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Simultaneous spectrophotometric flow injection determination of phosphate and silicate

J. Kozak*, K. Latocha, J. Kochana, M. Wieczorek, P. Kościelniak

Department of Analytical Chemistry, Faculty of Chemistry, Jagiellonian University in Krakow, Ingardena 3, 30-060 Krakow, Poland

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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 $1 < \mathrm{pH} < 2$) 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.

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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* Corresponding author. Tel.: +48 126632045.
E-mail address: j.kozak@uj.edu.pl (J. Kozak).

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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 2^2 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 $Na_2SiO_3 \cdot 5H_2O$ (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 $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ (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 $C_2H_2O_4 \cdot 2H_2O$ (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

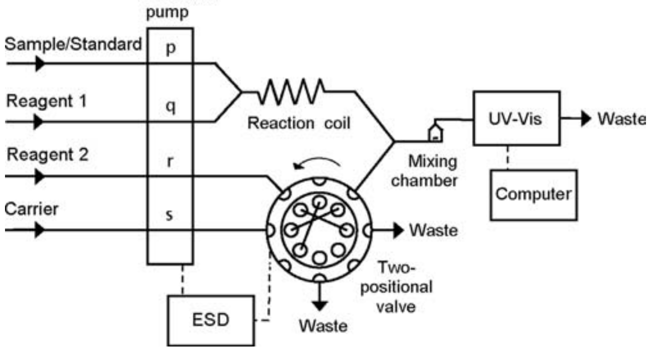

Fig. 1. Flow injection system dedicated to the developed method; *p*, *q*, *r*, *s* – flow rates ($p=0.5$ mL min^{-1}, $q=3.3$ mL min^{-1}, $r=2.3$ mL min^{-1}, $s=0.5$ mL min^{-1}); ESD – electronic steering device.

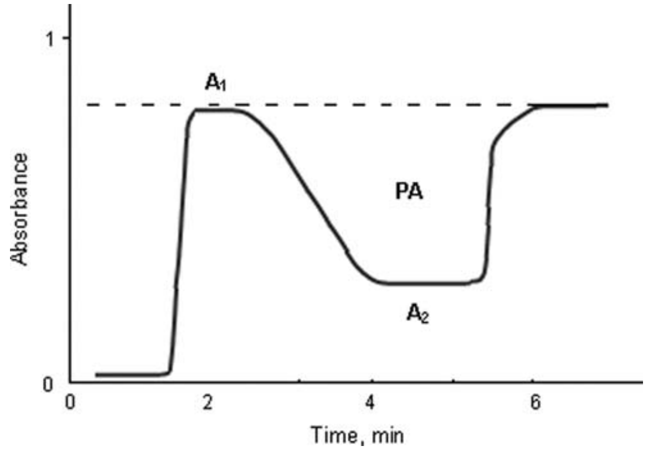

Fig. 2. An example of a peak registered in the system after injection of oxalic acid into a stream containing molybdophosphoric and molybdosilicic acids; peak area (PA) or signal A_1 can be the measure of phosphate concentration, signal A_2 measured at the peak minimum corresponds to silicate concentration.

Table 1
Parameters of the applied instrumental system.

Parameter	Value
Sample/Standard flow rate, mL min^{-1}	3.3
Carrier (H_2SO_4) flow rate, mL min^{-1}	0.5
Reagent 1 (Ammonium molybdate) flow rate, mL min^{-1}	0.5
Reagent 2 (Oxalic acid) flow rate, mL min^{-1}	2.3
Length of reaction coil (ID: 0.8 mm), m	1.2
Volume of injection loop, mL	0.5
Volume of mixing chamber, mL	0.8
Time of peak registration, min	3
Wavelength, nm	385

molybdate and carrier (H_2SO_4, 0.7 mol L^{-1}) flow rates and concentrations were selected in order not to dilute the sample too much and to obtain conditions (pH, reagent concentration) necessary for the reaction completion.

Volumes of injection loop (for oxalic acid) and mixing chamber were chosen in order to obtain peak with characteristic plateau A_2 (corresponding to the signal of molybdosilicic acid, Fig. 2) in relatively wide analytical range and to receive time of analysis as short as possible.

In order to select the volume of the injection loop for oxalic acid, two loops of volumes 300 and 500 μL were tested. Regarding the loop of volume 300 μL, it appeared that the injected amount of oxalic acid was not sufficient (in case of phosphate concentration in sample higher than 1.00 mg L^{-1}) to react with phosphate and, simultaneously, to reach a steady-state signal A_2 necessary for silicate determination. In the latter case (loop of capacity 500 μL), the amount of oxalic acid appeared sufficient to reach the steady-state signal in the studied concentration range of phosphate from 0.2 to 5.0 mg L^{-1}. Application of the loop of higher capacity lengthened the time of analysis but, on the account of oxalic acid precipitation, it was not possible to inject more concentrated oxalic acid solution, for instance, from a loop of smaller volume.

The volume of mixing chamber was selected on the basis of previous research [17,18]. Additionally, a mixing chamber of volume 1800 μL and a mixing coil of capacity 600 μL (ID 0.8 mm) were also tested. The use of the mixing chamber of volume 1800 μL did not significantly improve parameters of analytical curves obtained for the analytes, but lengthen the time of a single peak registration to about 4.5 min. On the other hand, the greater influence of phosphate (0.2–5.0 mg L^{-1}) on silicate determination (0.2–5.0 mg L^{-1}) was observed in case of using the mixing coil of capacity 600 μL than the mixing chamber of capacity 800 μL.

Length of reaction coil (see Fig. 1) was selected in order to allow the reactions between molybdate and phosphate as well as molybdate and silicate ions to go to completion. To this end, four reaction coils of length 0.6, 0.9, 1.2 and 1.8 m (in experimental conditions presented in Table 1) were tested. As a result of not sufficient time for the reaction between molybdate and silicate completion, randomly changing signals were registered for silicate (A_2), for coils of length 0.6 and 0.9 m and for samples of phosphate concentration in the range from 0.5 to 20.0 mg L^{-1} containing the same concentration of silicate (10.0 mg L^{-1}). In case of the reaction coils of length 1.2 and 1.8 m, the values of signals registered for silicate were practically the same in the studied concentration range. Therefore, on the account of the shorter time of analysis, the reaction coil of the length 1.2 m was selected for the research.

As a result of the above studies, the obtained time, necessary for registration of a single peak in the developed system, is about 3 min. Parameters characterized the developed flow system are summarized in Table 1.

In the next stage, the linearity of analytical curves responsible for phosphate and silicate determination was checked. To this end, sets of solutions containing phosphate or silicate in the concentration range from 0.20 to 20.00 mg L^{-1} were prepared and the peak area (PA) or the signal at the peak minimum (see Fig. 2) were measured for phosphate or silicate, respectively, using the designed FI system. As the signals were measured in transmittance mode, the appropriate values of transmittance were converted to absorbance A_2 values. The results showed that the calibration graphs are linear in the range from 0.20 to 5.00 mg L^{-1} of phosphate ($PA=308.07C^{3-}_{PO4}+233.73$; $R^2=0.9989$) and from 0.20 to 20.00 mg L^{-1} of silicate ($A_2=0.0422C^{2-}_{SiO3}-0.015$; $R^2=0.9991$). The linear range was also checked in situation when signals for phosphate in the presence of silicate were measured, and inversely. It appeared, that for phosphate measured in the presence of silicate, a significant decrease of sensitivity was observed for concentration of phosphate higher than 2 mg L^{-1}, therefore a narrower linear range was ascertained (0.20–2.00 mg L^{-1}; $R^2=0.9972$).

The possibility of applying the absorbance value measured at the steady-state signal A_1 (see Fig. 2) to broaden the analytical range for phosphate determination was also studied. To this end, two sets of standard solutions (one without silicate and the second containing silicate) were prepared. In both cases, the linearity in the studied concentration range from 0.20–20.00 mg L^{-1} of phosphate was proved ($A_1=0.0155C^{3-}_{PO4}+0.0014$; $R^2=0.9999$ on the basis of standard solutions without silicate and $R^2=0.9996$ – in the presence of silicate). As the signals were measured in transmittance mode, the appropriate transmittance values were converted to absorbance A_1 values. The presence of phosphate in a sample did not change the linear range for silicate determination ($R^2=0.9992$). Taking the relatively high values of absorbance measured for higher concentrations of phosphate in the presence of higher concentrations of silicate into account (values close to 1), the analytical range for determination of phosphate in the presence of silicate was assumed in the range from 0.20–15.00 mg L^{-1}.

Finally, the mutual influences of both analytes on their signals were studied. For this purpose, the developed system was used to prepare a set of analytical curves on the basis of two-component standard solutions containing: (1) phosphate in the range of 0.2–2.0 mg L^{-1} and silicate in the range of 0.0–2.0 mg L^{-1}, and (2) phosphate in the range from 0.2–5.0 mg L^{-1} and silicate in the range from 0.0–5.0 mg L^{-1}. Peak area or signal A_1 were the signals corresponding to phosphate concentration in cases (1) and

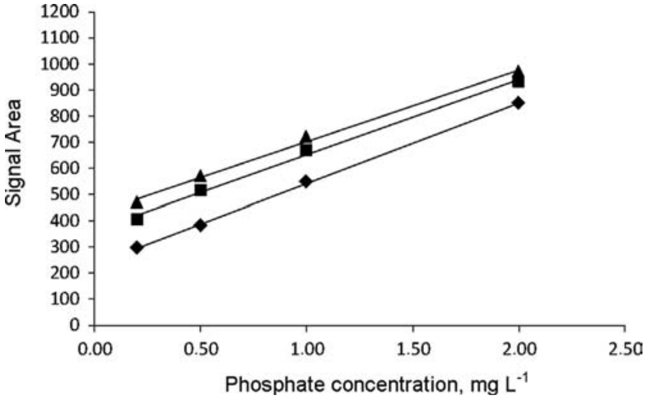

Fig. 3. Study of the influence of silicate on the signal (peak area) measured for phosphate (silicate concentration: 0.00 (◆), 1.00 (■), 2.00 (▲) mg L^{-1}).

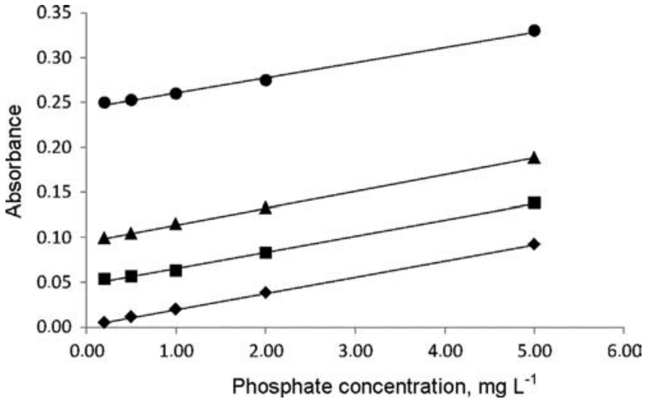

Fig. 4. Study of the influence of silicate on the signal (A_1, see Fig. 2) measured for phosphate (silicate concentration: 0.00 (◆), 1.00 (■), 2.00 (▲), and 5.00 (●) mg L^{-1}).

(2), respectively. The graphs obtained are presented in Figs. 3 and 4, respectively. Similarly, the influence of phosphate in the concentration: 0.20, 0.50, 1.00, 2.00 and 5.00 mg L^{-1} on the signals of silicate in the range of 0.0–5.0 mg L^{-1} was studied.

As seen in Figs. 3 and 4, significant influence of silicate on signals measured for phosphate (peak area and signal A_1, respectively) was observed, but the signal measured for silicate was not influenced by phosphate at the studied concentration range because a set of five analytical curves of nearly identical parameters was obtained. Therefore, to make possible simultaneous determination of both analytes, two-component calibration procedure based on four standard solutions containing the phosphate and silicate in concentrations established in accordance with 2^2 factorial design [19] was applied.

3.3. *Calibration procedure*

The linear relationships between the peak area or the absorbance A_1, and the concentration of the phosphate as well as between the absorbance A_2 and the silicate concentration have been revealed. Hence, the two-component calibration was performed as per the procedure described by Kozak et al. [17]. Appropriate systems of equations were prepared and solved in case of applying the peak area (PA) or absorbance (A_1) value as the signals corresponding to phosphate concentration and the absorbance (A_2) measured at the peak minimum as the signal responsible for silicate determination.

3.4. *Results and discussion*

The method was verified on the example of simultaneous determination of phosphate and silicate in synthetic samples and certified reference materials of groundwater, wastewater, and river water. Four standard solutions and ten samples containing phosphate and silicate in various concentrations were prepared. The concentration values were established on the levels close to the levels expected in natural samples. Peak area or absorbance A_1 were used as signals corresponding to phosphate concentration, depending on the concentration range of the analyte. Moreover, the possibility of applying standard solutions of different analyte concentrations was studied. The signals were measured two times for each standard and sample solution, and mean values were taken for calculations. The analytical results with calculated values of relative errors (RE, %) are presented in Table 2.

It is seen, that in most cases, phosphate ions were determined with relative errors not greater than 4.7% (in absolute values), and silicate generally with errors smaller than 3.9%. Greater errors of phosphate determination can be expected in case when higher concentrations of phosphate are determined in the presence of higher amount of silicate (samples No. 9 and 10). It can be also noted, that better accuracy of silicate determination was obtained when the steady-state signal (A_1) was applied for phosphate determination (instead of the peak area).

In the conditions defined above, the precision of the method was studied. For this aim five samples containing phosphate/silicate in concentrations 0.20/0.20, 0.20/5.00, 5.00/0.20, 2.00/2.00, and 5.00/5.00 mg L^{-1} were analyzed. Each analysis was performed six times. The precision found was 2.7 and 2.6% (RSD) for phosphate using peak area or the signal A_1, respectively, and 0.9% for silicate.

The limits of detection ($LOD=3.3s/a$) for each of the analytes were calculated on the basis of slope (a) of linear analytical curve and value of standard deviation (s) calculated for signals ($n=6$) measured when sample was replaced by blank solution. The obtained LOD values and the other analytical features of the method are summarized in Table 3.

The developed method was then applied to analysis of certified reference materials of groundwater, wastewater and river water samples. Samples were analyzed three times. The results of the determination and calculated values of confidence intervals are

Table 2
Results of simultaneous determination of phosphate and silicate in synthetic samples; for samples No. 1 and 2 – peak area used as the analytical signal for phosphate determination; standards composition (phosphate/silicate, mg L^{-1}): 0.50/1.00, 0.50/2.00, 2.00/1.00, 2.00/1.00; for samples No. 3-10 – absorbance A_1 (Fig. 2) used as the analytical signal for phosphate determination; standards composition (phosphate/silicate, mg L^{-1}): 0.50/0.50, 0.50/5.00, 5.00/5.00, 5.00/0.50 for samples No. 3-6, and 0.50/0.50, 0.50/10.00, 10.00/10.00, 10.0/0.50 for samples No. 7-10.

No.	Phosphate			Silicate		
	Concentration, mg L^{-1}		RE, %	Concentration, mg L^{-1}		RE, %
	Expected	Determined		Expected	Determined	
1	1.00	0.96	−3.7	1.00	0.96	6.2
2	2.00	2.02	1.2	1.00	0.96	−3.9
3	1.00	0.98	−1.9	1.00	0.97	−3.1
4	1.00	1.03	2.7	2.00	2.05	2.5
5	2.00	1.99	−0.7	1.00	1.01	1.4
6	2.00	1.98	−0.9	2.00	2.07	3.4
7	1.00	1.00	0.4	1.00	1.00	0.4
8	2.00	2.09	4.7	2.00	2.04	1.7
9	5.00	5.31	6.2	5.00	5.01	0.1
10	7.00	7.43	6.2	7.00	6.93	−1.0

Table 3
Analytical features of the developed method.

Parameter	Phosphate*	Phosphate**	Silicate
Analytical range, mg L^{-1}	0.20–15.00	0.20–2.00	0.20–20.00
Limit of detection, mg L^{-1}	0.054	0.040	0.092
Precision (RSD), %	2.6	2.7	0.9
Accuracy (|RE|), %	6.2	4.7	6.2

* Absorbance A1 (Fig. 2) applied as the analytical signal for phosphate determination.

** Peak area used as the analytical signal for phosphate determination.

Table 4
Results of determination of analytes in certified reference materials of groundwater (1), waste water (2) and river water (3); (a) – concentration added, (c) – concentration certified; CI – confidence interval, $\alpha = 0.05$.

No.	P		Si	
	Concentration ± CI, mg/L		Concentration ± CI, mg/L	
	Expected	Determined	Expected	Determined
1	$0.22^{(c)} \pm 0.03$	0.24 ± 0.01	$0.37^{(a)}$	0.37 ± 0.02
2	$0.86^{(c)} \pm 0.15$	0.84 ± 0.02	$1.48^{(a)}$	1.37 ± 0.02
3	$0.16^{(a)}$	0.15 ± 0.02	$1.16^{(c)} \pm 0.02$	1.12 ± 0.02

presented in Table 4. Silicate was added to samples No. 1 and 2, and phosphate to sample No. 3. It can be assumed, that the results are consistent with the certified and the expected (added) values of concentration. The results revealed that, the developed method can be applied to simultaneous determination of phosphate and silicate in various kind of water samples.

The influence of possible interferents, such as Ca^{2+}, Mg^{2+}, Fe^{3+}, Cl^{-}, bicarbonate and sulfate ions, can be also assessed on the basis of analysis of the certified materials of groundwater, river water and wastewater. It has been proved, that Ca^{2+} ions do not influence the results of phosphate and silicate determination to the concentration of 90 mg L^{-1}, Mg^{2+} to 20 mg L^{-1}, Fe^{3+} to 2 mg L^{-1}, Cl^{-} to 100 mg L^{-1}, sulfate to 110 mg $L^{-1}$and bicarbonate to 45 mg L^{-1}.

4. Conclusions

An approach to flow injection spectrophotometric, simultaneous determination of phosphate and silicate in water and wastewater samples has been presented. The approach constitutes an adaptation of the two-component method based on measuring parameters of a single peak (peak area and the signal measured at the peak minimum) registered in a flow injection system. The possibilities of the method have been enhanced by employing the signal corresponding to the sum of absorbance measured for the two formed heteropolyacids to two-component calibration based on four standard solutions containing the phosphate and silicate in concentrations established in accordance with 2^2 factorial design. This approach was used to broaden the analytical range of phosphate determination. For the method implementation a simple and easy operated flow injection system was developed.

From the analytical point of view, the developed method allows results to be obtained with acceptable accuracy and good precision, close to precision of other reported methods based on spectrophotometric detection [9–13,15]. The approach is performed in the room temperature and is characterized by relatively wide analytical ranges for both analytes and limits of detection comparable with limits obtained for the other reported method based on the same chemistry [15]. Regarding the time of analysis, registration of a single peak in the developed system takes up about three minutes, but to determine two analytes it is not necessary to obtain two peaks separately (like in many other flow injection methods) because parameters of the peak are sufficient for both analytes determination. The developed approach has the potential to be applied to routine analyses of water and wastewater samples.

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