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Simultaneous spectrophotometric flow injection determination of phosphate and silicate



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ABSTRACT

A method for the simultaneous determination of phosphate and silicate based on spectrophotometric measurement at 385 nm of a single peak using a flow injection system with two component calibration is described. In the system, a stream of sample containing both analytes is merged with a stream of ammonium molybdate to form (at $1 < \text{pH} < 2$) molybdophosphoric and molybdosilicic acids. Total absorbance of the compounds is registered in a form of a constant signal. Simultaneously, oxalic acid solution is injected into a carrier stream (H_2SO_4) and then merged with the stream of sample containing the mixture of heteropolyacids. A characteristic peak is registered as a result of selective decomposition of molybdophosphoric acid by oxalic acid. The area (or the absorbance measured at the constant signal) and the absorbance measured at the minimum of the peak can be used as measures corresponding to the phosphate and silicate concentrations, respectively. The time of the peak registration is about 3 min. Two-component calibration with the use of four standard solutions of the phosphate/silicate concentrations established in accordance with 2^2 factorial design was applied. Phosphate and silicate can be determined within the concentration ranges of 0.20–15.00 and 0.20–20.00 mg L^{-1} , with precision less than 2.7 and 0.9% (RSD), respectively and accuracy better than 6.2% (RE). The detection limit is 0.054 and 0.092 mg L^{-1} for phosphate and silicate, respectively. The method was applied to determination of the analytes in certified reference materials of groundwater, wastewater, and river water giving results consistent with the certified values.

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1. Introduction

Phosphorus and silicon play an important role in the metabolism of plants and animals, in the water environment as well as influence water quality and the possibilities of using water for various purposes.

Various analytical methods have been employed for the determination of concentration of phosphorus and silicon species in water and wastewater samples. Among them, UV/VIS spectrophotometry [1–3] and techniques involving separation are frequently applied [4–7]. Regarding application of the latter, ion-exclusion chromatographic separation and post-column derivatization [4], pre-column derivatization ion-pair liquid chromatography [5], ion-exclusion/cation exchange chromatography with dual detection [6], and capillary electrophoresis [7] were reported for determination of phosphate and silicate in environmental water and wastewater samples.

Generally, yellow β -molybdophosphoric and β -molybdosilicic heteropolyacids – the products of reactions of the analytes with

molybdate in acidic medium (pH 1–2) – constitute the basis for the spectrophotometric determination of both phosphate and silicate ions. The other method, used more frequently because of its better sensitivity, is based on detection of products of Mo(VI) to Mo(V) reduction, to form phosphomolybdenum or silicomolybdenum blue [8]. Examples of employing of vanadomolybdophosphate complex for phosphate determination can be also found [9].

Several concepts of implementation of flow techniques to simultaneous spectrophotometric determination of phosphate and silicate on the basis of molybdenum blue and vanadomolybdophosphate complex formation have been proposed since 2000 [9–13]. Among them, stopped-flow sequential injection [9] and sequential injection [10] analysis, cyclic injection [12], stopped-flow injection [13], and flow injection with solvent extraction [11] analysis are reported.

In general, as the chemistry of the developed methods is similar, the approaches employ different sequences of reagent addition [10,11], rely on different rates of reaction [9,11,13] and/or various instrumental approaches [9–13] to eliminate mutual interference during phosphate and silicate determination. In [14] application of flow techniques to determination of different ionic species in various water samples has been reviewed.

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Concerning the approaches based on molybdenum yellow method, a FIA system developed to simultaneous on-line determination of phosphate and silicate was reported [15]. In this method, total concentration of both analytes was determined when an injected plug of sample was passing through the first flow cell and subsequently the concentration of silicate was determined at a second flow cell of the same detector after continuously masking the molybdophosphoric acid in the sample zone. The concentration of phosphate was determined by difference. The analysis was performed at $\lambda=405$ nm, at temperature 50°C.

The developed approaches were applied to determination of phosphate and silicate in water [11–13], boiler water at power plants [15] and wastewater [9] samples as well as in environmental (sediment) samples, and in cell cultivation medium [10].

The present paper describes a quite different approach to the simultaneous determination of phosphate and silicate. It is based on an original way of performing two-component FIA analysis, developed for simultaneous flow injection spectrophotometric determination of Fe(II) and Fe(III) [16–18]. In this paper, a simple approach to simultaneous spectrophotometric determination of phosphate and silicate, based on measurements of parameters of a single peak and two-component calibration, is presented. A two-stream flow injection system was developed for the method implementation and the absorbance measured for the mixture of molybdophosphoric and molybdosilicic acids was applied to broaden the calibration range for phosphate determination. As it was observed that the presence of silicate influenced the analytical signal of phosphate, the calibration model based on preparation of four two-component standard solutions of analyte concentrations corresponding to a 2² factorial design was used. The approach was verified using synthetic and certified reference material samples of groundwater, wastewater, and river water.

2. Experimental

2.1. Reagents and solutions

A stock standard solution of phosphate (PO_4^{3-} , 1000 mg L⁻¹) was prepared by dissolving 0.72 g of KH_2PO_4 (POCh S.A., Poland) in water and making the solution up to 500.0 mL. Working standard solution of phosphate (100 mg L⁻¹) was prepared by appropriate dilution of the stock standard solution with water. A stock standard solution of silicate (SiO_3^{2-} , 100 mg L⁻¹) was prepared by dissolving 0.28 g of $\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$ (POCh S.A., Poland) in water and making it up to 1000.0 mL. Ammonium molybdate solution (8%, w/v) was prepared by dissolving 20.0 g of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ (POCh S.A., Poland) in about 150 mL water, adding 9 mL of sulfuric acid (2.0 mol L⁻¹) and making the solution up with water to 250 mL [15]. Oxalic acid solution (8% w/v) was prepared by dissolving 20 g $\text{C}_2\text{H}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ (POCh S.A., Poland) in water, adding 5 mL of sulfuric (2.0 mol L⁻¹) and making the solution up to 250 mL with water [15]. Solutions of sulfuric (0.5 and 0.7 and 2.0 mol L⁻¹) and hydrochloric (10%, v/v) acids were prepared by appropriate dilution of concentrated sulfuric (H_2SO_4 , 98%; Merck, Germany) and hydrochloric (HCl, 35–38%; Chempur, Poland) acids with water.

Analytical reagent grade chemicals and deionized water were used throughout. Solutions were prepared and stored in polyethylene flasks and containers. Flask, containers and glassware necessary for analysis were filled with HCl solution (10%, v/v), left for 48 h and washed with water. Between analyses the system was washed using sulfuric acid (0.5 mol L⁻¹) and subsequently with water.

Certified reference materials of groundwater (EnviroMAT Ground Water, High, ES-H-2, SCP Science, Canada), wastewater

(EnviroMAT Waste Water High, EU-H-3, SCP Science, Canada) and natural river water ION-96.3, Environment, Canada) were used for the method verification.

2.2. Instrumentation

The flow injection system developed for the research is presented in Fig. 1. It consists of a multichannel peristaltic pump (Gilson, France) equipped with Tygon pump tubes, a two-positional eight-channel injection valve (Perkin Elmer, USA), a glass mixing chamber of capacity 800 μL (made in our laboratory) with a magnetic stirring bar, and an MR 1000 magnetic stirrer (Heidolph, Germany). PTFE tubing (ID: 0.8 mm) was used as tubes and loops. The signals were measured with the use of a model SPEKOL 11 UV/Vis spectrometer (C. Zeiss, Germany) equipped with a flow cell of length 10 mm (Zhaofa, China). The measurements were performed in the transmittance mode. The operation of the pump and valve was controlled by an electronic control device (made in our laboratory). The dedicated software (developed in our laboratory) served for data acquisition, real-time signal visualization and peak parameters measuring.

3. Results and discussion

3.1. Method

The method is based on the reaction of molybdate with phosphate and silicate ions in an acid environment of pH 1–2. In the proposed approach, a stream of sample containing both analytes is merged with a stream of ammonium molybdate to form molybdophosphoric and molybdosilicic acids (see Fig. 1). Total absorbance of the compounds is registered in a form of a steady-state signal (A_1 , in Fig. 2) and measurements are performed at wavelength $\lambda=385$ nm, at which radiation is absorbed by both compounds. Simultaneously, oxalic acid solution is injected into a carrier stream (H_2SO_4) and then merged with the stream of sample containing the formed heteropolyacids. A characteristic peak is registered as a result of selective decomposition of molybdophosphoric acid by oxalic acid. The area (or the absorbance A_1 measured at the steady-state signal) and the absorbance measured at the minimum of the peak (A_2 in Fig. 2) were selected as the measures corresponding to the phosphate and silicate concentrations, respectively.

3.2. Preliminary studies

Preliminary studies were focused on searching for appropriate experimental conditions. Sample flow rate as well as ammonium

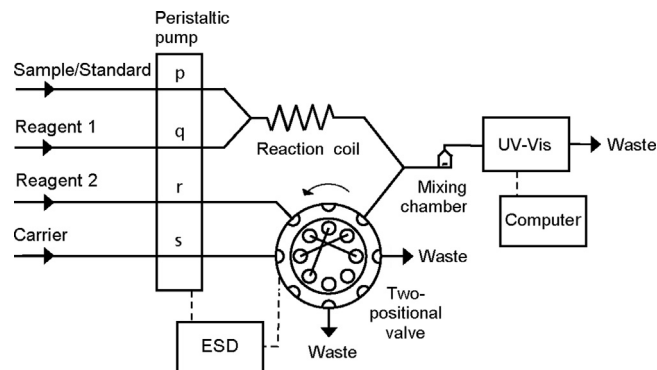


Fig. 1. Flow injection system dedicated to the developed method; p, q, r, s – flow rates ($p=0.5$ mL min⁻¹, $q=3.3$ mL min⁻¹, $r=2.3$ mL min⁻¹, $s=0.5$ mL min⁻¹); ESD – electronic steering device.

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