

Sequential injection system exploring the standard addition method for phosphate determination in high salinity samples: interstitial, transitional and coastal waters†

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A sequential injection system for phosphate determination within a wide concentration range was developed for water samples with high salinity levels. The determination is based on molybdenum blue chemistry using the standard addition quantification method. The detection system included a multi-reflective flow cell coupled to a light emitting diode, enabling the minimization of the schlieren effect. The developed system gave a LOD of 0.3 $\mu\text{mol P L}^{-1}$ and LOQ of 1.1 $\mu\text{mol P L}^{-1}$ with a sample consumption of 125 μL . A determination rate of about 30 h^{-1} was obtained, and the developed method was effectively applied to interstitial, transitional and coastal waters.

Introduction

Phosphorus is an essential macronutrient to all organisms and in natural waters it is present in its soluble form: orthophosphate (H_2PO_4^- and HPO_4^{2-}).^{1,2} Due to the low solubility of various minerals containing phosphorus, and the biological uptakes of phosphate (photosynthesis process), orthophosphates are usually present at low concentrations. In this context, fertilizers used in agriculture aim to increase orthophosphates levels, leading to an increase of the amount leaching to surface (river, estuaries and sea) and interstitial water. The excess of orthophosphates in water streams can lead to eutrophication, a massive growth of algae and plants which will deplete the dissolved oxygen and kill fishes and other aquatic life.¹

Consequently, the monitoring of phosphate levels in natural waters is an important indicator of contamination. Flow analysis techniques, namely sequential injection analysis, have been previously reported as an efficient tool for water analysis.³ Furthermore, several reviews about orthophosphates determination in waters using flow methods have been reported,^{1,4–6} and clearly indicate the importance of phosphate monitoring in water samples. Nevertheless, for the target complex water samples (with high variability in parameters, concentration levels and salinity) some alternative approaches must be developed. In fact,

samples from dynamic water systems, namely transitional, interstitial and coastal waters, present a wide range of salinity levels ranging from below 2 in transitional waters up to 35 in interstitial and coastal waters. Additionally, the determination of phosphate must be achieved, without salinity interference, to assess both low concentration values (for coastal and transitional waters) and high concentration values (for interstitial waters). In this context, the use of the standard addition method presents a valuable advantage: it maintains the level of salinity in the sample quantification. Moreover the standard addition approach avoids unnecessary reagent consumption, thus preparing the standards in deionised water.

In this work, a sequential injection (SI) method using a standard addition approach with the well-known molybdenum blue chemistry was developed for phosphate quantification in a wide concentration range. A multi-reflective cell (MRC), especially designed for minimization of the schlieren effect in high salinity samples,⁷ coupled to a light emission diode (LED) as the light source was used as the detection system. The application of this MRC–LED combination has been successfully used for the determination of phosphate in sea waters,⁸ and proved to be advantageous when compared to conventional flow cells.⁹ The developed methodology was applied to all the target high salinity water samples, coastal, transitional and interstitial, and also to some low salinity samples.

Experimental

Reagents and solutions

All solutions were prepared with analytical grade chemicals and boiled deionised water (specific conductance less than 0.1 $\mu\text{S cm}^{-1}$).

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The molybdate reagent was prepared daily by dissolving 0.32 g of ammonium heptamolybdate-tetra-hydrate ($(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$), 2.0 mg of potassium antimony(III) oxide tartrate hemihydrate ($\text{C}_4\text{H}_4\text{KO}_7\text{Sb}$) and 0.15 g of tartaric acid ($\text{C}_4\text{H}_6\text{O}_6$) in 3.9 mL of 4 mol L^{-1} sulfuric acid (H_2SO_4) and diluting to 20.0 mL with water to final concentrations of: 16 g L^{-1} $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$; 0.1 g L^{-1} $\text{C}_4\text{H}_4\text{KO}_7\text{Sb}$; 7.5 g L^{-1} $\text{C}_4\text{H}_6\text{O}_6$; and 0.78 mol L^{-1} H_2SO_4 . All reagents were obtained from Merck, Darmstadt, Germany. The 30 g L^{-1} ascorbic acid solution ($\text{C}_6\text{H}_8\text{O}_6$) was also prepared daily by dissolving 3.00 g of ascorbic acid, from Normapur (VWR, Leuven, Belgium), in 100.0 mL of water.

A phosphate stock solution (739 $\mu\text{mol L}^{-1}$) was prepared by dissolving 50 mg of the solid sodium dihydrogen phosphate monohydrate ($\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$), from Merck (Darmstadt, Germany), in 500.0 mL of water and stored in a refrigerator. Working standards in the range 14.8–73.9 $\mu\text{mol L}^{-1}$ were prepared by dilution of the phosphate stock solution.

The washing solution was prepared by dissolving 0.17 g of ammonium chloride in 0.75 mL of commercial ammonia solution ($d = 0.91$, 25%) and diluted to 20.0 mL of water. Both reagents were obtained from Merck, Darmstadt, Germany.

Sample collection and preparation

Surface water samples were collected from different aquatic systems: estuaries (transitional water) and sea waters (coastal water). Transitional and coastal waters were collected in polyethylene plastic bottles of 1 L capacity at about 20 cm depth.

The collected water samples from estuaries included not only surface water but also pore water (interstitial water). To collect interstitial water, sediment was collected from the estuary basin with a ponar sampler (a clamshell-type scoop activated by a counter-lever system) and then water from the sediment was aspirated with a plastic syringe (~ 25 mL). All the samples were introduced directly into the developed system without filtration.

Apparatus

Solutions were propelled by a Gilson Minipuls 3 (Villiers-le-Bel, France) peristaltic pump with PVC pumping tube, connected to the central channel of an eight-port electrically actuated selection valve (Valco VICI 51652-E8, Houston, USA). All tubing connecting the different components of the sequential injection system was made of Teflon from Omnifit (Cambridge, UK), with 0.8 mm id. The detection system was an especially designed multi-reflective flow cell (MRC),⁷ equipped with a red LED (λ_{max} at 660 nm) light source connected to a 12 V power supply regulated to 5 V using a multimeter. The output voltage was set to zero V while the LED was on and using deionised water. Analytical signals were recorded using a Kipp & Zonnen BD 111 (Delft, The Netherlands) chart recorder. Peak height (cm) was used for signal evaluation throughout the entire work. A personal computer (Samsung SD 700, Korea) equipped with a PCL818L interface card, running with a homemade software written in Quickbasic 4.5, controlled the selection valve position and the pump rotation sense and speed.

Sequential injection manifold and procedure

The sequential injection manifold used for the colorimetric determination of phosphate is depicted in Fig. 1.

The sequence of the steps, with the respective operation time and volume, for the standard addition determination of phosphate is shown in Table 1.

The protocol sequence initiates by sequential aspiration of the reagents, ascorbic acid and molybdate solutions, into the holding coil (steps A and B). Then, the sample is aspirated followed by the added standard solution (steps C and D). Afterwards, the plugs are propelled to the detector (step E), promoting the mixture and the absorbance signal registered.

To prevent the deposition of molybdenum blue in the reaction coil and flow cell walls, a washing solution,^{10,11} 1 mol L^{-1} $\text{NH}_4\text{Cl}/\text{NH}_3$, was aspirated and propelled to the detector at the end of the day's work.

Reference method

In order to evaluate its accuracy, results obtained with the proposed SIA system were compared with those obtained by the ascorbic acid method described in the standard methods for water and wastewater analysis (4500-P E).¹² Ammonium molybdate and potassium antimonyl tartrate react in acidic medium with orthophosphate to form a heteropoly acid—phosphomolybdic acid—that is reduced to intensely colored molybdenum blue by ascorbic acid.

Certified reference sample

To further assess accuracy, results obtained with the proposed SIA system were also compared to the certified value. The reference material, QC RW1 VKI-9-3-0702 water for nutrients from VKI, was prepared accordingly to the certificate instruction. The 50 fold dilution was made in different types of water resulting in different matrices with the certified phosphorus value.

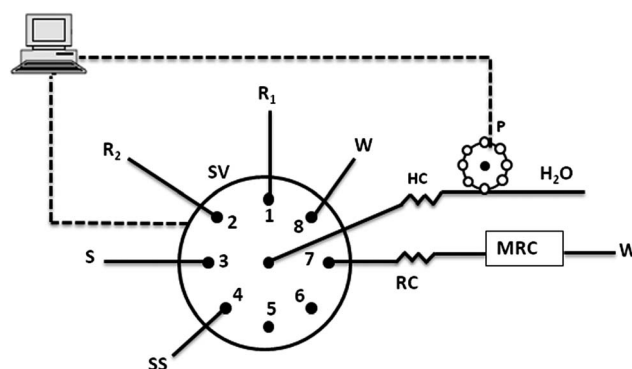


Fig. 1 Sequential injection analysis (SIA) manifold for the spectrophotometric determination of phosphate: P, peristaltic pump; SV, eight-port selection valve; HC, 4.25 m holding coil; RC, 1.82 m knitted reaction coil; S, sample; SS, standard solution; R_1 , ascorbic acid solution; R_2 , molybdate reagent; W, waste; MRC, multi-reflective flow cell coupled to a light emitting diode (660 nm).

Table 1 Sequential injection protocol for the standard addition determination of phosphate

Step	SV position	Time/s	Pump speed	Volume/ μL	Description
A	1	3	40	188	Aspiration of ascorbic acid solution
B	2	2	40	125	Aspiration of molybdate reagent
C	3	8 ^a /2.5	40	501/157 ^a	Aspiration of sample
D ^b	4	5.5	40	345	Aspiration of added standard
E	7	70	40	3760	Propel to detector ($\lambda = 660 \text{ nm}$)

^a Value for the determination without the standard addition. ^b Step absent in the determination without the standard addition.

Results and discussion

The choice of the well-known molybdenum blue chemistry for the chromogenic reaction was based on the reported high selectivity together with few possible interferences.¹³ It was an appropriate choice for highly complex water samples such as the transitional, interstitial and coastal waters. The chosen reaction being fairly slow, the length between the selection valve and the detector was set to 1.82 m. For molybdenum blue chemistry, different reducing agents can be used, and ascorbic acid was chosen due to its lower toxicity. The only significant interference reported, silicate, was minimized by adding 7.5 g L⁻¹ of tartaric acid to the molybdate reagent.⁹ This minimization is fully detailed in a previous work by Mesquita *et al.*⁹ where, for a silicate concentration of 65.7 μM , 18% interference was reduced to 2% with the 7.5 g L⁻¹ tartaric acid.

Physical parameters

Although some of the physical parameters of the phosphate determination had been previously addressed,⁹ some studies were revisited to enable the cover of a wide variation of sample characteristics and phosphate content.

Aspiration sequence and reagent volumes. According to the molybdenum blue chemistry, the intensely coloured compound results from the reduction of the phosphomolybdic acid by ascorbic acid, APHA 4500-P E.¹² The phosphomolybdic acid results from the reaction between orthophosphate and the mixture of ammonium molybdate/potassium antimonyl tartrate in acidic medium. This way, the molybdenum solution was chosen to be the middle plug.

In order to establish both the aspiration sequence and the aspiration volumes, a combined study was carried out using bromothymol blue (BTB) dye 0.03 mmol L⁻¹ in a carrier solution of 0.01 mol L⁻¹ sodium tetraborate (borax). This study was carried out using the protocol sequence (Table 1) without step D (no in-line standard addition). The idea was to simulate the overlapping of the stacked zones. Therefore, the aspiration sequence was studied introducing the BTB dye in different positions, as sample, as molybdate reagent and as ascorbic acid, and maintaining the two other plugs with borax. This way, the level of plug overlapping was assessed (Fig. 2). The two aspiration sequences tested were: sample–molybdate reagent–ascorbic acid solution and ascorbic acid solution–molybdate reagent–sample. The sample volume was studied within the range 501 to 752 μL . For the molybdate reagent, the range studied was 70.5–157 μL and the ascorbic acid volume was tested between 94 and 282 μL .

For the aspiration sequence: sample–molybdate reagent–ascorbic acid solution, the best mixture was obtained with the plug volumes 752, 157 and 219 μL so these were the chosen volumes (Fig. 2A). For the inverted aspiration sequence, ascorbic acid solution–molybdate reagent–sample, the best mixture was obtained with the volumes 188, 125 and 500 μL respectively (Fig. 2B), so those were the chosen volumes.

In the end, the BTB was replaced by the reagents of the phosphate reaction and calibration curves were made for each sequence. The sequence “ascorbic acid solution–molybdate reagent–sample” presented a better sensitivity, so it was chosen.

Sample and standard volumes—standard addition method. As previously mentioned, the standard addition method was employed to apply the phosphate determination to water samples with high salinity values since it minimizes matrix interference. To carry out the sequential injection standard addition method, the sample plug (previously set to 500 μL) was replaced by two stacked zones, sample and added standard. To establish the best ratio (sample/added standard), a study was performed using the certified reference material (QC RW 1) diluted in different water samples to a phosphorus concentration of 98.7 $\mu\text{g L}^{-1}$ and phosphate standards in the range 14.8–73.9 $\mu\text{mol L}^{-1}$. Sample/added standard volumes of 100/400, 125/375, 150/350, 200/300, 250/250, 300/200 μL were tested. The certified sample was analyzed for each ratio and the value obtained compared to the certified phosphorus concentration. The volume of 125 μL was chosen, resulting in an added standard volume of 376 μL , since a relative error of –3% was obtained. The effective overlapping of the chosen plug volumes was tested (Fig. 3) according to the procedure described for the volumes optimization in the previous section.

Reagents concentration

For the molybdate reagent, ammonium heptamolybdate-tetrahydrate and sulfuric acid concentrations were studied

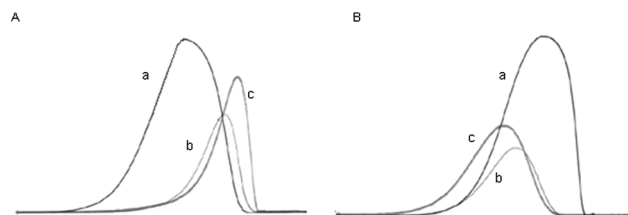


Fig. 2 Signal output for the zones overlapping study; (A) sequence: sample–molybdate reagent–ascorbic acid solution; (B) sequence: ascorbic acid solution–molybdate reagent–sample; a, BTB as sample; b, BTB as molybdate reagent; c, BTB as ascorbic acid solution.

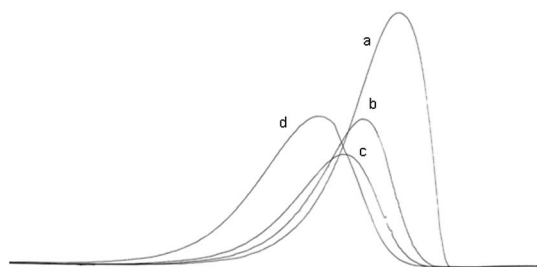


Fig. 3 Signal output for the zones overlapping in the standard addition method; aspiration sequence: ascorbic acid solution–molybdate reagent–sample–added standard; a, BTB as standard; b, BTB as sample; c, BTB as molybdate reagent; d, BTB as ascorbic acid solution.

simultaneously, keeping a ratio of 1 : 60 according to previous studies.^{14,15} The studied concentration ranges were 8–20 g L⁻¹ and 0.39–0.97 mol L⁻¹ for ammonium heptamolybdate-tetrahydrate and sulfuric acid, respectively. Since a higher sensitivity was obtained for 16 g L⁻¹ and 0.78 mol L⁻¹ of ammonium heptamolybdate-tetrahydrate and sulfuric acid, respectively, those were the concentrations chosen.

Antimony is included in the molybdate reagent due to its catalytic activity,¹⁶ resulting in an increase of the reduction rate. Potassium antimony(III) oxide tartrate hemihydrate was studied from no addition up to 1.0 g L⁻¹. From the concentrations studied, the sensitivity increased up to 0.1 g L⁻¹, so this was the value chosen (ESI Fig. S1†).

The purpose of ascorbic acid is to reduce the molybdenum yellow to molybdenum blue,¹⁶ and therefore it is important that this reagent is present in excess in order to assure the total reduction of the molybdenum yellow. So, the concentration of the ascorbic acid was studied in the range 10–35 g L⁻¹ (ESI Fig. S1†), and as the sensitivity increased up to 30 g L⁻¹ that was the chosen concentration.

Temperature

According to previous studies,¹⁶ the reduction of molybdenum yellow to the blue heteropoly compound is a rate-determining step. But this reduction can be accelerated, not only by adding the catalyst antimony, but also by increasing the temperature. So, the effect of temperature was studied, aiming for a faster reaction and a better sensitivity. Nevertheless, no significant changes were observed when the temperature was increased from room temperature (approximately 20 °C) to 30 and to 35 °C.

Salinity interference

The aim of the developed method was the application to water samples with high salinity levels. So, a study of salinity interference was a major priority. The salinity interference was assessed using a simulated sample obtained by preparing three phosphate standards with the expected salinity values for the target samples (transitional, coastal and interstitial waters) salinity 20 and 30. The salinity values were adjusted by adding sodium chloride to the standards. A standard addition curve was established for each of the simulated samples (with different salinity values) and the three resulting curves compared. The estimated slopes of the curves were assessed at the confidence

intervals at 95%. The quality of the regression was also tested by residual analysis (*i.e.* randomness and normality) and by the coefficient of determination (*i.e.* R^2 , which was above 0.897 in all cases). The estimated slopes were not statistically different, assessed by the CI95% which overlapped (Fig. 4) thus indicating that there is no interference of the salinity values in the determination.

To prove the efficiency of the standard addition procedure, a similar study was carried out using the sequence protocol without the standard addition (without step D) in order to observe the possible salinity interference in these conditions. Calibration curves using standard solutions with salinity values 0, 20 and 30, respectively, were compared; these solutions were also prepared by adding sodium chloride to the standards. The calibration curve with pure standards was compared to the calibration curve with standards with adjusted salinities and the estimated slopes of the curves were assessed at the confidence intervals at 95%. The quality of the regression was tested by residual analysis (*i.e.* randomness and normality) and by the coefficient of determination (*i.e.* R^2 , which was above 0.992 in all cases). The estimated slopes were statistically different, assessed by the confidence intervals at 95% (CI95%), which did not overlap (Fig. 4), therefore indicating that the increase of salinity interferes with the determination.

The results obtained with the salinity interference studies proved that the increase in salinity affected the slope of the calibration curve but not of the standard addition curve. However, the salinity influence in the slopes might not relate directly to the determination of phosphate in the water, namely in the standard addition method. So, simulated water samples were assessed using the standard addition method and the results were compared with a direct determination to prove the standard addition method efficiency. Three phosphate standards were prepared to simulate water samples; in two of them, salinity was adjusted to 20 and 30, respectively. The simulated samples were assessed and the interference percentage calculated (ESI Table S1†). The results showed that with the standard addition method, the presence of salinity had no significant influence on the obtained phosphate concentration, deviations <5%, unlike

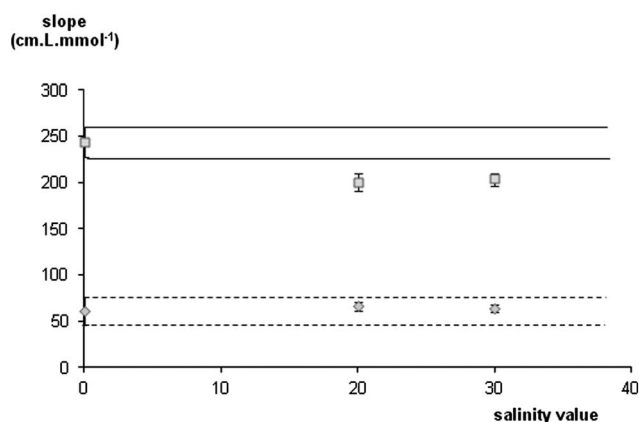


Fig. 4 Influence of salinity level in the sensitivity (three replicas): □, determination without standard addition (full lines, CI95% of the calibration curve); ◇, standard addition method (dashed lines, CI95% of the standard addition curve).

Table 2 Features of the developed SIA methodology

Dynamic range ^a / μmol L ⁻¹	Typical curve ^b	LOD/μmol L ⁻¹	LOQ/μmol L ⁻¹	Determination rate/h ⁻¹	Consumption per determination
14.8–73.9	$H^c = 0.079 (\pm 0.003)$ $C(\text{PO}_4^{3-}) + 0.18 (\pm 0.02)$	0.34	1.13	30	2.0 mg (NH ₄) ₆ Mo ₇ O ₂₄ ·4H ₂ O, 12.5 μg C ₄ H ₄ KO ₇ Sb, 0.94 mg C ₄ H ₆ O ₆ , 5.64 mg C ₆ H ₈ O ₆ , 9.59 mg H ₂ SO ₄

^a Concentration range of the added standards. ^b Values between brackets correspond to the standard deviation of the equation parameters ($n = 8$).

^c Peak height (cm).

with the direct determination method where presence of salinity caused a significant deviation, >10%.

Both interference studies proved the efficiency of the standard addition method for high salinity samples.

Features of the developed system

A summary of the main analytical features, the dynamic concentration range and typical curve, limits of detection (LOD) and quantification (LOQ), determination rate and consumption values, is shown in Table 2.

The LOD and LOQ were calculated as three and ten times, respectively, the standard deviation of the mean intercept (IUPAC recommendations¹⁷) of five standard addition plots.

The typical curve presented corresponds to the mean slope and intercept of eight curves with the respective standard deviations.

The determination rate was calculated based on the time spent per cycle. An analytical cycle is the sum of the time needed for each step plus the time necessary for the port selection in the selection valve and took about 2 min. The effluent production per determination is 3.76 mL and the sample consumption is 125 μL.

The repeatability was assessed by calculation of the relative standard deviation, RSD% (μmol PO₄³⁻ L⁻¹ ± SD). The RSD was obtained by the mean intercept of ten standard addition curves of two coastal waters: 4.73% (7.75 ± 0.37) and 4.43% (8.94 ± 0.40).

Application to water samples

To evaluate accuracy, certified reference material (QC RW 1, VKI-9-3-0702) was assessed. The certified material was prepared in transitional, interstitial and coastal waters in order to have a final phosphorus concentration of 98.7 μg P L⁻¹. The results obtained showed that there is no significant interference from the different water matrices with different salinity levels (Table 3).

To further evaluate accuracy, three water samples, two transitional and one coastal (T1, T2 and C), were assessed using the phosphate reference procedure, the ascorbic acid method¹² (RP). For the T1 sample, the phosphate concentration obtained with the RP was 456 μg P L⁻¹ and with the SI method 475 μg P L⁻¹, resulting in a relative error of 4.2%. For the T2 sample, the phosphate concentration obtained was 289 μg P L⁻¹ with the RP and 298 μg P L⁻¹ with the SI method, resulting in a relative error of 3.7%. As for the coastal water, C, the phosphate concentration obtained with the RP was 307 μg P L⁻¹ and with the SI method 312 μg P L⁻¹, resulting in a relative error of 1.6%.

The developed SIA methodology was used for the quantification of phosphate in water samples with high salinity levels, interstitial and coastal waters (ESI Table S2†).

Table 3 Application of the developed sequential injection to the phosphate determination in a certified reference material prepared in different water samples and comparison with tabulated values; RE, relative error; SD, standard deviation

Sample ID	G/mS cm ⁻¹	Salinity	Cert. value/ μg P L ⁻¹	SIA/μg P L ⁻¹ ± SD	RE (%)
<i>R_s</i>	47.1	34.3	98.7 ± 1.2	93.6 ± 2.6	-5.1
<i>R_d</i>	0.257	<2		102 ± 2	3.7
<i>R</i>	0.358	<2		98.8 ± 6.5	0.1
<i>R_{DOU}</i>	9.66	6.1		101 ± 4	2.6
<i>C_{Salg}</i>	28.1	19.4		90.6 ± 7.9	-8.2
<i>E_{Ave2}</i>	23.4	15.8		103 ± 9	4.2
<i>E_{Ave2B}</i>	30.3	21.1		106 ± 19	7.0
<i>C_{Int}</i>	44.8	32.5		90.4 ± 9.3	-8.4
<i>C_{Mat}</i>	47.1	34.8		102 ± 8	3.2

Conclusions

The developed SIA system enabled the determination of phosphate in a wide concentration range for water samples with high salinity levels, namely transitional, interstitial and coastal waters. Although aimed at high salinity water samples, the developed method proved to be also applicable to low salinity samples such as river water. This feature was necessary for the application to diverse dynamic water systems such as estuaries. All these types of samples were effectively analyzed without sample pre-treatment and the standard addition proved to efficiently avoid matrix interference. In fact, the developed methodology enabled the quantification of phosphate in: transitional waters (low salinity—low phosphate concentration); coastal waters (high salinity—low phosphate concentration) and interstitial water (high salinity—high phosphate concentration).

When compared to other flow methodologies previously described,^{9,11,14,16,18–24} (ESI Table S3†) the developed methodology has the significant advantage of enabling determinations in both fresh and high salinity waters. The standard addition method was a valuable improvement for coastal and interstitial waters. Furthermore, the detection limit obtained, 0.34 μM, is within the range of the previously reported methods, 1.4 nM–5.3 μM (ESI Table S3†).

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