environ. Anal. Chem., Vol. 43, pp. 71–78
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SIMULTANEOUS SPECTROPHOTOMETRIC DETERMINATION OF SILICATE AND PHOSPHATE BY FLOW INJECTION ANALYSIS

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(*Received 10 January 1990*)

A method is reported for the simultaneous determination of phosphate and silicate by flow injection analysis based on the different rate of formation of the heteromolybdic acids of the two anions. Measurements are based on the colour of the ion-pairs formed between the said molybdic acids and Rhodamine B. The method allows the determination of the two anions at a rate of 20 samples/h over the ranges 0.05–2.5 ppm (phosphate) and 0.8–15 ppm (silicate), which allows application to a variety of waters.

KEY WORDS: Flow injection analysis, simultaneous determination, spectrophotometry, silicate, molybdate, phosphate.

INTRODUCTION

The earliest application of flow injection analysis (FIA) involved the determination of phosphate based on the formation of heteromolybdophosphoric acid (12-MPA) and was reported by Ruzicka and Hansen.[1] It was followed by the development of a host of FIA procedures for phosphate and silicate, most of which were based on the formation of 12-MPA and silicomolybdic acid (12-MSA) or their reduction to Molybdenum Blue, which were detected spectrophotometrically,[2–8] voltammetrically[9–12] or coulometrically.[13]

Both phosphate and silicate react with molybdate in acid media to form the corresponding heteromolybdate. Thus, they seriously interfere with the determination of each other. The resolution of mixtures of the two anions has so far been addressed either by implementing a prior precipitation, selective extraction[14–16] or selective masking[17,18] step to isolate them, or by exploiting the kinetic differences arising from the acidity of the reaction medium used.[19–22] None of these methods is really selective; moreover, those involving separations are rather laborious and time-consuming. Some authors[23,24] have proposed the separation of phosphate, silicate and arsenate by introducing an ion-exchange column in the manifold.

A number of methods based on the formation of ion-pairs between the phosphomolybdate ion and some cationic dyes (e.g. Rhodamine B) have also been reported in the last few years. Thus, Liu and Wei[26] recently developed a highly sensitive non-FIA spectrophotometric method based on the reaction between silicium or phosphorus and the molybdovanadate/Rhodamine B system.

The FIA technique allows sample streams to be split into a number of channels. The resistance to flow circulation of each channel is normally a function of its length and inner diameter, which permits signals to be dephased as required. Valcárcel *et al.*[25] developed a method with splitting of the sample based on the faster formation kinetics of 12-MPA compared with 12-MSA. The heteropolyacids formed are used to oxidize thiamine to thiochrome, which is monitored fluorimetrically. This paper reports a method for the simultaneous determination of phosphate and silicate also based on the higher rate of formation of 12-MPA. The heteropolyacid is reacted with Rhodamine B to form an ion-pair which is detected spectrophotometrically.

EXPERIMENTAL

Reagents

- 0.2 M molybdate solution prepared from $(NH_4)_6Mo_7O_{24}\cdot H_2O$.
- 10^{-3} M solution of Rhodamine B.
- 5 M nitric acid solution.
- standard phosphate solution (1000 ppm), prepared from the corresponding monosodium salt.
- commercially available 34% silicate solution, purchased from Merck.
- 0.1% solution of polyvinyl alcohol (PVA) prepared by dissolution of the solid production in hot water and subsequent filtration.

Apparatus

The instrumental set-up used consisted of a Hewlett–Packard 8452A diode-array spectrophotometer furnished with a 18-μl Helma flow-cell, a Gilson Minipuls 2 eight-channel peristaltic pump and a Rheodyne 6-way valve.

RESULTS AND DISCUSSION

Preliminary studies on the individual determination of phosphate and silicate carried out by our group with the manifolds in Figure 1 revealed that the chief differences between the two systems lay in the marked influence of the temperature on the silicate system and in the type of acid to be used in each case: sulphuric for the determination of phosphate and nitric for that of silicate. Tables 1 and 2 summarize the optimum values of the chemical and physico-chemical variables involved in the individual determinations.[28,29]

As stated above, phosphomolybdic acid is formed more rapidly than silicomolybdic acid. This kinetic difference allows the analytical signals to be measured at a different time. Flow injection systems allow signals to be dephased by splitting the starting flow into two channels of different length and inner diameter. In order to achieve the best possible resolution, we aimed at minimizing and maximizing

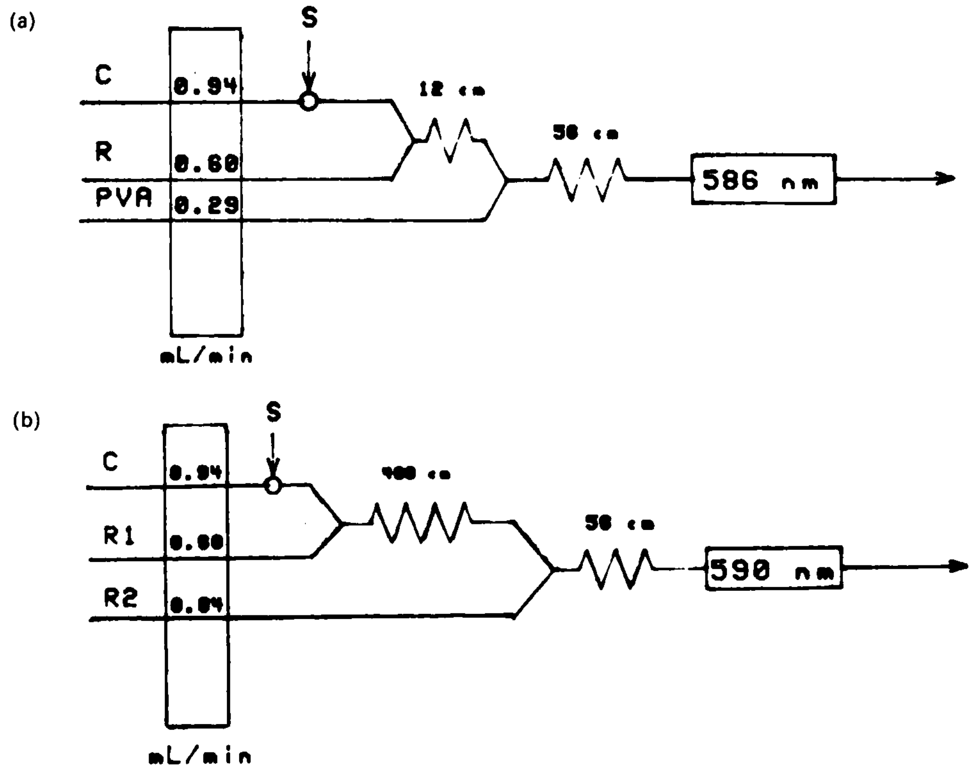

Figure 1 Manifolds for the individual determination of (a) phosphate and (b) silicate. S: sample; C: carrier (water). (a) R: molybdate/Rhodamine B solution. (b) R_1: molybdate solution; R_2: Rhodamine B/PVA solution.

Table 1 Optimum values of the variables involved in the individual FIA determinations of phosphate and silicate

Anion	*[Mo]* *(mol/l)*	*[Rhod]* *(mol/l)*	*[HNO_3]* *(eq/l)*	*[H_2SO_4]* *(eq/l)*	L_1 *(cm)*	L_2 *(cm)*	q_t *(ml)*	*Time* *(min)*	V_{inj} *(µl)*
PO_4^{3-}	0.026	8×10^{-5}	—/—	0.9	56	—	1.8	28	220
SiO_3^{2-}	0.024	1×10^{-4}	0.2[a]/1.0[b]	—	400	56	2.65	45–51	220

[a] Medium of the molybdate solution.
[b] Medium of the Rhodamine B solution.

the contribution of silicate to the first and second peak, respectively. We found that splitting the flow into two channels of 6 cm and 4 m with IDs of 0.3 mm and 0.5 mm, respectively, resulted in more than adequate peak resolution with no detriment to the sensitivity. Figure 2 shows the signals yielded by phosphate and silicate standards.

On the other hand, as the time required for the formation of silicomolybdic acid was the strongest limiting factor, the manifold used for the simultaneous determination of phosphate and silicate was similar to that employed in the individual

Table 2 Analytical data for the optimized individual FIA determinations of phosphate and silicate

Anion	*Equation*	*Linear range (ppm)*	*Correlation coefficient*	*RSD (%)*	*Sampling frequency (h^{-1})*
PO_4^{3-}	$A = 0.0016 + 0.3[PO_4^{3-}]$ ppm	0.02–2.0	0.999	5.0[a]	55
SiO_3^{2-}	$A = -0.01 + 0.3[SiO_3^{2-}]$ ppm	0.04–4.2	0.998	6.0[b]	40

[a] For 80 ppb.
[b] For 0.5 ppm.

determination of silicate, in which the molybdate and Rhodamine B solutions were kept from each other and the system was thermostated at 45 °C. This configuration and the values of the variables used are shown in Figure 3.

Calibration Graphs

Calibration curves were run by injecting 220 μl of various silicate and phosphate standards individually in order to obtain two curves per anion. Mixtures of the two ions were resolved by adding up the equations of the calibration curve of each peak. The equation of the first peak was linear for phosphate up to 2.5 ppm, while that of the second peak was linear for silicate over the range 0.8–15 ppm. The contribution of phosphate to the second peak was negligible at concentrations below 1 ppm, which are typical for natural water samples. On the other hand, the contribution of silicate to the first peak was quite significant at concentrations above 5 ppm. The sampling frequency achieved was 20 h^{-1}, and the detection limits were 0.05 ppm phosphate and 0.8 ppm silicate.

We studied the reproducibility of the proposed method by performing 10 and 9 injections of 0.5-ppm and 2-ppm standards, respectively, of phosphate. The relative standard deviation (RSD) was 6.8 % for the former standard and 2.5 and 8.3 % for the second (first and second peak, respectively). Nine injections of a 6.3-ppm standard of silicate yielded an RSD of 3 % for the second peak—it could not be calculated for the first peak because of its low intensity (0.009 μA). Table 3 summarizes the analytical features of the proposed simultaneous determination of phosphate and silicate.

Table 4 lists the results obtained in the resolution of mixtures of phosphate and silicate standards. As can be seen, the amounts found agree quite well with those added, with a maximum differences of 9 %.

Study of Interferences

Experimental work showed that Ce(IV) and V(V) were the most serious interferences with the determination of phosphate by the proposed method; they could be tolerated in ratios below 1:2. Iodide could be tolerated in a ratio of 2:1. Fluoride, sulphate, bromide, nitrate, nitrite, chloride, K(I), Na(I), Mg(II) and oxalic acid posed no interference in ratios up to 200:1 with the determination of 0.5 ppm phosphate. Cobalt(II), Cr(III), Zn(II) and Ca(II) did not interfere in ratios up to

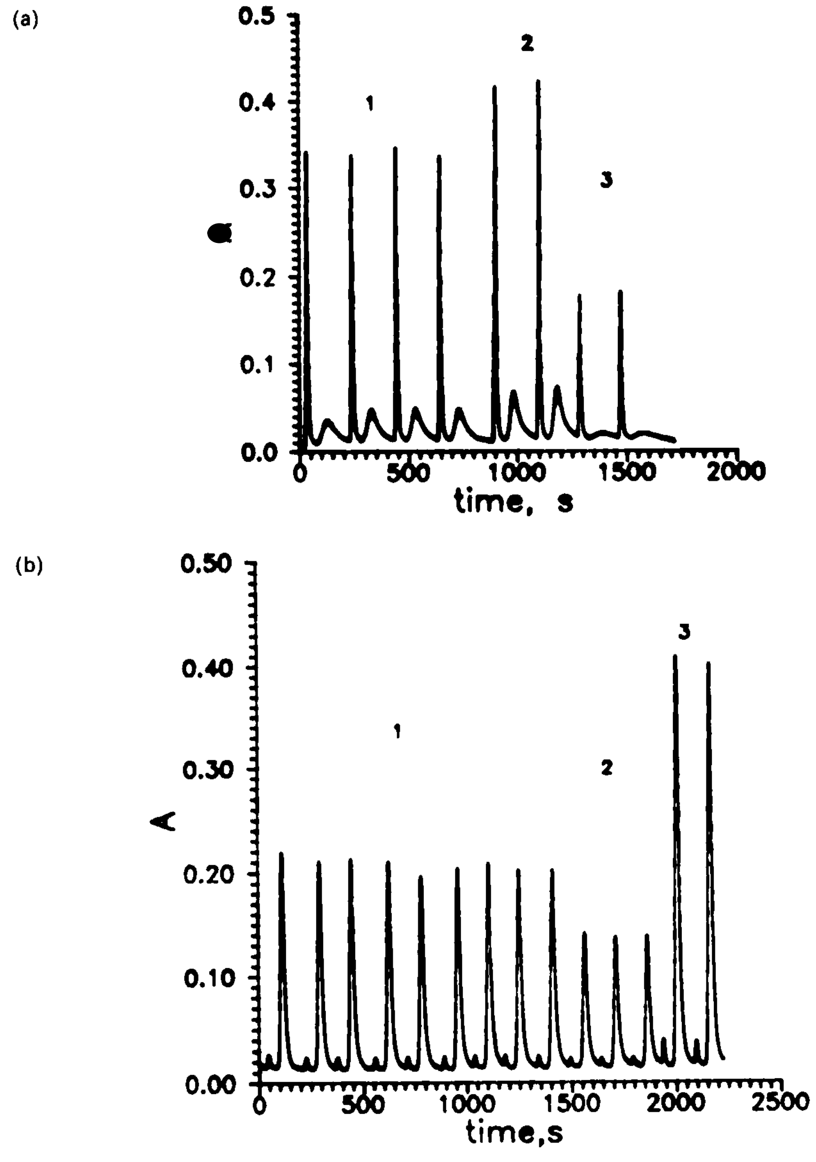

Figure 2 FIA recordings obtained upon injection of (a) phosphate and (b) silicate standards. Phosphate concentrations: (1) 2 ppm, (2) 2.5 ppm, (3) 1 ppm. Silicate concentrations: (1) 6.3 ppm, (2) 4.2 ppm, (3) 12.65 ppm. Wavelength, 590 nm.

100:1, and neither did As(V), Cu(II), Pb(II), Fe(III) or tartrate in a ratio of 10:1. Perchlorate and EDTA posed no problem either. As far as the ionic strength is concerned, a NaCl content of 0.6 M increased the second peak of phosphate, while contents below 0.15 M had no influence whatsoever.

As far as silicate is concerned, sulfate, bromide, nitrate, nitrite, chloride, K(I),

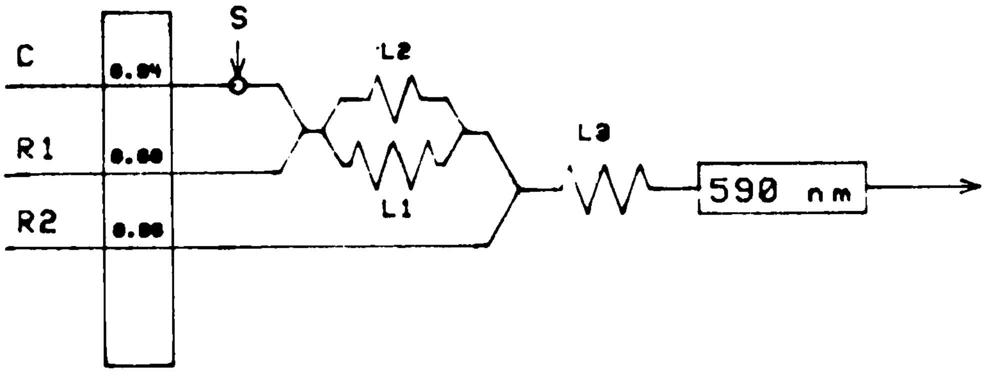

Figure 3 Manifold for the simultaneous determination of phosphate and silicate. S: sample; C: carrier (water); R_1: 0.024 M molybdate solution in 0.5 M HNO_3; R_2: 8×10^{-5} M solution of Rhodamine B in 1 M HNO_3 and 0.05% PVA; L_1: 4-m, 0.5-mm ID reactor; L_2: 6-cm, 0.3-mm ID reactor; L_3: 56-cm, 0.5-mm ID reactor.

Table 3 Analytical figures of merit for the simultaneous FIA determination of phosphate and silicate

Analyte	*Equation*[a]	*Correlation coefficient*	*RSD* (%)[b]
PO_4^{3-}	$A_1 = -2.97 \times 10^{-3} + 0.155[PO_4^{3-}]$ ppm	0.9997	2.5
	$A_2 = -3.65 \times 10^{-3} + 0.0423[PO_4^{3-}]$ ppm	0.9980	8.3
SiO_3^{2-}	$A_1 = -0.0135 + 0.003[SiO_3^{2-}]$ ppm	0.9984	—
	$A_2 = 5.52 \times 10^{-3} + 0.03[SiO_3^{2-}]$ ppm	0.9995	3.0

[a] Subscripts 1 and 2 denote the contribution of the first and second peak, respectively.
[b] For 2 ppm phosphate and 6.3 ppm silicate, respectively.

Na(I) and Mg(II) did not interfere with the determination of a 5-ppm standard in ratios up to 20:1—this was the maximum ratio assayed (100 ppm of the potential interferent). Fluoride was tolerated at concentrations below 10 ppm, while As(V), Cu(II), Pb(II), V(V), iodide and Fe(III) were tolerated in a ratio of 1:1—these ions are never found in higher ratios in waters. Cobalt(II), Cr(III), Zn(II), Ca(II) and EDTA did not interfere either in ratios up to 10:1. High salt contents (NcCl concentrations above 0.15 M) interfered with the determination. Finally, neither tartrate nor perchlorate had an appreciable effect on the silicate signal in ratios up to 100:1.

Applications

The proposed method was applied to the determination of silicate and phosphate in various types of water and the results obtained were compared with those provided by reference (non-FIA) methods, i.e. those using ascorbic acid and silicomolybdic acid for phosphate and silicate, respectively.[27] Table 5 lists the results obtained. As can be seen, consistency was more than acceptable in most

Table 4 Analysis of phosphate–silicate mixtures

Sample	*Phosphate (ppm)*		*Silicate (ppm)*	
	Added	*Found*	*Added*	*Found*
1	0.1	0.12	5.0	4.70
2	0.1	0.17	7.5	7.90
3	0.1	0.10	10.0	9.98
4	0.5	0.61	2.02	2.17
5	0.5	0.52	5.0	5.34
6	0.5	0.47	7.5	7.90
7	0.5	0.53	7.5	7.45
8	0.5	0.49	10.0	10.74
9	1.0	1.08	2.02	1.93
10	1.0	1.05	5.0	5.40
11	1.0	1.06	7.5	8.20
12	1.0	1.13	10.0	10.90
13	1.5	1.62	5.0	4.82
14	1.5	1.58	10.0	10.28
15	2.0	2.04	5.0	4.91
16	2.0	1.96	10.0	9.65
17	3.0	2.97	5.0	5.32
18	3.0	2.96	10.0	10.64

Table 5 Determination of phosphate and silicate in real samples

Sample	*Phosphate (ppm)*		*Silicate (ppm)*	
	Proposed method	*Reference method*	*Proposed method*	*Reference method*
Tank	0.051	0.046	3.83	3.81
Well 1	<0.05	0.018	14.9	13.3
Well 2	<0.05	0.022	8.97	8.74
Tap 1	0.420	0.404	10.3	10.7
Tap 2	0.543	0.470	20.2	17.1
Bottled 1	<0.05	0.051	93.0	85.1
Bottled 2	<0.05	0.023	45.3	45.5
Waste 1	16.9	19.0	24.5	32.3
Waste 2	23.6	28.3	28.8	39.6
Fountain	<0.05	0.030	20.8	20.6

cases. As one would expect, the largest differences arose in waste water samples and were probably caused by matrix effects.

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