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Determination of soluble phosphates in water samples using ytterbium(III) and dynamic measurements of light scattering intensity at long wavelength

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Abstract

A selective and fast method has been developed for the determination of phosphates by measuring the formation of ytterbium(III) phosphate through the variation of the light scattering intensity with time. The low solubility of this compound causes an efficient dispersion of the radiation at 490 nm, which is measured at 980 nm using the second-order grating effect. This approach minimizes potential background signals from the sample matrix. The initial rate of the system is automatically obtained in only 0.5 s by stopped-flow mixing technique. The variable optimization study has been carried out using univariate and multivariate methods. The dynamic range of the calibration graph is 0.09–7.9 mmol L^{-1} (Pearson's correlation coefficient = 0.9999) and the detection limit is 0.03 mmol L^{-1}. The precision of the method, expressed as relative standard deviation, is 2.3%. The study of the potential interference of different inorganic anions showed that arsenate is the main interferent, although it is tolerated in a molar ratio of 5.5. The method has been satisfactorily applied to the determination of soluble phosphates in tap, ground and river water using a previous preconcentration step with a Dowex 1 (1 × 4–400) anionic resin. A 500-fold concentration has been achieved, which has allowed to decrease the detection limit up to 60 mmol L^{-1}. The recovery range is 97.5–102.5%. The results obtained are consistent with those obtained with the standard molybdenum blue method.

Keywords: Phosphates; Ytterbium(III); Light scattering; Stopped-flow; Water analysis

1. Introduction

The concentration of phosphates in water is an important quality factor of water as they are essential nutrients for aquatic life. Clean natural water should have less than 0.1 mg L^{-1} (1.05 μmol L^{-1}) of phosphates [1]. A higher concentration can lead to eutrophication, a condition of excessive algal growth, which can be harmful to the environment because it reduces the amount of free oxygen in the water. The main sources of phosphates present in waters are municipal wastewaters and agriculture, since phosphates can be present in detergents and fertilizers. A number of countries have been successful in reducing eutrophication through implementation of measures to reduce phosphate loads. On the other hand, phosphates are used in the potable water treatment to perform several functions such as iron and manganese control, scale inhibition and removal, corrosion control and chlorine stabilization.

Most methods for phosphate determination in water are based on the formation of phosphomolybdate and its reduction to molybdenum blue, which has been widely used in several automated flow injection systems [2–6]. Some modifications of this classical photometric approach involve the formation of an ion pair between phosphomolybdate and a cationic dye, such as Rhodamine B [7] or Malachite Green [8], or the addition of antimony to form phosphoantimonylmolybdenum blue, which has been used to develop a spot test for phosphate based on the formation of a colored band in an adsorption column [9]. Analytical features and applications of flow methods for phosphorus determination have been recently reviewed [10–12].

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The method described here reports a new and relatively simple alternative approach that involves the measurement of the initial rate of ytterbium(III) phosphate formation, by monitoring the variation of light scattering intensity with time. The solubilities of lanthanide phosphates are so low that their solubility and activity products essentially have the same value, the ytterbium(III) phosphate being one of the most insoluble of these phosphates, with a pK of 26.17 [13].

Ytterbium(III) has been scarcely described as analytical reagent, unlike other lanthanide ions such as europium(III) and terbium(III), which have been widely used in numerous luminescent methods [14,15]. Although several luminescent ytterbium(III) chelates have been reported, their luminescence in solution is easily quenched by dissolved oxygen or –OH oscillator vibrations [16,17]. Recently, a kinetic method for sulfite determination in wine samples has been described, which is based on the formation of the ytterbium(III)-sulfite precipitate and the measurement of the variation of light scattering intensity with time [18]. Phosphate ions were the main interference of this method, as they contributed to the scattering phenomenon in the same way as sulfite ions did. However, this interference was avoided by preparing a calibration graph with two series of standards and treating one of them with hydrogen peroxide to transform sulfite into sulfate, so that the initial rates obtained for these standards were taken as the blank signals as sulfate did not interfere up to a concentration 20 times higher than that of sulfite. The behavior of phosphate ions in this sulfite method has been taken as the starting point to develop a selective kinetic method for the determination of these species, as the interference of sulfite can be avoided by treating previously the sample with hydrogen peroxide. Univariate and multivariate methods have been used to carry out the optimization of the chemical system. The application of a composite central design (CCD) to perform the multivariate optimization of the ytterbium(III) concentration and the sample pH, which are two critical variables of the system, showed that both variables are independent. The results provided by this method have been compared to those by univariate method, which assumes the independence of variables as an initial premise. The detection limit of the method has been improved using a preconcentration step with an anionic exchange resin.

2. Experimental

2.1. Materials

All chemicals used were of analytical reagent grade and ultrapure MilliQ water (Millipore, USA) was used throughout. A 0.02 mol L^{-1} ytterbium(III) solution was made by dissolving an appropriate amount of ytterbium(III) nitrate pentahydrate (Sigma–Aldrich, Schnelldorf, Germany) in water. A 0.01 mol L^{-1} solution of di-sodium hydrogen phosphate anhydrous (Merck, Darmstadt, Germany) was prepared in water and stored at room temperature. A sodium hydroxide (Merck) solution (1 mol L^{-1}) was used to adjust the pH. A Dowex 1 (1 × 4–400) strongly basic anion exchanger (Sigma–Aldrich) was used for the preconcentration step.

2.2. Apparatus

An SLM Aminco (Urbana, IL) AB2 luminescence spectrometer equipped with a 150 W xenon lamp was used. A 9050 visible and NIR monochromator and an R636-10 Hamamatsu red-sensitive photomultiplier tube, both supplied by ScienceTech (London, Ont., Canada), were fitted to the T-format configuration of the instrument to obtain long-wavelength measurements. The instrument was also furnished with a stopped-flow module [19]. The observation cell of the module has a path length of 1 cm, and the excitation and emission slits were adjusted to provide 4 and 16 nm band-pass, respectively. Initial rate measurements were obtained at room temperature. A 24-port Visi-Prep vacuum device from Supelco (Bellefonte, PA, USA) was used for the ion exchange step.

2.3. Procedure

One of the two 2-mL drive syringes of the stopped-flow module was filled with an aqueous solution containing ytterbium(III) (0.02 mol L^{-1}, pH 6.7). The other syringe was filled with standard or water solution containing from 0.09 to 7.9 mmol L^{-1} phosphate at pH 9.0. A volume of 0.15 mL of each solution was mixed in the mixing chamber in each run, and the variation of the light scattering signal throughout the reaction was monitored at λ_{ex} 490 and λ_{em} 980 nm for 2 s. Kinetic data were obtained by applying the initial rate method to the values acquired from the detector, which were processed by the computer, furnished with a linear regression program for application of this kinetic method. The initial rate was measured in only 0.5 s, and each standard or sample was assayed in triplicate. The blank signal was subtracted from each measurement.

2.4. Analysis of water samples

The pH of the water sample (1 L) was adjusted to 7.30 with 1 mol L^{-1} sodium hydroxide, and it was passed through a microcolumn packed with 0.5 g of a strongly basic anion-exchange resin (Dowex 1, 1 × 4–400), previously conditioned with 5 mL of NaCl (0.1 mol L^{-1}) and 5 mL of distilled water. After sample application, phosphate was eluted with 1.5 mL of 0.1 mol L^{-1} HCl. The pH of this solution was adjusted to 9.0 with sodium hydroxide and the solution was diluted to a final volume of 2 mL. This solution was treated as described above for phosphate determination.

3. Results and discussion

3.1. Study of the system

The features of ytterbium(III) phosphate have been widely described using X-ray diffraction and IR and Raman spectroscopies [20]. Also, the optical and spectroscopic properties of ytterbium(III)-doped phosphate glasses have been studied with the aim of applying these glasses as laser materials [21,22]. However, the potential use of ytterbium(III) as analytical reagent for phosphate determination has not been described up to date, although the measurement of the formation of the ytterbium(III) phosphate can be a simple and useful approach for this purpose owing to its low solubility [13].

The use of a spectrofluorimeter allows to follow the formation of this compound by measuring the variation of the light scattering intensity with time and using the initial rate of this reaction as the analytical parameter. As the reaction is very fast, the mixture of the reactants has been automatically performed using stopped-flow mixing technique, which allows the measurement of high initial rate values. Each kinetic measurement is carried out in only 0.5 s. The optimum excitation (λ_{ex}) and emission (λ_{em}) wavelengths of the instrument were selected by obtaining a synchronous spectrum with $\lambda_{ex} = \lambda_{em}$. The highest light scattering intensity and initial rate were obtained at 490 nm. The measurement of the analytical signal at this wavelength could be interfered by the presence of fluorescent species that absorb or emit at a wavelength close to 490 nm. However, this effect can be minimized using the second-order grating effect, in which the emission wavelength is changed at 980 nm [18]. The spectrofluorimeter was furnished with a near infrared emission monochromator and a sensitive detector to obtain dispersion signals at long wavelength.

The study of the effect of several organic solvents on the chemical system showed that all of them caused a decrease in the initial rate. The initial rate obtained in the presence of 0.67% ethanol, acetonitrile, acetone or methanol was 88.8, 85.1, 79.5 and 51.1%, respectively, of the initial rate obtained in water. Other species such as α-cyclodextrin and polyvinyl alcohol also have a negative effect on the initial rate (62.6 and 61.3%, respectively, of the value obtained in water), while the presence of gelatin prevented the formation of the precipitate. Also, the surfactants cetyltrimethylammonium bromide, sodium dodecyl sulfate and Triton X-100 were assayed at concentrations below and above their critical micellar concentration, but the initial rate of the system did not improve in any case the value obtained in the aqueous medium alone.

3.2. Optimization of variables

The variables affecting the system were optimized using univariate and multivariate methods, with the aim of comparing the values obtained in both instances. All reported concentrations are initial concentrations in the syringes (twice the actual concentrations in the reaction mixture at time zero after mixing) and each kinetic result is the average of three measurements. Those values yielding the minimum possible standard deviation for the initial rate, under conditions where the reaction order with respect to the species concerned was zero or near zero, were taken as optimal.

Several assays carried out on the system showed that the two main critical chemical variables are the pH in the mixing chamber and the ytterbium(III) concentration. The optimization of the pH using the univariate method was carried out by studying separately the effect of the pH of both ytterbium(III) and phosphate solutions on the initial rate of the system. Fig. 1A shows that the optimum pH range of the ytterbium(III) solution is very narrow, obtaining the best initial rate value at pH 6.7, while the optimum pH values for the phosphate solution (Fig. 1B) range from 8.9 to 10.0. Under these conditions, the pH in the mixing chamber was 6.4–6.6, which was measured in the waste. This decrease in the pH of the reaction medium could be ascribed to the hydrolysis reaction of the ytterbium(III) excess [23]. The pH of both ytterbium(III) and phosphate solutions was adjusted using hydrochloric acid and/or sodium hydroxide solutions, because the initial rate of the system decreased in the presence of several buffer solutions assayed [hexamethylenetetramine (hexamine), imidazole and ammonium acetate]. The initial rate of the system was independent of the ytterbium(III) concentration when the value of this variable was in the range 18–27 mmol L^{-1} (Fig. 2).

A central composite design (CCD) was used to apply the response surface methodology for the multivariate optimization of the system. This experimental design was chosen by assuming that only two input variables or critical factors (CF), namely

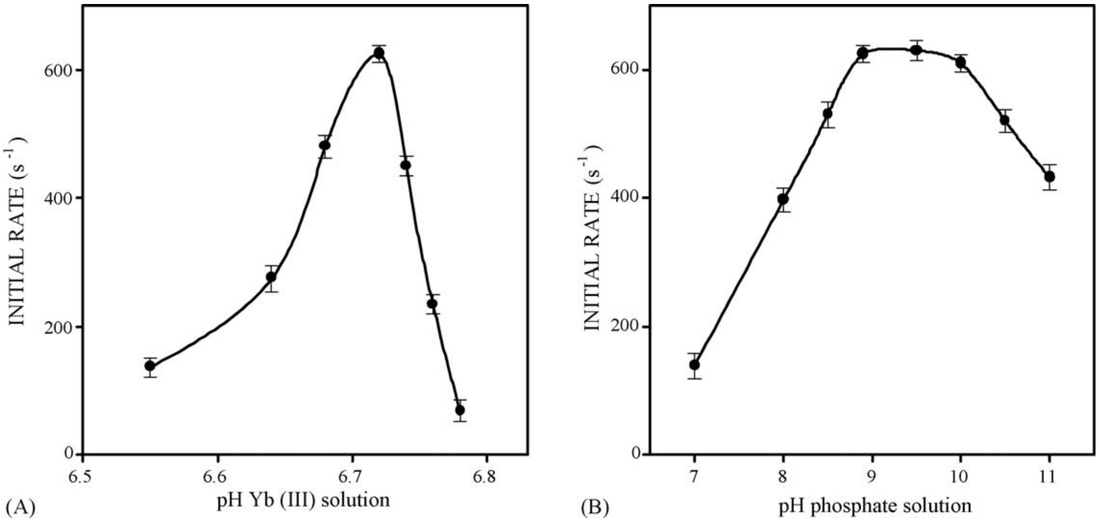

Fig. 1. Variation of the initial rate of the system with the pH of the ytterbium(III) (A) and phosphate (B) solutions. [Yb(III)] = 20 mmol L^{-1} and [phosphate] = 5.3 mmol L^{-1}.

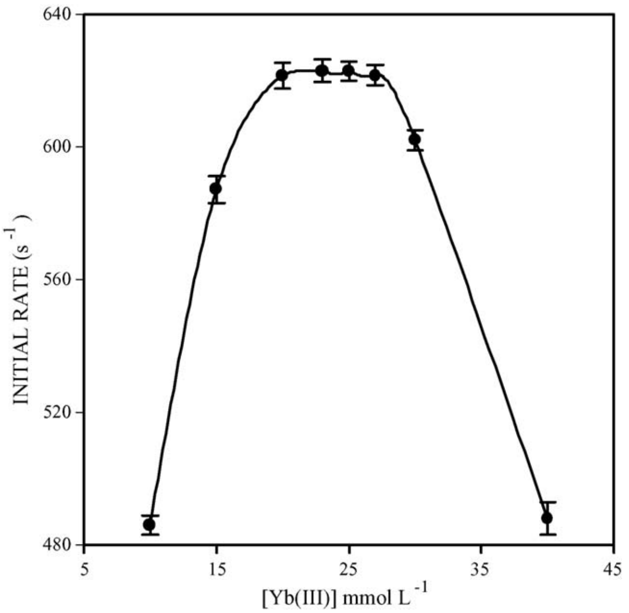

Fig. 2. Variation of the initial rate of the system with the ytterbium(III) concentration. [Phosphate] = 5.3 mmol L^{-1}.

the ytterbium(III) concentration and the pH of the phosphate solution, are considered. The CCD used was made rotatable by using an axial spacing (α) value of 1.41, as it corresponds to a 2-CF design [24]. As it is known, the rotatability of the system means that the variance of the estimated response is the same for all the points at the same radial distance from the origin. These designs protect the system from biased correlation coefficients in a more effective way than orthogonal designs do. Table 1 shows both CF in actual (Y_R and pH) and coded (X_1 and X_2) forms, respectively. The coded form of variables is defined as dimensionless with zero as mean and with the same standard deviation [25]. Coded factors were assayed in five levels, also expressed in coded form, as it can be seen in Table 1.

Three responses were measured, the pH of the blank reaction (R_1) and the pH of the sample reaction (R_2), which were measured in the waste, and the initial rate of the system (R_3), for both X_1 and X_2. The CCD was carried out by using 10 experiences (Table 2). Numbers in run column of this table are those for experiments arranged in the logical order for combinations of coded levels for each factor, while trial is the performance sequence of experiences. As it can be seen, they are randomly performed in order to avoid or minimize potential experimental errors from non-controlled sources of variability.

Table 1
Levels of factors for optimization of assay conditions according to a central composite experimental design

Factors	Symbol		Levels				
	Coded	Actual	−1.41	−1	0	1	1.41
Ytterbium concentration (mmol L^{-1})	X_1	Y_R	18.7	22.0	30.0	38.0	41.3
pH	X_2	pH	8.89	9.10	9.40	9.70	9.82

Table 2
Central composite experimental design and results obtained for R_1, R_2 and R_3

Run	Trial	X_1	X_2	R_1[a]	R_2[a]	R_3[a]
8	1	0	1.41	6.75	6.30	398.36
3	2	1	−1	6.52	6.49	354.81
10	3	0	0	6.70	6.41	575.49
1	4	−1	−1	6.68	6.43	582.83
4	5	1	1	6.58	6.46	338.02
7	6	0	−1.41	6.59	6.44	618.36
9	7	0	0	6.71	6.42	572.19
6	8	1.41	0	6.62	6.52	253.50
2	9	−1	1	6.76	6.36	486.35
5	10	−1.41	0	6.77	6.30	500.41

[a] R_1: pH of the blank reaction; R_2: pH of the sample reaction; R_3: initial rate of the system.

The response surface experiment was done by fitting the responses to both coded factors by a quadratic model using the expression:

$$\xi = b_0 + b_1X_1 + b_2X_2 + b_{11}X_1^2 + b_{22}X_2^2 + b_{12}X_1X_2 + \varepsilon,$$

where ξ is each response, X_1 and X_2 the CF, X_1X_2 the term for two-factor interactions and ε is the model error. The regression coefficients are given by b_0 (intercept), b_1 and b_2 (linear), b_{11} and b_{22} (quadratic) and b_{12} (cross product). Quadratic regression terms ($b_{11}X_1^2$ and $b_{22}X_2^2$) are indicative of the response surface curvature while the cross product regression term ($b_{12}X_1X_2$) gives the interaction degree between both CF. Table 3 shows the significant effects of both CF to each response, in which can be seen that two of the responses (R_1 and R_2) are correlated by linear effects, while the initial rate (R_3) is a quadratic function of the ytterbium(III) concentration. This variable has the most significant effect on the initial rate, which agrees with the results obtained using the univariate method. The effects have been considered significant if $p < 0.05$ (within 95% confidence interval). The empty cells in Table 3 correspond to effects with p-values higher than 0.05. As can be seen, the term X_1X_2 was found to be negligible, what means that both factors are independent, and in this instance, the results obtained by using both univariate and response surface methods will lead to similar optimum data. The values for the coefficient of multiple correlation (R^2) indicate a good fitness of the experimental data which confirms that the initial choice of both CF involved was correctly done.

Table 3
Significant effects ($p \leq 0.05$) in terms of coded factors on R_1, R_2 and R_3 obtained from the central composite experimental design

Factor	Responses		
	R_1[a]	R_2[a]	R_3[a]
X_1 (linear)	−4.52	3.68	−7.24
X_1 (quadratic)	–	–	−5.97
X_2 (linear)	2.99	−2.33	−4.23
X_2 (quadratic)	–	–	–
X_1X_2	–	–	–
R^2	0.89	0.83	0.96

[a] R_1: pH of the blank reaction; R_2: pH of the sample reaction; R_3: initial rate of the system; R^2: correlation coefficient.

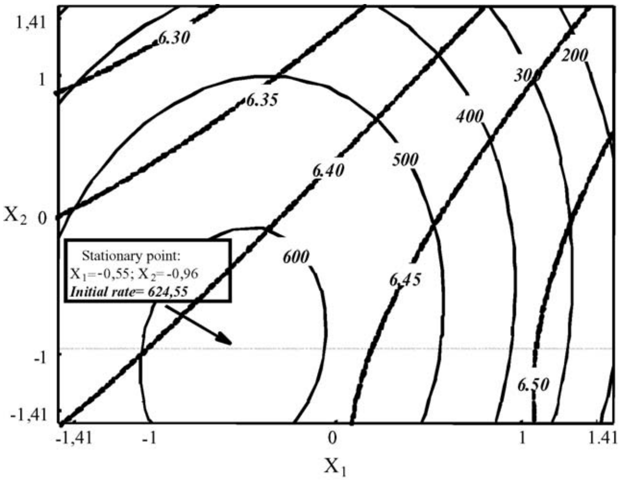

Fig. 3. Location of the stationary point by the multivariate method. X_1: levels of ytterbium(III) and X_2: levels of pH of the phosphate solution. Solid lines correspond to initial rate values (R_3) and dotted lines correspond to pH values of the reaction medium measured in the waste (R_2).

The location of the stationary point is shown in a two-dimensional plot (Fig. 3). Solid lines give the response curves for initial rate and dotted lines for the pH of the sample reaction waste. The stationary point is given by (−0.55,−0.96), which corresponds to 25.5 mmol L^{-1} ytterbium(III) and 9.11 for the pH of the phosphate solution. An increase in the ytterbium(III) concentration from the optimum value causes a notable decrease in the initial rate of the system. The pH of the sample reaction waste can act as a control response, since the stationary point is located between the curves corresponding to 6.40 and 6.45. Thus, a rapid pH measurement would afford the detection of any error that could deviate the system from its optimum working conditions. The results obtained from the two optimization methods show that they reach similar results for the two variables studied and that they are independent variables.

3.3. Features of the method

The kinetic curves obtained under optimum conditions and using λ_{ex} 490 nm and λ_{em} 980 nm for different phosphate concentrations were processed by monitoring the variation of light scattering intensity with time and measuring the initial rate of the system, which was obtained in 0.5 s. The analytical parameter used to obtain the calibration graph was the difference between the initial rate obtained in the presence and in the absence of phosphate. The dynamic range of the calibration graph was 0.09–7.9 mmol L^{-1}. The regression equation obtained was $v = -(8 \pm 10) + (120.3 \pm 0.7)C$, in which v is the initial rate, expressed in s^{-1}, and C is the phosphate concentration expressed in mmol L^{-1}. The Pearson's correlation coefficient (r) was 0.9999, which suggests a good linearity of the regression. The detection limit calculated according to IUPAC recommendations [26] was 0.03 mmol L^{-1}.

The precision of the method, expressed as the percentage of the relative standard deviation, was evaluated using standards at two different phosphate concentrations, 0.50 and 1.00 mmol L^{-1}, giving 2.3 and 0.7%, respectively. The selectivity was studied by assaying some anions that can be present in water samples, which could be considered as potential interferents. Table 4 shows the maximum tolerated interferent/analyte molar ratio. A substance was considered not to interfere if the initial rate obtained in the presence of the interferent was within one standard deviation of the signal obtained in its absence. Arsenate is the main interferent, but it is tolerated in a 5.5-fold molar excess. Although sulfite ions would interfere at the same concentration level as that of the analyte, this interference is easily avoided by treating the sample with hydrogen peroxide (0.2%) for 2 min to achieve the oxidation of sulfite to sulfate, which is tolerated up to a molar concentration 20 times higher than that of phosphate.

Table 4
Influence of anionic species over the determination of 0.5 mmol L^{-1} phosphate

Compound	Maximum tolerated interferent/analyte molar ratio
Cl^-	300
$NO_3{}^-$	200
$NO_2{}^-$	200
F^-	50
S^{2-}	30
$SO_4{}^{2-}$	20
$SO_3{}^{2-}$	20[a]
$AsO_4{}^{3-}$	5.5

[a] After treatment with hydrogen peroxide.

3.4. Applications

The application of the proposed method to the determination of phosphate in water samples has been carried out using a preconcentration step. Several methods have been described for this purpose, which involve different approaches, such as the use of a molybdate-form anion exchange resin [27], a Zr-SP cartridge [28] and a silica-gel collector containing iron(III) [7], among others. In our case, we have obtained good results using a Dowex type I strongly basic anion-exchange resin, achieving a preconcentration factor of 500 for a sample volume of 1 L and thus, a LOD of about 60 mmol L^{-1}. This process has been carried out using a 24-port vacuum device, which allows the preparation of several samples at the same time. Also, the use of a cap at the upper side of the microcolumn with a Teflon tubing inserted in the cap provides an unattended loading of the sample to the column, with increased automation degree of the sample preparation.

The method has been applied to the analysis of three different water samples: tap, ground and river water. Each sample was treated according to the procedure described above, and the analyte concentration was calculated by interpolating on the calibration curve. The results obtained are summarized in Table 5, which also shows the values obtained using the standard molybdenum blue method. The application of the paired t-test [29] showed that there were not any significant differences in the results given by both methods. Table 5 also shows the analytical recoveries obtained by the proposed method, which were calculated by adding three different amounts of phosphates to each

Table 5
Analysis of water samples

Sample	Photometric method[a]	Proposed method[a]			
	Content (μmol L^{-1})[a]	Content (μmol L^{-1})[a]	Recovery study		
			Added (μmol L^{-1})	Found[a] (μmol L^{-1})	Recovery (%)
Tap water	0.22 ± 0.02	0.25 ± 0.06	0.4	0.39 ± 0.01	97.5
			0.6	0.60 ± 0.02	100.2
			0.8	0.79 ± 0.01	98.8
Ground water	0.42 ± 0.02	0.43 ± 0.03	0.4	0.41 ± 0.01	102.5
			0.6	0.61 ± 0.05	101.7
			0.8	0.79 ± 0.03	98.8
River water	0.41 ± 0.02	0.40 ± 0.02	0.4	0.39 ± 0.02	97.5
			0.6	0.61 ± 0.07	101.7
			0.8	0.79 ± 0.06	98.8

[a] Mean ± confidence interval (95%, $n = 5$).

sample and subtracting the results obtained from similarly prepared unspiked samples. As can be seen, the recoveries ranged from 97.5 to 102.5%.

4. Conclusions

The proposed method describes a fast and relatively simple approach for phosphate determination using ytterbium(III) as reagent and measuring the initial rate of the system by monitoring the variation of the light scattering intensity with time at a long wavelength. The use of a stopped-flow mixing technique simplifies the mixing of reagents and allows the automatic acquisition of kinetic data, obtaining each measurement in only 0.5 s. Although the detection limit of the method is relatively high, it is improved using a preconcentration step, which is usual in other methods for phosphate determination [7,27,28].

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