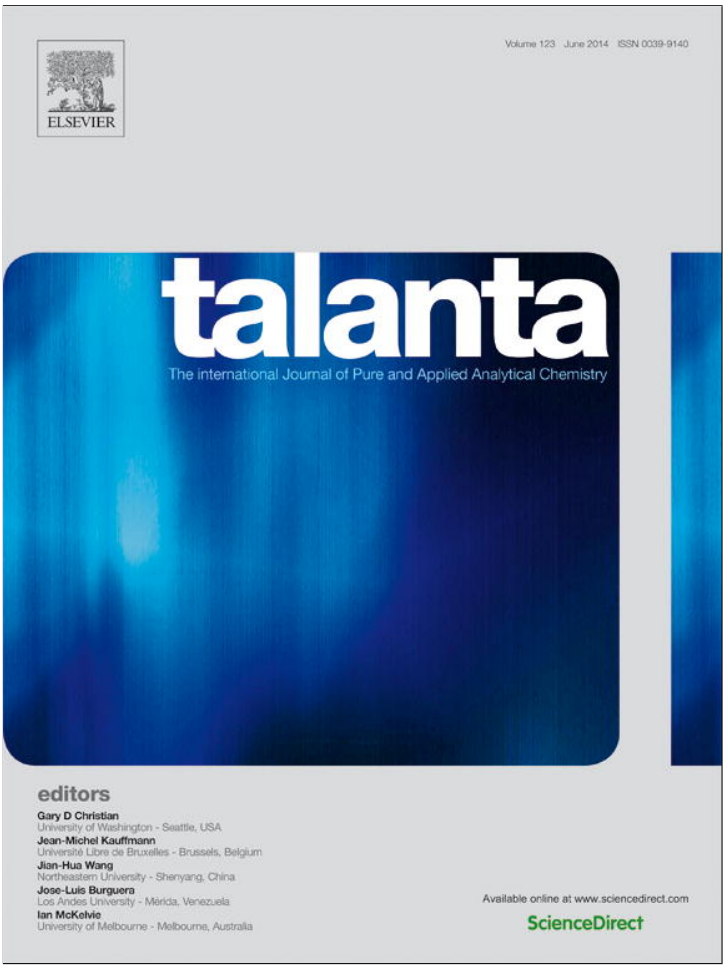

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Loop flow analysis of dissolved reactive phosphorus in aqueous samples

Jian Ma*, Quanlong Li, Dongxing Yuan

State Key Laboratory of Marine Environmental Science, College of the Environment and Ecology, Xiamen University, Xiamen 361005, Fujian, China

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ABSTRACT

The current flow based method for the determination of dissolved reactive phosphorus (DRP) suffers interference from salinity (e.g. index refractive difference) and the incidentally formed bubbles, which can be a problem for optical detection. Here we reported a simple and robust loop flow analysis (LFA) method for accurate measurement of DRP in different aqueous samples. The chemistry is based on the classic phosphomolybdenum blue (PMB) reaction and the PMB formed in a novel cross-shaped flow cell was detected at 700 nm using a miniature spectrophotometer. The effects of reagents on the kinetic formation of PMB were evaluated. The detection limit was 32 nM with an optical pathlength of 1 cm and the relative standard deviations for repetitive determinations of 1, 2 and 8 μM phosphate solutions were 1.8% ($n=113$, without any stoppage during repeating analysis for >7 h), 1.0% ($n=49$) and 0.39% ($n=9$), respectively. The analysis time was 4 min sample^{-1}. The effects of salinity and interfering ions (silicate and arsenate) were evaluated and showed no interference under the proposed protocol for DRP analysis. Using the LFA method, different aqueous samples with a salinity range of 0–34 were analyzed and the results showed excellent agreement with the reference method (slope 0.9982 ± 0.0063, $R^2=0.9987$, $n=34$). Recoveries for spiked samples varied from 95.4% to 103.7%. The proposed method showed insignificant interference from salinity, silicate and arsenate, higher reproducibility, easier operation and was free of the bubble problem.

1. Introduction

Phosphorus is an essential nutrient for living organisms in both terrestrial and aquatic environments, and its major inorganic form, orthophosphate, plays a key role in photosynthesis (i.e., primary productivity) and could be a typical limiting nutrient in the marine environment [1,2]. On the other hand, excessive loading of nutrients (e.g. phosphorus) can result in eutrophication, which is widely considered as a cause of aquatic system degradation [2]. Therefore, extensive and continuous monitoring of phosphate in aqueous samples is required in different research areas including oceanography, environmental science, and domestic/industrial wastewater treatment.

Many methods are available for phosphate analysis [3] and a special issue on the topic *Analysis of Phosphorus in Environmental and Agricultural Samples* is available in *Talanta* [1]. Among these published techniques, the modified phosphomolybdenum blue (PMB) method [4] is the most widely used technique for the determination of phosphate [5]. The PMB method is based on the reaction of phosphate and molybdate in acidic medium in the presence of antimony to form phosphomolybdenum yellow (i.e. 12-molybdophosphoric acid), which is subsequently reduced to PMB using a reducing agent (e.g. ascorbic acid) to increase the sensitivity [6]. Dissolved reactive phosphorus (DRP) is therefore operationally defined as phosphate which passes through a 0.45 μm membrane [7] and it is measured using the PMB technique, which includes orthophosphate and a small quantity of acid hydrolysable organic or condensed phosphorus compounds [8].

Due to their amenability to automation, high sample throughput, and low risk to contamination, the flow based methods were widely used for the determination of phosphate, which have been comprehensively reviewed [9–12]. Besides flow/sequential injection analysis, segmented-flow analysis (SFA) is still the mainstream for nutrient analysis in seawater. For example, among 53 laboratories from 18 countries who took part in the 2006 Inter-laboratory Comparison Study for Reference Material for Nutrients in Seawater, more than 90% of the participants used a segmented-flow analyzer [13].

The flow based methods may suffer from some problems such as refractive index (RI) changes (Schlieren effect) caused by salinity difference between samples and the washing solution/carrier leading to interference in absorbance measurements [14].

* Corresponding author. Tel.: +86 592 2186916.
E-mail address: jma@xmu.edu.cn (J. Ma).

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A reversed FIA manifold with the injection of molybdate into NaCl solution or RI-matched sulfuric acid carrier has been designed to compensate for the salinity variation [7,14], and these methods have been used for the determination of DRP in different salinity samples. Sample dilution [15] and a salinity calibration curve [6] have also been used for resolving the salinity interference problem. Recently, the matrix effects in the SFA have been re-examined and the authors find that a semi-automated procedure is needed for measuring and correcting the sample and RI blanks [13]. However, these corrections are time and labor consuming and may not be possible in shipboard laboratories. Therefore, a salinity interference free method is urgently needed in order to eliminate the Schlieren effect in the determination of DRP in estuarine and coastal waters, where the sample salinity varies.

Another challenge to optical detection in flow analysis is the incidental bubbles formed owing to the reagent mixing, pressure change or sample heating [16,17]. A planar debubbler was constructed to overcome the disruption of bubbles, but an erroneous detector response from air bubbles in the flow stream was still obtained [18]. A multi-reflection and total internal reflection photometric detection cell has been designed to avoid the Schlieren effect and gas bubble trapping problem [16,17], but it is still not easy to eliminate the bubble interference. For example, although equipped with an on-line debubbler and a total internal reflection flow cell, almost 30% of the underway data had to be discarded because of bubbles causing distortion to the collected peaks [19]. Very recently, a novel cross-shaped flow cell for total alkalinity analysis in seawater was designed [20]. The optical path is perpendicular to the flow path of the cell, which is called "cross-shaped". Therefore when the cell is positioned with the light path horizontal and flow path vertical, the bubbles in the cell float and leave the optical path free.

Loop flow analysis (LFA) has been introduced for nutrient analysis in seawater [21], and commercial instruments are available (www.systea.it). The hermetic closed loop provides full protection against background interference, but the construction of the instrument is complicated and the bubble problem still remains. Here we reported the combination of the modified LFA and cross-shaped flow cell for the determination of DRP in aqueous samples. Two main problems for flow analysis of DRP, the Schlieren effect and bubble interference, were resolved using this simple and robust LFA method. The interference of silicate and arsenate were investigated and real samples of different salinity were analyzed and compared with the results obtained with a reference method [8]. The resulting method is well suited for shipboard/underway applications in marine science and in on-line environmental monitoring applications.

2. Experimental

2.1. Reagents

All chemicals were reagent grade or better, purchased from Sinopharm Chemical Reagent Co., China and used as received. All solutions were prepared in ultrapure water (UPW) obtained from a Millipore water purification system (Millipore Co., MA, USA). A stock mixed reagent (MR) solution for color development was prepared [22], and stored at 4 °C. The working MR solution was diluted three times and prepared daily. Ascorbic acid (AA) solution of 25 g/L was prepared daily.

Phosphate stock solution (10.31 mM) was purchased from the National Research Center for Certified Reference Materials (Beijing, China). Silicate stock solution of 10 mM was prepared from Na_2SiF_6 dried at 105 °C for 1 h. Arsenate stock solution (1000 mg/L) was purchased from ChemService Co., USA. Working standards were prepared as required using suitable serial dilution.

2.2. Analytical system

The LFA system used in this study is shown in Fig. 1. The main part is an FIA 3110 flow injection analysis processor (Beijing Titan Instruments Co., Beijing, China) including two 8-roller peristaltic pumps equipped with 2.0/1.0 mm i.d. PVC tubing (Baoding Longer Precision Pump Co., China) and an 8-way rotary valve. The light source (tungsten halogen lamp LS-1-LL), two fiber-optic cables (QP600-2-SR), a miniature charge coupled device spectrophotometer (USB 2000+) and data collecting software (Spectrasuite) were purchased from Ocean Optics Inc., USA. The detection wavelength was 700 nm. The cross-shaped flow cell was made of optical glass and positioned with the light path horizontal and the flow path vertical. The detailed structure and description of the cross-shaped flow cell and data process can be found in our previous work [15,20].

The analytical program is shown in Table 1. During step 1, a new sample was introduced into the sample loop (total volume of ~3 mL) using pump 1. The fresh sample could flush out the residual of the previous sample and clean the flow cell. After 60 s, pump 1 was kept working and pump 2 was used to propel the MR and AA into the reagent loop of ~120 μL (step 2) for 30 s and the spectrophotometer was set to zero (100% transmittance). During step 3, when the valve was switched from "Inject" to "Fill" position (Fig. 1), the sample and reagent were mixed for 30 s, which gave sufficient mixing based on our preliminary experiment (data shown in Supplementary materials, Fig. S1); then in step 4, both pumps were stopped for the formation of the PMB, which was monitored using a detector for 120 s. After step 4, the program returned to step 1 and these four steps repeated, unless it was stopped manually.

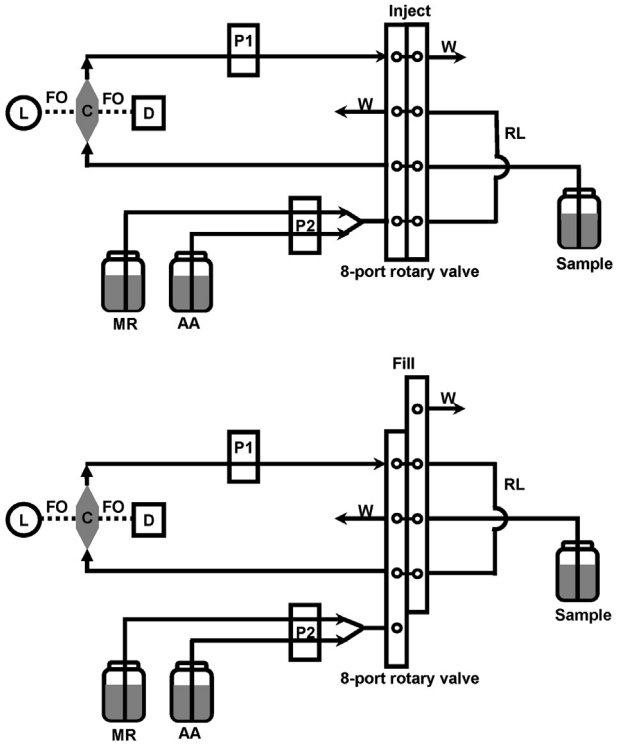

Fig. 1. Manifold of the LFA for DRP determination (L: light source; FO: fiber optics; C: cell; D: detector; P1/2: pump 1/2; W: waste; RL: reagent loop; MR: mixed reagent; and AA: ascorbic acid).

Table 1
The descriptions of the proposed loop flow analysis program.

Step	Time (s)	Pump 1 flow rate (mL/min)	Pump 2 flow rate (mL/min)	Valve position	Description
1	60	9.0	0	Inject	Adding new sample into sample loop and flushing out the residual of last sample
2	30	9.0	1.2	Inject	Continuous adding new sample into sample loop, filling the reagent loop, spectrophotometer setting zero (100% T)
3	30	9.0	0	Fill	Sample and reagent mixing
4	120	0	0	Fill	Waiting for formation of PMB, data recording

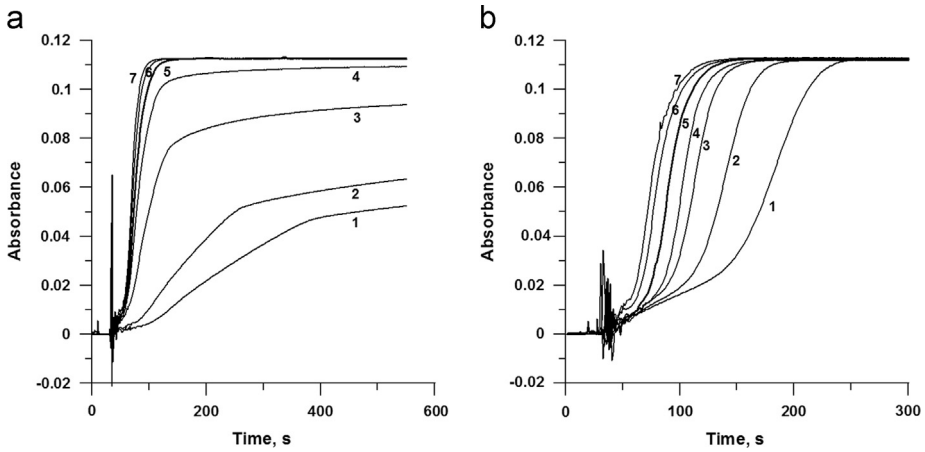

Fig. 2. The effect of (a) the MR percentage in the stock solution: 1–5%, 2–10%, 3–15%, 4–20%, 5–25%, 6–30% and 7–35% (AA kept at 25 g/L) and (b) the AA concentration: 1–5 g/L, 2–10 g/L, 3–15 g/L, 4–20 g/L, 5–25 g/L, 6–30 g/L and 7–35 g/L (MR kept at 25% dilution) on the signal of an 8 μM sample. The optimized values are shown with bold lines.

The blank and a 2 μM phosphate solution were used as data quality control samples throughout the experiments in order to check the measurement deviation and provide sound data.

2.3. Sample collection and treatment

Four river water samples were collected from the Jiulong River, Fujian, China; 17 coastal water samples were collected in Xiamen Bay, Fujian, China; and five ocean seawater samples were collected at different depths from the South China Sea. After collection, these samples were filtrated through 0.45 μm nitrocellulose membrane (Heaion Co., Tianjin, China), frozen, transported to the laboratory and analyzed within 1 week. Before analysis, the samples were completely thawed and mixed, and then 2–3 determinations were performed depending on the sample volume. The salinities of these samples were measured using a refracting salinity meter (Link Optical Instrument Co., Fuzhou, China). Five bottled mineral water samples from different vendors were purchased from local markets and kept sealed until analysis. Three reclaimed wastewater samples from different irrigation locations in Xiamen University were collected and stored in clean plastic bottles and analyzed within 1 h after filtration.

3. Results and discussion

3.1. Effect of concentration of the color developing reagents (MR and AA)

Many researchers have studied the parameters that affect the formation of PMB, which include temperature, phosphate concentration, pH and $[H^+]$:[Mo] ratio [4,5,23–25]. The $[H^+]$:[Mo] ratio is found to be a crucial parameter which not only influences the form of the final reduced complex (PMB), but also plays a key role in controlling the reaction kinetics [23]. The optimum $[H^+]$:[Mo] ratio is between 50 and 80 in order to achieve complete formation of the PMB complex while avoiding self reduction of the molybdate [4,24]. Therefore, in our work the ratio was fixed at 74 when preparing the stock MR solution. The effects of dilutions of the stock MR and AA were evaluated and are shown in Fig. 2.

The lower MR concentration gave a slow or even insufficient reaction rate, whereas when the MR concentration was higher than 25% of the stock solution, the PMB reaction could reach a maximum in <2 min (Fig. 2(a)). The final pH of the mixed sample and reagent was around 1.2, which was sensitive, there was less interference from other elements [5], and the coating of the tubing and cell with PMB could be inhibited at this pH level [18]. The effect of AA concentration on the PMB reaction was studied in the range 5–35 g/L as shown in Fig. 2(b). For a min reaction time, no significant absorbance increases were found when the AA concentration was higher than 25 g/L. These results are consistent with those of earlier studies [5,24], which show that the PMB reaction time is only 2 min at room temperature at a $[H^+]$:[Mo] ratio of 70 in the presence of Sb as catalyst. The concentrations of MR and AA used in all subsequent experiments involved a 1:3 dilution of the MR stock solution and 25 g/L based on the balance of analysis time and reagent consumption.

3.2. Effect of salinity

Two types of errors/anomalies in absorbance measurements occur because of the RI changes between sample and carrier/washing solution: one is the physical influence referred to as the Schlieren effect and the other is the chemical influence of ionic strength or solution composition variations [26]. In order to study the effect of salinity, samples containing 2 and 4 μM phosphate

were prepared in UPW and oligotrophic seawater (< 10 nM, measured with a solid phase extraction method [27]) over a range of salinities and analyzed with the LFA system. It should be noted that the spectrophotometer was set to zero only when the cell was filled with UPW matrix sample.

It was found that the baseline shifted when the sample salinity changed (raw data shown in Fig. S2). The resultant absorbance from the baseline shift (i.e. RI difference) was converted to phosphate concentrations. The measured RI of the system was directly proportional to salinity as follows (calibration curve is shown in Fig. S3):

$$[P]_{RI} = (0.0304 \pm 0.0011)S - (0.0562 \pm 0.0235) \quad (R^2 = 0.0029,\ n = 8)$$

where $[P]_{RI}$ is a correction for RI interference for the sample phosphate concentration in μM, and S is the salinity of samples. This result was consistent with an earlier evaluation of the salinity effect on DRP analysis when using a liquid waveguide capillary flow cell based continuous-flow analysis system [6].

Although the baseline shifted, the salinity had no effect on the formation of PMB as reflected by the net absorbance signal shown in Fig. 3. Following our analysis protocol, the spectrophotometer was set to zero (100% transmittance) during step 2 when the cell was filled with a fresh sample at a different salinity. Therefore, the RI difference was corrected and the proposed method could be applied to various seawater samples without salinity calibration, which meant a wider application, especially for coastal areas.

3.3. Analytical figures of merit

Using the 1:3 diluted stock MR solution and 25 g/L AA as reagent and the analytical procedure tabulated in Table 1, a calibration curve was obtained over a concentration range between 0 and 10 μM (inset of Fig. 4). The regression equation, given as Absorbance = $(0.01402 \pm 0.0008) \times C_P$ (μM) − (-0.0013 ± 0.003), with $R^2 = 0.9979$ ($n = 64$), was created on the data obtained over several days. The linear range could be increased up to 50 μM when MR and AA were applied at higher concentrations. Fig. 4 also shows the typical detector output for sample concentrations between 0 and 10 μM. The sample throughput for the optimized conditions was 15 h^{-1}, which should be fast enough for routine sample analysis and online or underway monitoring. The sample rate could be further improved using a higher reagent

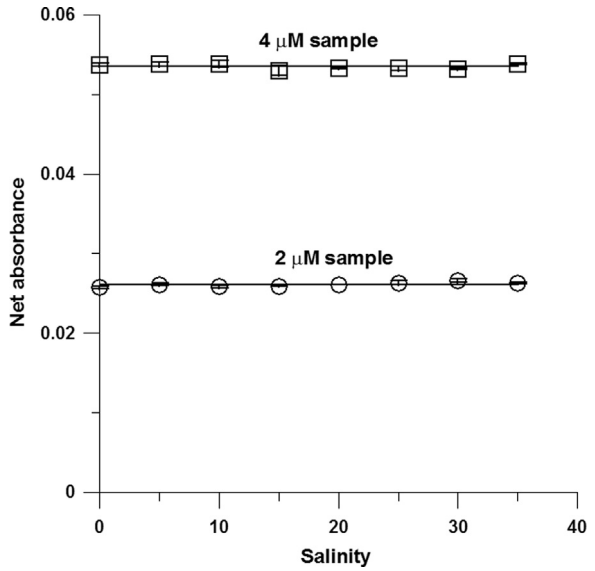

Fig. 3. The effect of salinity on the net absorbance. Results are shown as an average ± the standard deviation (SD, $n = 3$).

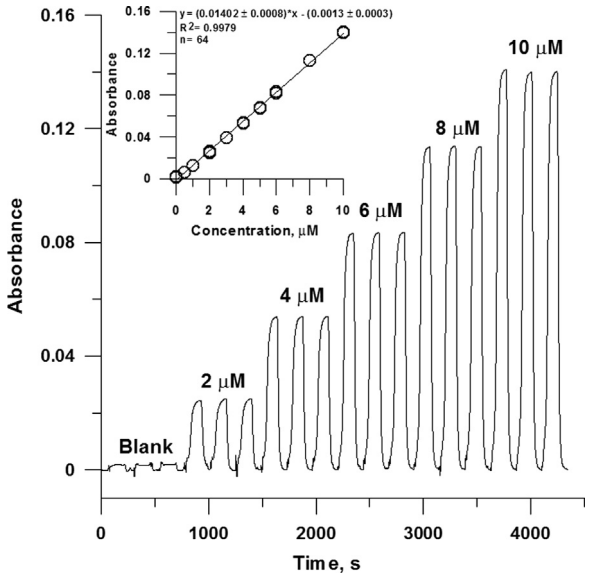

Fig. 4. Typical signal output and, inset, calibration curve with standard samples in the range 0–10 μM.

concentration as the kinetics show in Fig. 2, and at elevated temperature if needed.

The detection limit of the system, estimated as three times the standard deviation of the measured blanks ($n = 9$), was 32 nM, which was equivalent to an absorbance uncertainty of ± 0.0006. The relative standard deviations for repetitive determinations of 1, 2 and 8 μM phosphate solutions were 1.8% ($n = 113$), 1.0% ($n = 49$) and 0.39% ($n = 9$). It should be noted that the analyzer showed very repetitive and reliable results during unattended repeating analysis of low concentration samples (e.g. 1 μM) for > 7 h (the raw data was plotted as shown in Fig. S4). Two national phosphate standards (GBW08623, The Second Institute of Oceanography, SOA) were analyzed, and the detected values (1.56 ± 0.05 and 3.21 ± 0.07 μM) showed good agreement with certified values (1.60 and 3.20 μM).

Carryover effects were investigated using a modification of Zhang's scheme [28], and a 0.8 μM phosphate sample was analyzed twice, with an average observed absorbance of 0.0117 ± 0.0004. Next a 10-fold phosphate sample (8 μM) was analyzed twice and the average absorbance was 0.1172 ± 0.0003. Subsequently, the 0.8 μM phosphate sample was analyzed again, and the observed absorbance was 0.0116 ± 0.0004. The difference between the two measurements of the 0.8 μM sample was insignificant, indicating that sample carryover is negligible. During the experiment, the residual in the cell was sufficiently washed by the new sample and the short contact time reduced the possibility of coating of the PMB on the inner wall of the cell and tubing. More data for alternate analysis of high/low concentration samples can be found in Fig. S5.

3.4. Interferences from silicate and arsenate

Because silicate and arsenate can form similar molybdate heteropolyacid compounds with PMB reagent, they are considered as two of the main species interfering with the determination of DRP using the PMB method [29,30]. The effect of silicate and arsenate on DRP determination using the proposed method was studied, with samples containing phosphate and various amounts of silicate and arsenate.

For silicate concentrations between 0 and 400 μM, which are the common concentrations found in different seawater and mineral waters, the absorbance showed no significant variation within the tested silicate concentration range (Fig. 5(a)). The result

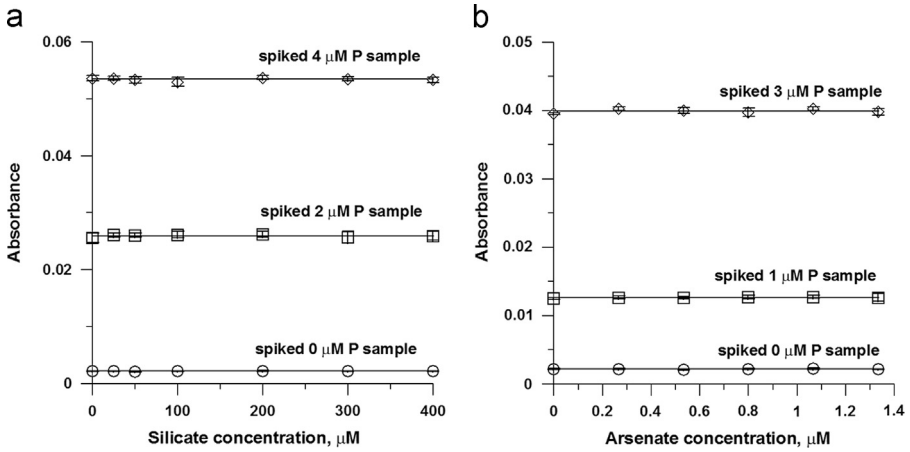

Fig. 5. The effect of silicate (a) and arsenate (b) on the signal of phosphate samples. Results are shown as an average ± SD ($n=3$).

Table 2
Summary of DRP concentrations measured with LFA in aqueous samples of different matrix.

Sample type	Salinity range	Concentration range measured by LFA (μM)	Spiked (μM)	Recovery (%)	Sample numbers, *n*
River water	0	1.76–4.39	2	97.8–103.1	4
Coastal water	5–26	1.55–2.80	2	95.7–103.7	17
Ocean seawater	34	0.39–2.45	2	95.9–100.8	5
Reclaimed wastewater	–	2.09–7.44	2	95.8–103.2	3
Mineral water	–	ND to 1.36	2	95.4–98.1	5

ND, not detected.

was in accordance with that obtained previously [5], where silicate interference could be minimized under optimal reaction conditions including a pH in the final solution of 1.0 (1.2 in the proposed method), room temperature, a $[H^+]$:[Mo] ratio of 70 (74 in the proposed method) and the addition of Sb.

Different from silicate, arsenate interference on DRP analysis is considered to be more serious and depends on the phosphate concentration in the sample [30]. However, as shown in Fig. 5(b), arsenate concentration at the tested range of 0–1.33 μM (80 μg/L) showed no interference on phosphate measurement. The main reason is that the kinetics of the arsenate reaction is much slower than that for phosphate, which needed ~1 h to complete the reaction. In addition, the molar absorption coefficient of arsenic molybdenum blue is ~10% of PMB under the optimized PMB formation protocol (the kinetics of arsenic molybdenum blue formation in a 133 μM arsenate sample are shown in Fig. S5). As a matter of fact, arsenate concentration is at a low level in most natural waters, for example < 30 nM in the open ocean [31], less than 0.04 μM in Xiamen Bay coastal water (measured with ion chromatography-hydride generation-atomic fluorescence spectrometry [32]), and below the limit of 0.13 μM in safe drinking water [33]. Therefore, in most cases using the proposed method the influence of arsenate could be ignored. In areas with arsenic pollution or hydrothermal activity, the addition of reducing reagents to transform arsenate to arsenite, which is non-reactive with molybdate reagents, is recommended [5].

3.5. Application

The LFA system described above was used to determine the concentrations of DRP in various aqueous samples with salinity ranging from 0 to 34. The samples were also spiked with 2 μM phosphate to examine recoveries. A summary of the results of these analyses is given in Table 2 and a detailed comparison of the data from different samples can be found in Supplementary materials.

Recoveries for spiked samples varied from 95.4% to 103.7%, indicating little matrix interference on the determination of DRP using the proposed method. The samples were also analyzed with the standard phosphate protocol as a reference method [8] using a 1 cm cell. A comparison of the two methods exhibited excellent agreement. The DRP measured with the LFA method = (0.9982 ± 0.0063) × DRP measured with the reference method ($R^2=0.9987$, $n=34$).

4. Conclusions

A simple and robust LFA method was developed and applied to the determination of DRP aqueous samples. Relative to previous flow based methods for DRP analysis, the procedures developed in this work exhibited enhanced performance with respect to insignificant interference from salinity, silicate and arsenate, higher reproducibility, less operator intervention and no waiting time needed for baseline stabilization. The application of the novel cross-shaped flow cell avoided the bubble problem which can interfere in the optical detection for flow analysis. Based on the proposed method, a compact loop flow analyzer is under development, which will be applied for the on-line monitoring of wastewater and in an underway system for mapping nutrients in coastal areas.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.talanta.2014.02.020.

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