Continuous-flow Analysis: a Capillary Column with Hydrophobic Inner Surface for the Simultaneous Determination of Calcium and Magnesium

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A capillary tube with a hydrophobic inner surface, which was non-covalently coated on-line with quinalizarin, has been used for the simultaneous determination of Ca and Mg by segmented-flow analysis.

Improvement of the on-line sorption preconcentration and separation stage can be used for the development of new multicomponent high-performance methods for in-flow determination. The first and only attempt to replace a conventional filled sorption microcolumn with a capillary tube in the manifold of a segmented-flow analyser was made by Snyder for protein determination.[1] The separation was provided by interaction with the hydrophobic surface of the capillary tube. The application of capillary columns with a hydrophobic inner surface in conjunction with being coated with non-covalent complexing agents is promising for metal determination.

The performance characteristics of these systems depend on signal dispersion. The influence of various factors on the sample dispersion was studied in the case of an ideal laminar flow without sorption interaction.[2,3] The use of capillary tubes with their hydrophobic inner surface acting as sorption columns may lead to additional signal dispersion; thus, their application assumes the study of the influence of both the hydrodynamic parameters and the chemical factors of the system.

Our first experiments on the application of coated capillary tubes for the on-line preconcentration of Co, Cu and Fe led to promising results.[4] The main advantages of using capillary tubes compared to microcolumns are increased column capacity, lack of hydrodynamic difficulties, improvement of metal separation and broadening of pH range. Therefore, we decided to further develop this method for the well-known and important simultaneous determination of Ca and Mg using segmented-flow analysis. A lot of work has been devoted to flow-injection and continuous flow determination of Ca and Mg.[5–9] In the majority of cases a photometry detector was used to determine the total hardness and then, after masking, one of the components. Another component was determined from the signal difference. Typical productivity was 15–30 h^{-1}. The fact that quinalizarin interacts in the alkaline media only with magnesium could be used for the separation of Ca and Mg in the flow system.

Our aim was the investigation of the possible application of capillary tubes with hydrophobic inner surfaces in the determination of Ca and Mg. This implied on-line non-covalent immobilisation of a complexing agent and the study of the influence of various parameters of the flow system on signal dispersion.

Apparatus.– Photometric determination of Ca and Mg was performed with a continuous-flow analyser RFA-300 (Alpkem, USA). The analyser included (1) a sampler; (2) a peristaltic pump; the manifold inxcluding flexible tubes, (3) a capillary tube and (4) a coil; (5) a spectrophotometer with a flow cell and (6) a recorder (Fig. 1). The capillary column was a molybdenum-glass tube (l = 10 m, i.d. = 0.45–1 mm). Its inner surface was chemically etched and then coated *in situ* with organosilicon compounds [dichlorohexylmethylsilane (C$_6$) and dichlorodiphenylsilane (Ph)] according to the literature procedure.[10] A water–ethanol (9:1, v/v) solution of chemically pure quinalizarin (1×10^{-4} M) was used for coating.

On-line Reagent Immobilisation and Flow Determination of Metals.– The quinalizarin solution was placed in the sampler-cup tube (Fig. 1) and the reagent entered the system *via* the sampling tube during t_s. The reagent concentration provided maximal tube capacity at a flow rate of 287 µl min^{-1} over 25 s. The excess reagent was removed by washing during t_w. An ammonia solution of Eriochrome Black T was used as the photometric reagent. Other sampler cups were filled with the samples to be analysed. The sample interacted with the capillary tube during t_s. Magnesium was quantitatively sorbed and the sample containing only calcium was mixed with the carrier and the photometric reagent, segmented by the air stream, mixed in the coil and detected photometrically in the flow cell. This stage was followed by washing with the buffer solution that was used as the eluent. Magnesium was quantitatively desorbed, and a second signal peak was observed. The column was regenerated by washing with ethanol over t_s, which led to complete removal of the reagent.

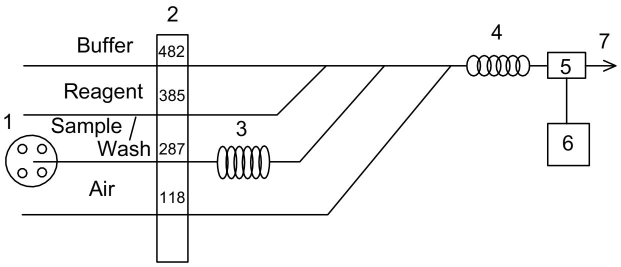

Fig. 1 The apparatus used for the flow determination of calcium and magnesium: (1) sampler; (2) peristaltic pump; (3) capillary sorption tube (l = 10 m; i.d. = 0.5 mm); (4) coil; (5) flow spectrophotometer; (6) recorder and (7) waste.

The immobilisation of quinalizarin was studied for two types of capillary tubes: with C$_6$ and C–Ph. The capacities of capillary tubes for 10% of ethanol were 1.25 ± 0.05 and 1.90 ± 0.05 µmol, respectively. The increase in the ethanol concentration in the coating solution led to a decrease in the column capacity. To provide more versatility in the system the C–Ph tubes were used in subsequent studies. This provides a good coating of a large amount of reagent.

The stability of the column coating was dynamically studied. It was found that the action of 500 ml of buffer solution with pH 3.0–10.5 or 200 ml of 1.4 M NaOH solution resulted in a decrease in the capacity to 2–6%. The coated column was suitable for use in a sorption-elution cycle over 10–12 h.

The rate of immobilisation of the reagent depends on the concentration of the coating solution.[4] The maximal capacity of the C–Ph column was reached by single sampling for t_s = 25 s.

Metal Sorption.– The interaction of Ca and Mg with quinalizarin immobilised was dynamically studied. Conditions providing quantitative sorption of magnesium were chosen as the optimum. Under these conditions the sorption of calcium is minimal (concentration range of NaOH 0.01–0.08 M). This working mode provides high throughput capacity (calcium was determined over t_s and magnesium after quantitative desorption by washing over t_s). Acetate buffer solutions with pH 3.6–4.8 were most suitable as the eluent, since they provided fast (t_s = 40 s) desorption and did not interfere the detection conditions.

The parameters of the flow system were optimised for the chosen conditions. It was found that magnesium sorption and

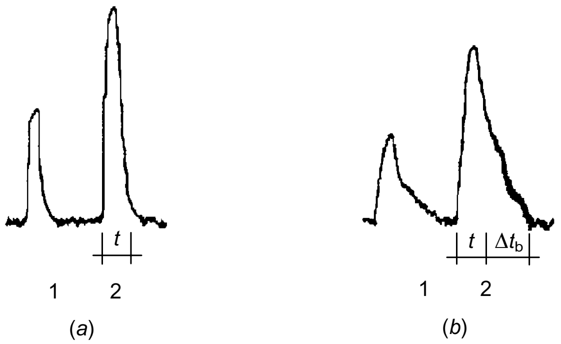

Fig. 2 Analytical signal curves of magnesium (1, $C_{\mathrm{Mg}} = 5$ mg dm^{-3} and 2, $C_{\mathrm{Mg}} = 10$ mg dm^{-3}) for capillary tubes coated with quinalizarin. Tube diameters (*a*) 0.5 mm; (*b*) 1 mm.

sample dispersion are affected mainly by sample flow rate, inner diameter and length of the capillary tube. These parameters were estimated from the Δt_{b} parameter introduced by Korenaga[2,3] (Fig. 2). The value of Δt_{b} is defined as the difference between the width of the foot of the signal peaks with the column and without it. Fig. 2 shows that the decrease in the dispersion leads to lower parameter values. It was found that the tubes with inner diameter of 0.5 mm gave lower sample dispersion ($\Delta t_{\mathrm{b}} = 3.5$) than the tubes with inner diameter 1 mm ($\Delta t_{\mathrm{b}} = 8$). The length of the tube in the range 1–10 m did not affect sample dispersion. The sample flow rate strongly affected sample dispersion and sorption of magnesium (R%) (Fig. 3). Thus, the rate of 287 μl min^{-1} was chosen as the maximal (for minimal dispersion) rate providing quantitative sorption.

Under the optimal conditions found the influence of cations and anions on the simultaneous determination of calcium and magnesium was studied. The choice of interferent was determined on the one hand by the composition of real materials, *e.g.* sea, fresh or rain waters and on the other hand by competitive interaction of quinalizarin with other metals.

The main characteristics of flow-photometric determination of calcium and magnesium are shown below.

(1) The linear calibration ranges: Ca, 2–32; Mg, 1–22 mg dm^{-3}.

(2) The limits of detection (3σ-criterion) Ca, 0.5; Mg, 0.3 mg dm^{-3}.

(3) The relative standard deviation ($C_{\mathrm{Me}} = 10$ mg dm^{-3}, $n = 4$) Ca, 3%; Mg, 2%.

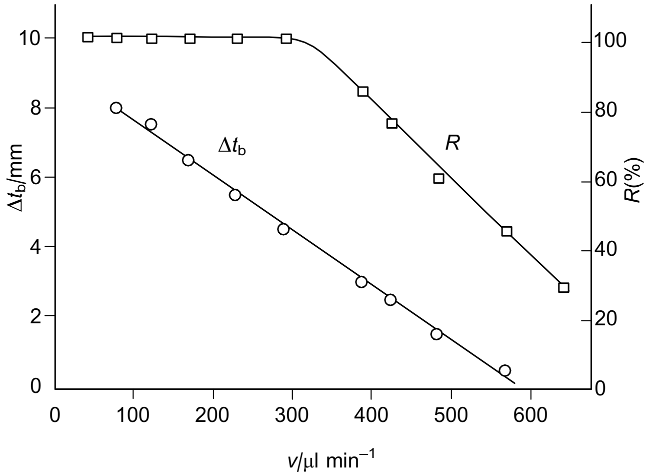

Fig. 3 The dependence of sorption of magnesium [R(%)] and sample dispersion (Δt_{b}) on the flow rate v/μl min^{-1}.

Table 1 Determination of calcium and magnesium in atmospheric sediments.

Sample and date		Found/mg dm^{-3}			S_{r} ($n = 4$)
		CFA	AAS	IC[a]	
Snow	Ca	2.45 ± 0.04	2.48	2.50	0.02
January 1–2, 1994	Mg	1.40 ± 0.05	1.45	1.49	0.04
Sleet	Ca	13.56 ± 0.04	13.58	13.60	0.01
January 26, 1994	Mg	2.40 ± 0.04	2.40	2.40	0.02
Rain	Ca	7.80 ± 0.03	7.79	–	0.01
March 14, 1994	Mg	2.85 ± 0.06	2.90	–	0.02

[a] Ion chromatography with conductivity detection.

(4) The sample composition, t_{s}: 0.03 M NaOH, 25 s.

(5) The wash pH, t_{s}: 4.2, 40 s.

(6) Performance: 55 samples h^{-1}.

(7) The determination of Mg and Ca in the range 2–20 mg dm^{-3} is not affected by a 1000-fold excess of K and Na; 350-fold excess of Al; 100-fold excess of Zn and by a 10 000-fold excess of chloride ions; 1000-fold excess of nitrate and hydrocarbonate ions; 500-fold excess of sulfate ions and 300-fold excess of fluoride ions.

The procedure was used to determine Ca and Mg in atmospheric sediments (Meteorological Observatory of M. V. Lomonosov Moscow State University, Table 1). The results obtained are in good agreement with the results obtained by using other analytical methods, *e.g.* atomic absorbance spectrometry and ion chromatography with conductivity detection. Since the determination, in contrast with known methods,[5–9] is based on the use of individual peaks produced after the separation of Ca and Mg, it provides increased performance and simplifies the treatment of results.

Capillary tubes with a hydrophobic inner surface used in conjunction with non-covalent immobilisation of organic reagents show much promise for use in analytical flow methods.

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