Sequential determination of silicate and phosphate in waters by flow-injection spectrophotometry

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SUMMARY

A flow-injection kinetic procedure using intermittent flows is proposed for the sequential determination of phosphate and silicate in waters. The intermittent flows are attained with a single commutator and permit the implementation of two different methods in the same manifold. With stream intermittence, selectivity is enhanced because the differences in the rates of formation of heteropolyacid and molybdenum blue are emphasized. Effects of sample volume, flow rates, coil lengths, acidity, order of reagent addition and reagent concentrations were studied. Sixty samples can be analyzed per hour, precise results (r.s.d, < 1%) being obtained within the 2.50 - 15.00 mg Si l^{-1} and 0.25 - 1.50 mg P l^{-1} ranges. For phosphate determination, the detection limit is 0.02 µg P l^{-1}. The results are in agreement with those obtained by classical procedures.

INTRODUCTION

Originally proposed to speed-up flow-injection procedures based on relatively slow chemical reactions and to achieve merging zones[1], intermittent flows were used also to avoid baseline drift in turbidimetry[2], and in connexion with simultaneous determinations[3,4]. With intermittence, two states can be defined for a single manifold each with its own characteristics[5]. Therefore, selectivity in differential kinetic analysis is improved by adding intermittent flows to modify the

reaction conditions thus emphasizing the differences in reaction rates. Sequential determinations taking advantage of this feature are easily carried out especially when commutation is exploited to provide intermittent flows[6] and coil replacement[7].

This is demonstrated in the flow-injection system proposed here for the sequential spectrophotometric determination of silicate and phosphate in waters. The methods are based on the molybdenum blue formation after reaction with ammonium molybdate under different acidic conditions, followed by reduction of the heteropolyacid by stannous chloride[8,9]. Oxalic and sulfuric acids are alternatively added to suppress the phosphate contribution to the silicate analytical signal, and to increase the differences in reaction rates[10-12].

EXPERIMENTAL

Standards, reagents and samples

All solutions were prepared with distilled-deionized water and analytical-quality reagents. Sample and standard solutions were stored in polyethylene vials.

The R_1, R_2 and R_3 reagents (Fig. 1) were 3.0 % w/V ammonium molybdate, 2.0 M H_2SO_4 and 10 % w/V oxalic acid aqueous solutions. The R_4 reducing reagent (0.1 % w/V $SnCl_2$) was prepared immediately before use by dilution of a stock reagent with water. This stock solution was prepared by dissolving 5.0 g $SnCl_2$ in 20 ml conc HCl and making the volume up to 100 ml with water; after adding metallic stannous, the solution was kept in a refrigerator. The C_S carrier stream was prepared with the same acidity as the samples (0.018 M H_2SO_4) in order to avoid the establishment of undesired pH gradients along the sample zone[13]

The silicate (1000 mg Si l^{-1}) and phosphate (100 mg P l^{-1}) stock standard solutions were prepared by dissolving 5.0595 g $Na_2SiO_3.9H_2O$ or 0.2292 g Na_2HPO_4 in water and completing the volume up to 500 ml with water. Mixed working standard solutions within the 0.00 - 15.00 mg Si l^{-1} and 0.00 - 1.50 mg P l^{-1} ranges, were also 0.018 M in H_2SO_4.

River water samples from the Piracicaba region (S. Paulo State - Brasil) were collected into 500-ml polyethylene vials, filtered through 0.45 μm membrane filters, preserved with 5 ml 1.8 M H_2SO_4 solution[14] and

analyzed.

Apparatus

The system consisted of a mpl3 GJ4 Ismatec peristaltic pump with accessories, a B352 Micronal commutator with built-in T-shaped connectors, transmission lines and reaction coils (0.8 mm i.d. polyethylene tubes), a model B342 II Micronal spectrophotometer with flow cell (14 mm optical path) and a REC 61 Radiometer recorder.

Flow diagram

The flow-injection system with intermittent streams (Fig. 1) was dimensioned to permit the silicate and phosphate determinations to be carried out in a single manifold.

In the situation specified in Fig. 1, the sample is aspirated through the L_2 sampling loop, the R_3 reagent recycles outside the analytical path, and the carrier stream transports the sample volume selected by the L_1 loop through the analytical path. The sample zone receives the R_1 and R_2 reagents at the x confluence, and the hetero-polyacid is formed inside the B_1 and B_2 coils. The R_2 addition increases the acidity thus speeding up the rate of the reaction with phosphate and impairing the reaction with silicate[12]. The R_4 reagent merges with the sample zone at the z confluence, starting the molybdenum blue formation inside the following B_3 coil. Stannous chloride is used as reducing agent because in flow-injection systems better sensitivity for phosphate is attained with this reagent[10]. Parallel tests indicated that sensitivity did not improve when a 1 % w/V hydrazin sulphate solution or ascorbic acid solutions at high concentrations (up to 10 % w/V) were employed. When the processed zone passes through the detector, the molybdenum blue is monitored at 735 nm. This wavelength was experimentally selected in order to provide maximum sensitivity for phosphate because in this procedure sensitivity for phosphate is a limiting factor. The height of the recorded peak reflects the phosphate content in the sample.

After switching the commutator, another state is defined for the system, in which the L_1 loop is placed in the sampling position, the L_2 loop is intercalated into the carrier stream, the R_2 reagent is re-
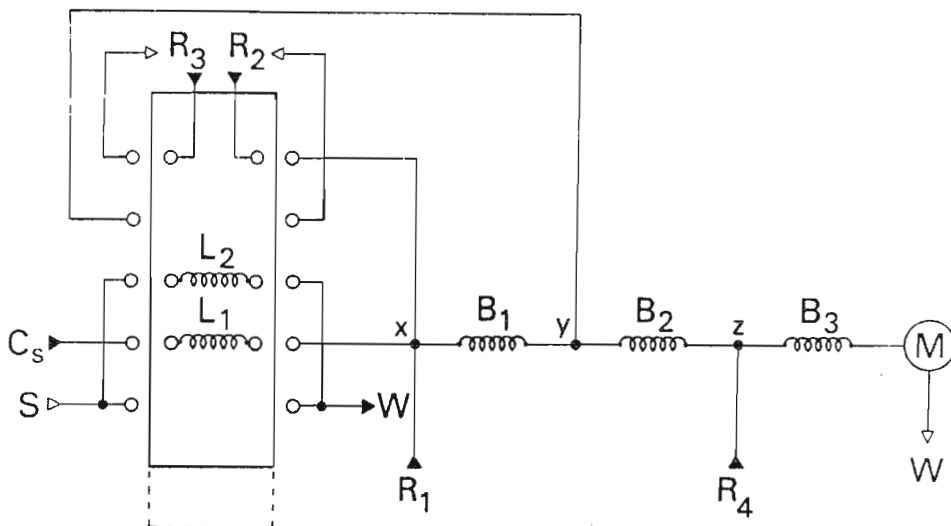
Fig. 1. Flow diagram of the flow-injection system for the sequential determination of silicate and phosphate in waters. S: sample aspirated at 4.0 ml min^{-1}; L_1 and L_2: 100 and 50 cm loops; C_S: carrier stream at 4.9 ml min^{-1}; R_1, R_2, R_3 and R_4: ammonium molybdate, sulfuric acid, oxalic acid and stannous chloride solutions at 0.42, 0.60, 0.42 and 0.42 ml min^{-1}, respectively; B_1, B_2 and B_3: 100, 150 and 50 cm reaction coils x, y and z: confluence points; M: spectrophotometer at 735 nm; W: waste. The boxed components are associated with the central movable portion of the commutator, dashed lines indicate the next commutation state. Black arrows indicate where pumping is applied.

cycled, and the R_3 reagent is directed towards the analytical path (**y** confluence). The injected sample reaches the R_1 reagent at the **x** confluence and mixing is improved in the B_1 coil. The R_3 reagent is added to inhibit the reaction with phosphate in the B_2 coil[10]. Thereafter, the sample zone is similarly processed, the quantified species being proportional to the silicate content of the sample.

Procedure

Single phosphate and silicate standard solutions were injected in triplicate to permit system optimization and selectivity evaluation. The L_1 and L_2 loop lengths were initially fixed as 100 cm. Effects of the sulfuric acid (1.25 - 3.0 M range), ammonium molybdate (1 - 5 % w/V range) and stannous chloride (0.05 - 0.3 % w/V range) concentrations, were investigated. The oxalic acid concentration was always 10 % w/V; in this situation, the R_3 reagent was close to saturation.

After defining the reagent concentrations, the lengths of B_1, B_2 and B_3 coils were varied within the 25 - 250 cm range. The possibility of removing the B_1 coil was also investigated. With $B_1 = 100$ cm, $B_2 = 150$ cm and $B_3 = 50$ cm, the effect of pumping speed (75 and 125 % of the flow rates of Fig. 1) was investigated. Thereafter, the sample loops were dimensioned.

The proposed system was then applied to water analysis. Precision was evaluated as the relative standard deviation of ten results associated with successive injections of typical samples and accuracy was confirmed by running several samples already analyzed by classical procedures[15].

RESULTS AND DISCUSSION

Two baselines are observed with the proposed system (as shown in Fig. 3), each corresponding to a different manifold state and reflecting the extent of molybdenum blue formation in the absence of phosphate or silicate. The highest baseline is associated with phosphate determination which is carried out under more acidic conditions[10,11]. With ammonium molybdate and stannous chloride concentrations of 3.0 % w/V and 0.1 % w/V, the recorded peak height increased when the sulfuric acid concentration in the R_2 reagent varied from 1.25 to 2.0 M. This effect was less marked in the 1.75 - 2.0 M range. The silicate contribution to the phosphate analytical signal, observed under lower acidities, disappeared when the R_2 reagent concentration was higher than 1.75 M. In this case, the differences in baseline were not relevant. These differences became more pronounced with R_2 acidities higher than 2.5 M. In fact, when the sulfuric acid concentration was 3.0 M, the

difference in baselines was about 0.1A and sensitivity deteriorated. The R_2 reagent was then defined as 2.0 M in sulfuric acid which corresponds to an acidity of 0.2 M inside the B_1 and B_2 coils, similar to that used earlier[9]. Stopped-flow experiments suggested that an unstable condition is established with such acidity. After stopping the peristaltic pump, a continuous increase in the baseline absorbance was observed, which emphasizes the tendency for spontaneous molybdenum blue formation: maximum sensitivity for phosphate determination was then achieved. This instability is being used in the present flow-injection procedure which yields reproducible results without silicate interference.

When the commutator rested in the position for silicate determination, the pH inside the B_2 coil was measured as 1.6 which is in agreement with the 1.4 - 1.8 recommended range[11]. This value depends strongly on the carrier stream acidity which is matched with the mean sample acidity (0.018 M). For samples without acid preservation, the carrier stream should be water and the molybdate reagent (R_1 - Fig. 1), 0.2 M in sulfuric acid. With this acidity, the contribution of a 3.00 mg P l^{-1} standard solution to the silicate analytical signal was not observed, indicating that the oxalic acid concentration was suitable.

To prevent the interaction between the R_2 reagent inside the B_1 coil immediately after commutation and the sample zone to be analyzed for silicate, a 20-cm transmission line was placed between the injection port and point **x**. This carry-over effect should always be taken into consideration when designing flow-injection systems with alternating streams.

The B_1 coil length has a marked effect on the yellow heteropolyacid formation associated with silicate (Fig. 2 a-c). No transient signal was detected when this coil was removed. As the yellow heteropolyacid formation increases with the sample residence time inside B_1, longer B_1 coils improve the sensitivity for silicate. However, since sensitivity was not critical for this determination, and the use of a too long coil implied in sampling rate deterioration, the B_1 coil length was selected as 100 cm.

The silicate analytical signal depends also on the B_2 coil length (Fig. 2 a,d,e) because this length is proportional to the available time

for the yellow heteropolyacid formation. The slight decrease in peak height when the B_2 coil was increased from 150 to 200 cm was due to dispersion effects[13]. The B_2 coil length should be enough to provide a suitable time for quantitative phosphate masking without deterioration of the silicate analytical signal. The phosphate peak height was less dependent on the B_2 coil length, and underwent reduction with the B_2 increase as a consequence of sample dispersion. For this work, the B_2 length was chosen as 150 cm.
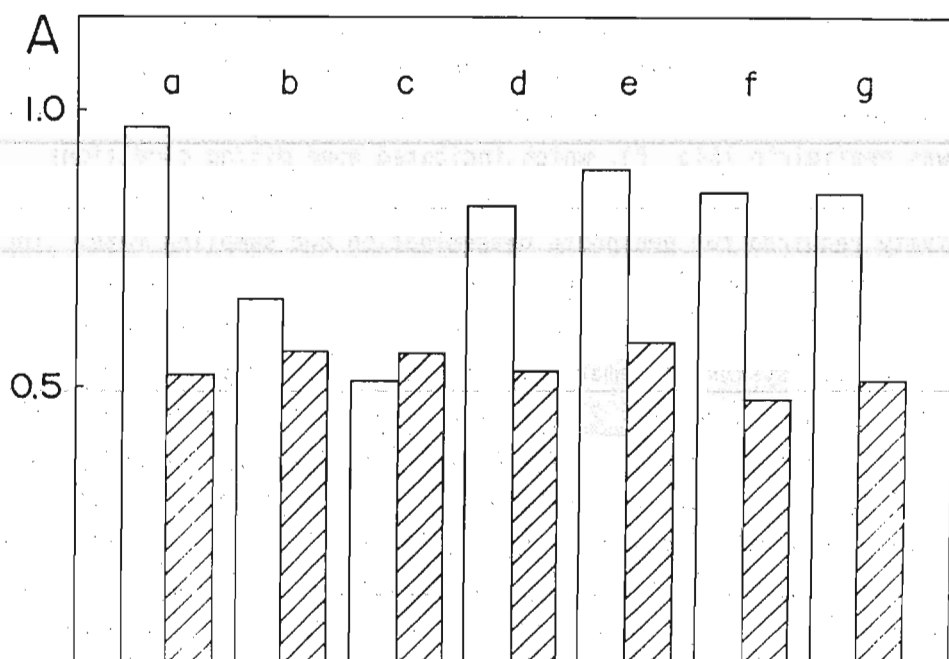

Fig. 2. Effects of the B_1, B_2 and B_3 coil lengths. The histogram columns are peak heights, in absorbance units, corresponding to 1.00 mg P l^{-1} (dashed) and 15.00 mg Si l^{-1} (white) standards. The B_1, B_2 and B_3 coil lengths are: 100, 150 and 50 cm (a); 75, 150 and 50 cm (b); 50, 150 and 50 cm (c); 100, 200 and 50 cm (d); 100, 100 and 50 cm (e); 100, 150 and 25 cm (f); 100, 150 and 100 cm (g).

The B_3 coil length has little effect in both the phosphate and silicate signals (Fig. 2 a,f,g) because a fast reaction is attained with stannous chloride as reducing agent[9]. When the stannous chloride concentration was increased from 0.1 to 0.3 % w/V, the peak height increased only slightly (about 15 %) and the spontaneous molybdenum blue formation determined a pronounced baseline drift. On the other hand, the peak height decreased with lower R_4 reagent concentrations. With 0.05 % w/V stannous chloride concentration, both the phosphate and silicate analytical signals were about 30 % lower in relation to the proposed system and the linearity of the calibration equations deteriorated. Again, the slight decrease in peak height observed when B_3 changed from 50 to 100 cm was due to dispersion effects. Therefore, B_3 was chosen as 50 cm and the stannous chloride concentration 0.1 % w/V. The required sensitivity for phosphate was then achieved and the baseline noise was negligible (Fig. 3), which indicated good mixing conditions.

The L_1 loop length was chosen as 100 cm, as a compromise between sensitivity required for phosphate determination and sampling rate. The dispersion coefficient[16] was determined as 1.2. Sensitivity was not critical for silicate, therefore a shorter L_2 loop (50 cm) was used.

The proposed system is remarkably stable. After 8-h continuous work, only minor changes (usually < 2 %) in the linear coefficients of the calibration equations were observed. About 60 samples are run per hour, at the 1 % carry-over level, including 120 determinations. When manual-ly operated, this rate diminishes to 40 h^{-1} (Fig. 3) because there is a tendency for the operator to wait for baseline restoration. After incorporation of this procedure into routine analysis, it was observed that with an electronically operated commutator[5], sampling rate can be almost doubled by accepting a constant 5 % carry-over which is easily subtracted. Highly precise results are obtained, the relative standard deviations of results for typical samples being usually around 2%. The detection limit for silicate was not determined because this ion occurs often in the 2 - 15 mg Si l^{-1} range; for higher silicate concentrations, the L_2 loop should be reduced accordingly. The detection limit for phosphate (peak height about three times baseline noise) was determined

Tab. 1. Silicate and phosphate concentrations in river waters determined by the proposed flow-injection system (FIA) and by standard procedures[15] (APHA). Data in mg P l^{-1} or mg Si l^{-1}.

SAMPLE	FIA		APHA	
	phosphate	silicate	phosphate	silicate
1	0.80	2.40	0.80	2.42
2	0.19	2.14	0.17	2.29
3	0.51	0.59	0.48	0.54
4	1.49	6.00	1.46	5.69
5	0.76	2.28	0.74	2.13
6	*	0.90	ND	0.98
7	0.12	0.62	0.14	0.64
8	0.18	5.21	0.20	5.17

* about 0.02 mg P l^{-1}; ND - not determined.

as 20 μg P l^{-1}. The results are little affected by variations in the r.p.m. of the peristaltic pump; even with pronounced r.p.m. variations (75 to 125 % of that related to Fig. 1) the recorded peak heights underwent only a 20 % decrease. Analysis of Tab. 1 reveals that the results obtained with the proposed procedure are in agreement with those obtained by classical procedures[16].
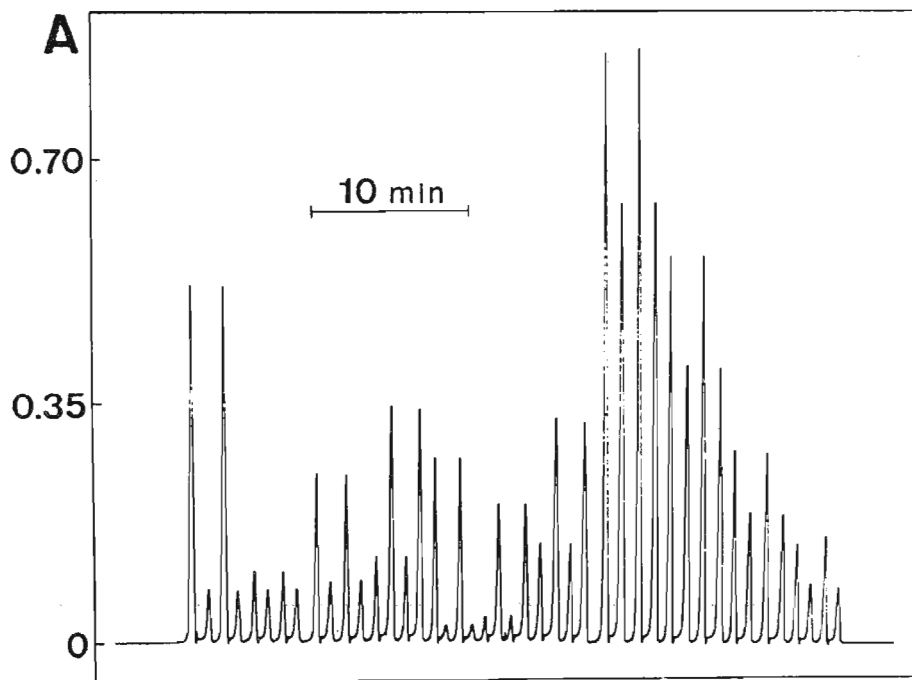
Fig. 3. Recorder output of a routine analysis. From right, four mixed standard solutions (0.25 - 0.50 - 1.00 - 1.50 mg P l^{-1} plus 2.50 - 5.00 - 10.00 - 15.00 mg Si l^{-1} followed by seven river water samples. The first recorded peak refers to phosphate.

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