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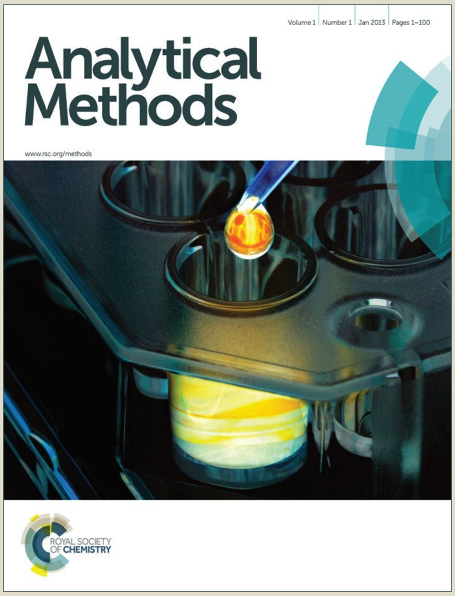

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A sensitive flow-injection analysis method with iminodiacetate chelation and spectrophotometric detection for on board determination of trace dissolved aluminum in seawater

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Abstract

A flexible, flow injection analysis method for shipboard use was developed for the on-line determination of trace dissolved aluminum (dAl) in seawater. The analytical system included a Towed Fish underway sampler and a modified flow injection analysis system with a solid phase extraction-spectrophotometric detection device. Determination was based on the spectrophotometric detection of a complex of chrome azurol S and dAl. In this study, the dAl in the samples was efficiently extracted onto an SPE cartridge, packed with iminodiacetate chelating resin. The extracted dAl was rapidly eluted with hydrochloric acid and reacted with the reagents to form a complex, which was detected at 620 nm with a 30 mm flow cell. Compared with the commonly used methods, the proposed method offered the benefits of improved sensitivity, negligible salinity effect and low cost. Experimental parameters were optimized based on a univariate experimental design, and the matrix effect of seawater was preliminarily investigated. The proposed method had high sensitivity with a detection limit of 0.80 nmol·L^{-1}. The linearity range was 1.0 to 250 nmol·L^{-1} with a 120 s sample loading time and the upper limit was extended to 1.0 μmol·L^{-1} when choosing longer sample loading times. The recoveries were between 96.8 and 99.8% and the relative standard deviation was 2.6% (n=8) for an aged seawater sample spiked with 5.0 nmol·L^{-1} dAl. The analytical results obtained with the proposed method showed good agreement with those using a reference method. The proposed method has been successfully applied to a shipboard underway analysis of dAl in the Jiulongjiang Estuary, Fujian, China.

Keywords: Trace dissolved aluminum; Solid phase extraction; Flow injection analysis; Iminodiacetate; Chrome azurol s; Seawater

1. Introduction

Aluminum (Al) is the most abundant metal element in the Earth crust, and can be found in water from a variety of sources. The acidification of the environment causes an increased concentration of dissolved Al (dAl, <0.45 μm) in natural waters, and the oceanic levels of dAl are found at trace concentrations (nanomolar) [1]. The major sources of dAl in the open ocean include atmospheric inputs, riverine inputs, and dissolution from sedimentary particles [2]. Al is characterized by its relatively short residence time (2-6 year) in surface seawater [3]. The concentrations of dAl in surface waters seem to be driven primarily by atmospheric dust deposition. The distribution of dAl in surface waters can offer reliable estimates of atmospheric dust fluxes to the ocean [4]. The concentration of dAl in surface seawater has been successfully used as a proxy for dust deposition in the ocean. Estimates of dust deposition onto surface waters can be used to provide information on the atmospheric delivery of bio-limiting trace elements, for example, iron. Therefore, it is very important to accurately measure the distribution of dAl in real-time with high spatial and temporal resolution for better understanding the biogeochemistry of dAl.

There are numerous methods for Al determination, including graphite furnace atomic absorption spectrometry (GF-AAS) [5, 6], electrothermal atomic absorption spectrometry (ETAAS) [7], inductively coupled plasma optical emission spectrometry (ICP-OES) [8], inductively coupled plasma mass spectrometry (ICP-MS) [9-11], fluorometry [12-18] and spectrophotometry [19-21]. However, there are limitations in these methods, such as the severe matrices effect, complicated procedures, and shipboard analysis. GF-AAS and ICP-MS are accepted reference methods for the determination of total Al in natural waters. However, when GF-AAS and ICP-MS are applied to seawater dAl analysis, the results of both methods can be severely interfered with by the high salt content in samples [22]. Moreover, these methods are difficult to apply shipboard or to *in situ* analysis. In order to avoid matrix interference and obtain lower detection limits, a pre-concentration or solid-phase extraction step is often required prior to the determination. A shipboard flow injection fluorescence method for trace dAl analysis in seawater has been developed and successfully used in the GEOTRACES program, which delivers preconcentrated dAl onto a column of resin-immobilized iminodiacetate (IDA) [14].

Spectrophotometric methods, because of their low cost, fast analysis, good precision and simple operation, are widely used in trace metal determination. Many examples of spectrophotometric determinations of dAl can be found in the literature. For example, using morin [20], eriochrome cyanine R [22] and pyrocatechol violet [23]. Because of the severe interference and their toxicity, those reagents are not the ideal choice for determination of dAl. The chrome azurol S (CAS) spectrophotometric method is the most common and widely adopted method for dAl determination in natural waters [24], and has the advantages of good selectivity and stability. However, it suffers from shortage of low sensitivity and high matrix interference; and the detection limit of this method (185 $nmol\cdot L^{-1}$) is not low enough to accurately quantify trace dAl in seawater. Although a traditional method for the determination of trace dAl in fresh water [24], spectrophotometry cannot be directly used in seawater analysis, owing to the seawater matrix interference.

Solid phase extraction (SPE) is adopted for the separation and preconcentration of metal ions from complicated matrices and can be easily applied for on-line operation [25, 26]. Among various sorbent materials, toyopearl AF-chelate 650M (IDA resin, Tosohass, Japan) [14] is very popular owing to its affinity for binding several metals, and IDA resin with a macroporous methacrylate backbone is particularly useful.

Because of the automaticity, preciseness, robustness, simplicity and low risk of contamination, flow injection analysis (FIA) is widely used for the determination of trace metals and nutrients [27-29]. By coupling spectrophotometry and an SPE technique, FIA has become a widespread method for the long term on-line monitoring of trace metals (Fe, Mn, Al) [14, 30, 31].

In our work, a flexible FIA method with an SPE technique based on a classic spectrophotometric method has been developed for the determination of trace dAl in seawater. The dAl was efficiently extracted onto an IDA column and separated from the seawater matrix. Our work has provided a rapid, simple and highly sensitive shipboard method for underway determination of trace dAl in seawater, and the method is capable of achieving high spatial and temporal resolution of dAl data.

2. Experimental

2.1 Reagents and solutions

All solutions were prepared with fresh ultrapure water (resistivity ≥ 18.20 MΩ·cm), obtained from a Millipore Purification Water System (Millipore, USA). The preparation of standard and reagent solutions was conducted in a clean airflow bench. Plastic ware for storing standard and reagent solutions as well as water samples was low-density polyethylene (LDPE) bottles (Nalgene, USA), washed following the previously described procedure [32]. CAS stock solution (5.00 $\mathrm{mmol \cdot L^{-1}}$) was prepared by dissolving 0.152 g CAS (Fluke, USA) into 50 mL ultrapure water. The solution was stored at 4^{o}C while not in use. Cetyltrimethylammonium bromide (CTAB) stock solution (10.0 mmol·L^{-1}) was prepared by adding 0.182 g CTAB (Sinopharm Chemical Reagent, China) into 50 mL ultrapure water. The CAS-CTAB mixed solution was prepared by mixing 10.0 mL CAS stock solution with 2.5 mL CTAB stock solution, and brought up to 100 mL with ultrapure water. A 1.5 mol·L^{-1} ammonium acetate column conditioning solution was made with appropriate dilution of 25% (v/v) ammonium solution (Emsure, Merck, Germany) and 100% (v/v) glacial acetic acid (Emsure, Merck, Germany). The pH of the column conditioning solution (1.5 mol·L^{-1}) was 6.5 ± 0.1, and after mixing with sample or standard solution, the final pH was 5.5 ± 0.1. The pH of the ammonium acetate buffer (1.0 mol·L^{-1}) was 5.6 ± 0.1. A 0.10 mol·L^{-1} hydrochloric acid (HCl) solution was prepared by diluting 30% HCl (v/v) (Suprapur®, Merck, Germany) with ultrapure water. The ascorbic acid stock solution (0.10 mol·L^{-1}) was obtained weekly by dissolving 0.440 g ascorbic acid (99.7%, Sinopharm Chemical Reagent, China) in 25 mL ultrapure water and was stored in an LDPE bottle at 4°C. Thiourea stock solution (0.10 mol·L^{-1}) was prepared weekly by dissolving 0.190 g thiourea (99.0%, Sinopharm Chemical Reagent, China) in 25 mL ultrapure water and was stored in an LDPE bottle at 4°C. The mixed solution of buffer and masking reagent (10.0 mmol·L^{-1} ascorbic acid and 10.0 mmol·L^{-1} thiourea) was prepared daily by diluting the correct amount of ascorbic acid stock solution and thiourea stock solution with 1.0 mol·L^{-1} ammonium acetate solution. Al standard solutions were prepared with appropriate dilution of commercial Al standard solution (1000 mg·L^{-1}, Merck, Germany) in ultrapure water and stored at 4°C. Working standards were obtained daily by appropriate dilution of the stock solutions with ultrapure water.

The SPE column (Supelco, America) was packed with the IDA chelating resin in a manner similar to that described elsewhere for 8-hydroxyquinoline resin [33]. The IDA chelating resin was toyopearl AF-chelate 650M (Tosohass, Japan), which has a nonswelling hydroxylated methacrylic polymer base bead (Toyopearl HW-65) derivatized with IDA functional groups at a concentration of about 35 μmol/mL of wet resin. The column was 10 mm in inner diameter and 40 mm high [14]. The IDA column was washed with column conditioning solution before use, with ultrapure water and column conditioning solution after use, and stored in 20% ethanol (v/v) before the next experiment.

2.2 Apparatus

The configuration of the detection manifold and underway sampling system is shown in Fig. 1. Two four-channel peristaltic pumps (Baoding Longer Precision Pump, Hebei, China) were used to deliver sample, carrier and reagents. An eight-position selection valve with a microelectronic actuator (Valco Instruments, USA) was used for the selection and injection of sample and standard solutions. A six-port, two-position injection valve with a microelectronic actuator (Valco Instruments, USA) was used for injecting the eluted solution into the reagent stream. The detection system included a 30 mm flow cell (Yixing Jingke Optical Instrument, Yixing, China), a miniature tungsten halogen lamp (LS-1-LL, Ocean Optics Inc., USA) and a variable wavelength spectrophotometer (USB 2000+, Ocean Optics, USA). The underway sampling system (Fig. 1) was similar to that described elsewhere [30], and consisted of a

Towed Fish, a BT100-2J one-channel peristaltic pump (Baoding Longer Precision Pump, Hebei, China), a one-channel peristaltic pump (MASTERFLEXs, Cole Parmer Instrument USA), a 0.45 μm pore-size membrane filter (Millipore, USA) and a conductance-temperature-depth (CTD) sensor (Yellow Spring Instrument Co. USA) for sample delivery, on-line filtering and real-time measurement of temperature, pH and salinity of water samples.

All manifold tubing was 1.58 mm o.d. and 0.75 mm i.d. transparent polytetrafluoroethylene (PTFE) tubing (Valco Instruments, USA) except for the peristaltic pump tubing, where silicone tubing (Baoding Longer Precision Pump Co., Hebei, China) was used. The tubing of the Towed Fish sampler was PTFE tubing of 10 mm i.d. Two mixing coils, one 100 cm and one 200 cm, were made as two knotted reactors. ICP-MS (7700 Series, Agilent Technologies, USA) was used to analyze dAl in the samples for intercomparison with the proposed method.

Fig. 1

2.3 Manifold and procedures

The underway sampling system using a homemade Towed Fish was towed at the end of a boom at a distance of 3 m from the side of the ship [30]. As shown in Fig. 1, the surface seawater was on-line filtered with a 0.45 μm pore-size membrane filters and acidified to pH 1.7 by mixing with 0.30 mol·L^{-1} HCl. Fresh ultrapure water was used as a carrier. The acidified sample or standard solution and column conditioning solution were introduced using the eight-position selection valve. The system operation program for dAl analysis is given in Table 1. In Step 1, the IDA chelating column was first rinsed with 0.10 mol·L^{-1} HCl for 5 s. The rotary injection valve was then switched from position A to position B, and the column was rinsed with column conditioning solution for 10 s (Step 2). After the sample or standard solution was pre-filled into the tubing (Step 3), the sample or standard solution was loaded onto the column for a selected time depending on the dAl concentration in the sample. During the sample loading time (Step 4), the HCl mixed with the reagent stream to produce a reagent blank signal. When sample loading was finished, the IDA chelating resin was rinsed out with column conditioning solution to remove impurity (Step 5). In Step 6, the dAl enriched on the column was rapidly eluted with the HCl solution, and then mixed with the reagents in the mixing coils, leading to the formation of the dAl-CAS-CTAB complex. During the elution time (Step 6), a new sample or standard solution was introduced. The complex was delivered through the 30 mm flow cell for detection against reagent blank at 620 nm wavelength. A reference wavelength of 700 nm was adopted to correct shift of the light source and any refractive index difference between the carrier and sample. The whole analysis procedure, including data acquisition, was automatically controlled using the graphical user software programmed in LabVIEW (National Instruments, USA).

Table 1 System operation program for dAl analysis

Step	Duration time (s)	Injection valve position*	Selection valve position	Comments
1	5	A	1	Rinsing IDA chelating column with HCl solution (R2)
2	10	B	1	Conditioning IDA column with column conditioning solution (R1)
3	15	A	3	Pre-fill
4	120	B	3	Loading sample onto IDA column (preconcentration of dAl)
5	5	B	1	Rinsing IDA column with column conditioning solution (R1)
6	45	A	1	Eluting IDA column with HCl solution (R2)

* A and B correspond to the solid and dashed line for valve 2 in Fig. 1.

During the experiment, a 50 nmol·L^{-1} standard dAl solution was used as the data quality control sample and inserted every 10 samples to check the measurement deviation. In order to eliminate carryover, before and after use the manifold was sequentially flushed with ultrapure water, 0.10 mol·L^{-1} HCl solution, and again ultrapure water. Bubbles could affect the stability of the output signal; therefore, a narrow-bore poly-ether ether ketone (PEEK) tubing (1.58 mm o.d. and 0.25 mm i.d., Shimadzu, Japan) was connected to the outlet of the flow cell to provide back pressure and eliminate bubble formation in the carrier stream.

2.4 Sampling

An underway measurement was carried out in Jiulongjiang Estuary on-board R/V Haiyang II on 16 June 2015. The Estuary receives freshwater from the Jiulongjiang, the second largest river in Fujian Province. Several coastal water samples were collected using an underway sampling system. The seawater samples were transferred to acid-washed LDPE bottles. Water samples were stored in the dark at 4^{o}C immediately after collection. All water samples were filtered through a 0.45 μm pore-size membrane within 12 h to remove suspended particles. The filtered water samples were acidified to pH 1.7 with 0.30 mol·L^{-1} HCl, then stored at 4°C in the dark until analysis. Ultrapure water was used to prepare field blanks and procedural blanks for sample collection and handling, as data quality control samples.

3. Results and discussion

3.1 Parameter optimization

3.1.1 Selection of detection wavelength

The absorption spectra of the reaction product obtained with different concentrations of CTAB solutions are shown in Fig. 2, and the absorption spectra of the reagent blank obtained with different concentrations of CTAB are shown in Supplementary Material (Fig. S1). The cationic surfactant CTAB enhances the dissociation of the organic dyes, thus increasing the number of chromogenic molecules or formation of ternary complexes containing surfactant monomers. Without CTAB, the maximum absorbance of the dAl-CAS complex occurred at 545 nm. When CTAB was added, the maximum absorbance shifted from 545 to 610 nm, accompanied by a considerable enhancement of absorptivity. However, increasing the concentration of CTAB increased correspondingly the reagent blank [34]. The increase of CTAB concentration caused intensive increase in the blank absorption value at the maximum absorbance wavelength of 610 nm. Therefore, the wavelength of 620 nm was selected as the detection wavelength, and the blank was low, while the method sensitivity was not significantly decreased.

Fig. 2

3.1.2 Influence of the reagent concentration, reaction pH and flow rate

The possible affecting factors, including reagent concentrations, reaction pH, reagent flow rates and salinity, were investigated. A univariate experimental design was based on the results of preliminary experiments. A 50 nmol·L^{-1} dAl standard solution was used as the test sample. The results shown as the averaged value ± standard deviation (SD) are given in Fig. 3. The analytical method sensitivity and analysis time were taken into consideration to evaluate the optimum parameters.

Fig. 3

The effects of CAS concentrations ranging from 0.30 to 0.70 mmol·L^{-1} on signal intensity are shown in Fig. 3(A). Higher concentrations of CAS increased signal intensity. When the concentration of CAS was higher than 0.50 mmol·L^{-1}, the SD of signal intensity was higher. To reach an acceptable sensitivity, a concentration of 0.50 mmol·L^{-1} CAS was selected.

As shown in Fig. 3(B), the signal intensity increased as the CTAB concentration increased and reached a maximum at a concentration of 0.25 mmol·L^{-1}. Considering the sensitivity, the 0.25 mmol·L^{-1} CTAB concentration was selected for subsequent experiments.

The reaction pH was the pH of the mixed solution of the eluent and the reagent. Fig. 3(C) shows the absorbance variation of the complex in the reaction pH ranging from 4.9 to 6.2. When the pH was higher than 5.6, hydroxyl ions competed with CAS-CTAB for dAl, and lowered the signal intensity. On the other hand, as the pH decreased (<5.6), the protonation of the ligand increased, resulting in decreased signal intensity. Therefore, pH 5.6 was used as the optimum for further experiments.

The effect of elution HCl concentration on a signal intensity ranging from 0.05 to 0.25 mol·L^{-1} is illustrated in Fig. 3(D). When the elution HCl concentration was 0.05 mol·L^{-1}, the strength of acidity was not high enough to elute the dAl from the IDA chelating column. If the concentration of HCl was higher than 0.10 mol·L^{-1}, the reaction pH was decreased, resulting in decreased signal intensity. It should be pointed out that the elution solution HCl in the present study was prepared in ultrapure water, which was different from that in the literature [16], where a much more expensive low dAl seawater was used. It was found that the 0.10 mol·L^{-1} HCl was suitable to elute the dAl-CAS-CTAB complex.

The effects of a CAS-CTAB flow rate ranging from 0.30 to 0.50 mL·min^{-1} and an eluting flow rate from 0.70 to 1.10 mL·min^{-1} were investigated, and the results are shown in Figs 3(E) and (F). In Fig. 3(E) the signal intensity increased with the increase of CAS-CTAB flow rate and reached a maximum at 0.45 mL·min^{-1}, and so a 0.45 mL·min^{-1} CAS-CTAB flow rate was selected as the optimum. As shown in Fig. 3(F), the signal intensity increased with the increase of eluting flow rate and reached a maximum between 0.90 and 1.00 mL·min^{-1}. However, the reproducibility was worse at a flow rate of 1.00 mL·min^{-1}. For a better sensitivity and reproducibility, an eluting flow rate of 0.90 mL·min^{-1} was selected.

3.2 Interference

In theory, Zn^{2+}, Co^{2+}, Ni^{2+}, Mg^{2+}, Ca^{2+}, Cu^{2+} and Fe^{3+} are believed to have a potential interference on the signal of the proposed method. However, in seawater, Zn^{2+}, Ni^{2+} and Cu^{2+} are the predominant forms of strongly bound organic complexes, which limit their complexation with a CAS reagent and reduce the interference with dAl. Because IDA chelating resin can preconcentrate different metal ions under different pH conditions, the interference from the foreign metal ions could be eliminated with the proposed method since, at the selected pH, only Fe^{3+} and Cu^{2+} contributed a higher than 10% interference absorbance.

Ascorbic acid and thiourea were chosen for masking the interfering ions Fe^{3+} and Cu^{2+}. With the masking reagent, the tolerance limit was 100 for Fe^{3+} and 50 for Cu^{2+}. In fact, in seawater the concentrations of dissolved Fe^{3+} (0.03 to 3 nmol·kg^{-1}) and dissolved Cu^{2+} (0.4 to 5 nmol·kg^{-1}) are lower than that of dAl (0.3 to 40 nmol·kg^{-1}) [35]. Therefore, the interference of Fe^{3+} ions and Cu^{2+} ions could be neglected. Phosphate, surfactants, ethylene diamine tetraacetic acid, citrate, oxalate and tartrate are also known to interfere with the reaction of dAl-CAS-CTAB; however, their concentrations in seawater are generally not high enough to cause interference.

3.3 Effect of salinity

The sensitivity of the analytical method was affected by the seawater matrix.

Based on the Debye-Hückel equation, the activity coefficients for ions in the sample solution decrease as the ionic strength increases [36]. Calibration curves with different dAl concentrations were obtained by spiking standard dAl solution into seawater matrices with different salinities (ranging from 0 to 35), which were prepared by diluting aged seawater collected from the surface of the South China Sea with ultrapure water. The relative standard deviation (RSD) of slopes of the calibration curves with different salinity matrices was less than ±5%, indicating that the salinity effect was negligible.

3.4 Analytical figures of merit

Table 2 summarizes the optimum parameters for the proposed method. The sample volume consumed for the determination of dAl was 8.0 mL. Several calibration curves with different sample loading time obtained over a range of dAl concentrations from 1.0 to 1000 nmol·L^{-1} are shown in Supplementary Material (Fig. S2). The RSD for repetitive determinations of 5.0 nmol·L^{-1} dAl in an aged seawater sample (salinity 35) was 2.60% (n=8), showing good precision.

Table 2 Recommended analytical parameters*

Parameter	Range of tested values	Recommended value
CTAB concentration, mol·L^{-1}	0.10-0.35	0.25
CAS concentration, mol·L^{-1}	0.10-0.80	0.50
Reaction pH	4.9-6.2	5.6 ± 0.1
Sample flow rate, mL·min^{-1}	2.00-5.60	4.00
CAS-CTAB flow rate, mL·min^{-1}	0.30-0.50	0.45
Eluting flow rate, mL·min^{-1}	0.70-1.10	0.90
Concentration of elution HCl, mol·L^{-1}	0.05-0.25	0.10
Eluting time, s	30-50	45

*sample loading time 120 s

The limit of detection (LOD) was estimated using the method introduced by Berger et al [37]. Eight aliquots of the ultrapure water spiked at 2.5 nmol·L^{-1} dAl were analyzed. The LOD was calculated using the following equation:

$$\mathrm{LOD}=\mathrm{SD}\times t_{0.02}=0.80\ \mathrm{nmol{\cdot}L^{-1}}$$

where $t_{0.02}$, the Student's two-tailed t-statistic at the 98% confidence level with eight degrees of freedom, was 2.998; and SD (0.27 nmol·L^{-1}) was the SD of the eight analyses. The LOD was low enough for the determination of Al in most open seas. The LOD could be further lowered by extending the sample loading time. The sample throughput was 18 samples per hour, which was fast enough for achieving high spatial and temporal resolution of the dAl data.

3.5 Validation of the method

3.5.1 Recovery

The recovery of the proposed method was examined to evaluate matrix interference. Aged seawater samples collected from the South China Sea were spiked with dAl at different concentrations and analyzed using the proposed method. As shown in Table 3, the recoveries of the dAl in spiked samples were between 96.8 and 99.8%, indicating that the determination of dAl did not interfere with the seawater matrix.

Table 3 Recovery of dAl from seawater samples using the proposed method (n=3)

Sample	Added, nmol·L^{-1}	Found, nmol·L^{-1}	Recovery, %
SW1	0	8.5 ± 0.6	--
	25	32.7 ± 2.1	96.8
SW2	0	49.3 ± 1.9	--
	50	99.0 ± 1.1	99.4
SW3	0	146.6 ± 2.2	--
	100	246.4 ± 4.2	99.8
SW4	0	99.6 ± 2.9	--
	200	297.3 ± 4.9	99.3

3.5.2 Application

The proposed method was applied underway to analyze the concentration of dAl in seawater. The dAl distribution and salinity variation obtained in the underway analysis of the Jiulongjiang Estuary, China are shown in Fig. 4. The highest dAl concentration was found in the low salinity sea area, which expressed runoff from the Jiulongjiang. Downstream, the Jiulongjiang Estuary was affected by the influx of seawater, thus a higher salinity and lower concentrations of dAl were observed.

Fig. 4

3.5.3 Comparison with a reference method

In fact, there is no suitable certified seawater reference material for dAl, therefore, an intercomparison experiment was performed to evaluate the accuracy of the proposed method. Several samples collected from the South China Sea were spiked with dAl at different concentrations and analyzed using both the proposed method and a reference method, ICP-MS [11], the result is shown in Supplementary

Material (Fig. S3). Fig. S3 illustrates good agreement between the two methods within a range of 50 to 600 nmol·L^{-1} of dAl.

The estuary samples collected from the Jiulongjiang Estuary were analyzed using both the proposed method and the standard reference method. As shown in the results in Table 4, the calculated *t*-values were lower than the critical *t*-values, indicating no statistically significant difference between the two methods.

Table 4 Comparison of the analytical results of the proposed method and the ICP-MS method

Sample no.	Concentration ± standard deviation (n= 3, nmol·L^{-1})		Calculated *t*-value	Critical *t*-value (P=0.95)
	Proposed method	ICP-MS		
1	53.4±1.5	53.8±5.0	0.26	2.78
2	99.1±2.8	103.0±2.8	1.12	2.78
3	124.9±2.5	119.8±5.5	1.64	2.78
4	192.3±3.0	189.7±7.4	1.20	2.78

3.6 Comparison of the method with others

Recent reported methods for on-line determination of dAl in natural waters are compared and listed in Table 5. As shown in Table 5, only two of the reported flow injection fluorescence methods could be applied for the determination of dAl in seawater samples. Based on spectrophotometric technique, this research aimed at exploring a new method for the determination of dissolved Al in seawater. Compared with the widely used lumogallion fluorescence method, the proposed method had the advantages of high sample throughput and simple apparatus (without heating). The spectrophotometric instruments are more compact and stable than the fluorescence instruments. The fluorescence method can be affected by many factors, such as solvent, temperature, excitation wavelength and fluorescence quenching. This apparatus was of higher accuracy with simple and efficient device and could meet the requirements of the practical determination.

Table 5 Characteristics of some reported methods for the on-line determination of dAl in natural waters

Detection	Key reagents	Technique	Matrix	LOD and precision[a]	Ref.
Fluorometry	N-o-vanillidine-2-amino-p-cresol	FIA	Seawater	LOD: 2.1 nmol·L^{-1} P: 0.6% at 0.1 μmol·L^{-1}	38
Fluorometry	Morin and Tween-20	SIA	Natural water	LOD: 70.3 nmol·L^{-1} P: 2.9% at 70.3 nmol·L^{-1}	39
Fluorometry	Salicylaldehyde picolinoylhydrazone	rFIA	Drinking water	LOD: 0.7 μmol·L^{-1} P: not reported	40
Fluorometry	8-Hydroxyquinoline-5-sulphonic acid	MSFIA	Drinking water	LOD: 18.5 nmol·L^{-1} P: 0.6% at 1.1 μmol·L^{-1}	41
Fluorometry	Lumogallion	In-syringe dispersive LLME	Coastal seawater	LOD: 8.0 nmol·L^{-1} P: 1.5% at 200 nmol·L^{-1}	17
Fluorometry	Lumogallion and Brij-35	FIA, preconcentrated onto an IDA SPE column	Seawater	LOD: 0.1 nmol·L^{-1} P: 2.5% at 5.0 nmol·L^{-1}	14
UV-vis	CAS and CTAB	FIA	Tap water	LOD: 0.19 μmol·L^{-1} P: 0.46% at 3.7 μmol·L^{-1}	24
UV-vis	Quercetin and CTAB	rFIA	Tap water	LOD: 0.26 μmol·L^{-1} P: 1.1% at 7.4 μmol·L^{-1}	42
UV-vis	CAS and CTAB	FIA, preconcentrated onto an IDA SPE column	Seawater	LOD: 0.8 nmol·L^{-1} P: 2.6% at 5.0 nmol·L^{-1}	TW

[a] Concentrations reported in the original articles have been converted to μmol·L^{-1} or nmol·L^{-1} for comparison purposes.

SIA, Sequential injection analysis; rFIA, reverse flow injection analysis; MSFIA, multisyringe flow injection analysis; LLME, liquid-liquid microextraction; Ref., reference; TW, this work.

4. Conclusions

A simple and flexible shipboard FIA analytical method coupled with spectrophotometric detection and an SPE technique was developed for underway determination of trace dAl in seawater. The proposed method had the advantages of low detection limit, high precision, high recovery, high sample throughput, wide linear range and negligible salinity effect. In addition, another advantage of the proposed method was the possibility of on-board application. The analytical method was successfully applied *in situ* for the on-line monitoring of trace dAl in the surface seawater of the Jiulongjiang Estuary. By adjusting the sample loading time, this method could be applied in both open ocean (<10 nmol·L^{-1}) and coastal (<1.0 μmol·L^{-1}) environments. There was no statistically significant difference between the results obtained from the proposed and the ICP-MS method.

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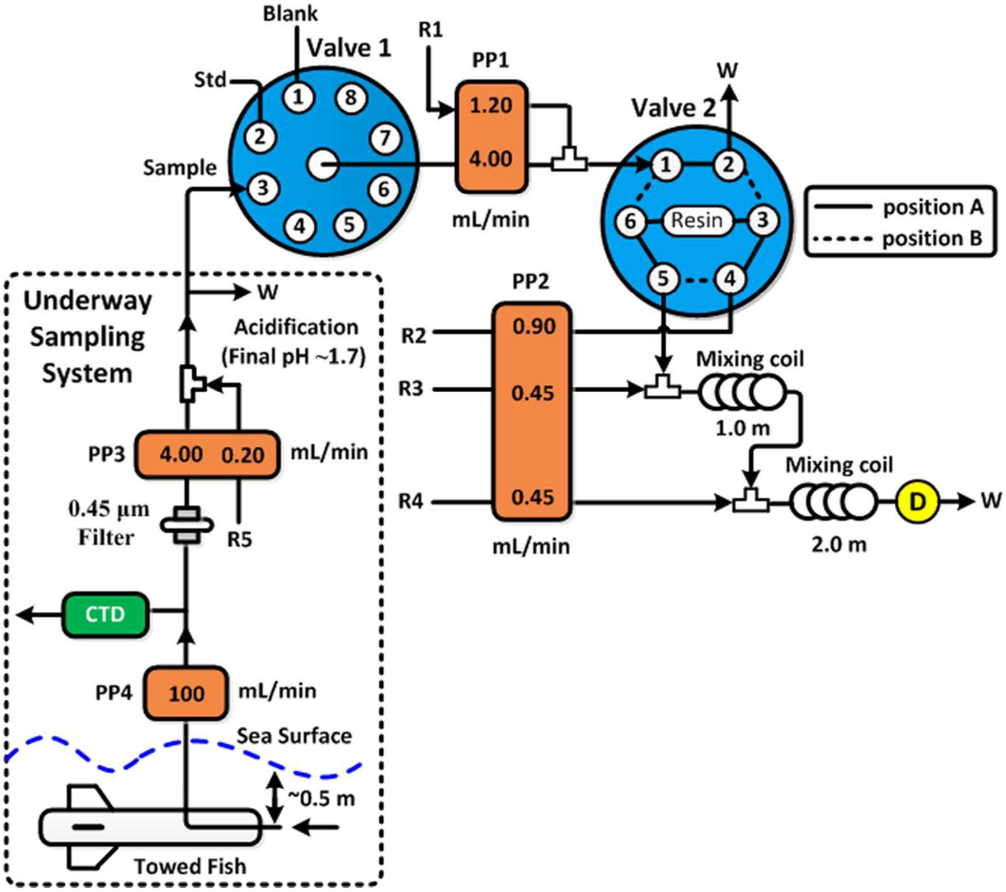
Figure Caption

Fig. 1 Configuration of detection manifold and underway sampling system (Valve 1, eight-position selection valve; Valve 2, rotary injection valve; CTD, conductivity-temperature-depth sensor; PP, peristaltic pump; R1, column conditioning solution; R2, 0.10 moL·L^{-1} HCl; R3, the mixed solution of buffer and masking reagent; R4, CAS-CTAB mixed solution; R5, 0.30 mol·L^{-1} HCl; W, waste)

Fig. 2 Absorption spectra of dAl-CAS-CTAB complex solutions with various CTAB concentrations (concentration of dAl, 1000 nmol·L^{-1}; concentration of CAS, 0.25 mmol·L^{-1}; pH 5.6)

Fig. 3 Influence of the different parameters on detection signal intensity (A, concentration of CAS; B, concentration of CTAB; C, reaction pH; D, concentration of elution HCl; E, CAS-CTAB flow rate; F, eluting flow rate. The concentration of the test sample was 50 nmol·L^{-1} dAl (n=3))

Fig. 4 Distribution of dAl (a) and salinity (b) in the Jiulongjiang Estuary (The figure was created using the Ocean Data View software)



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233x208mm (150 x 150 DPI)

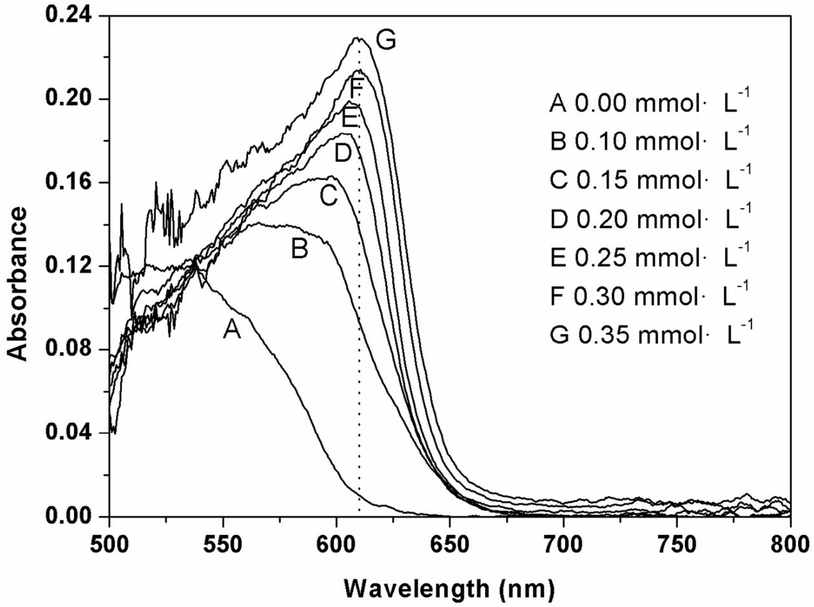
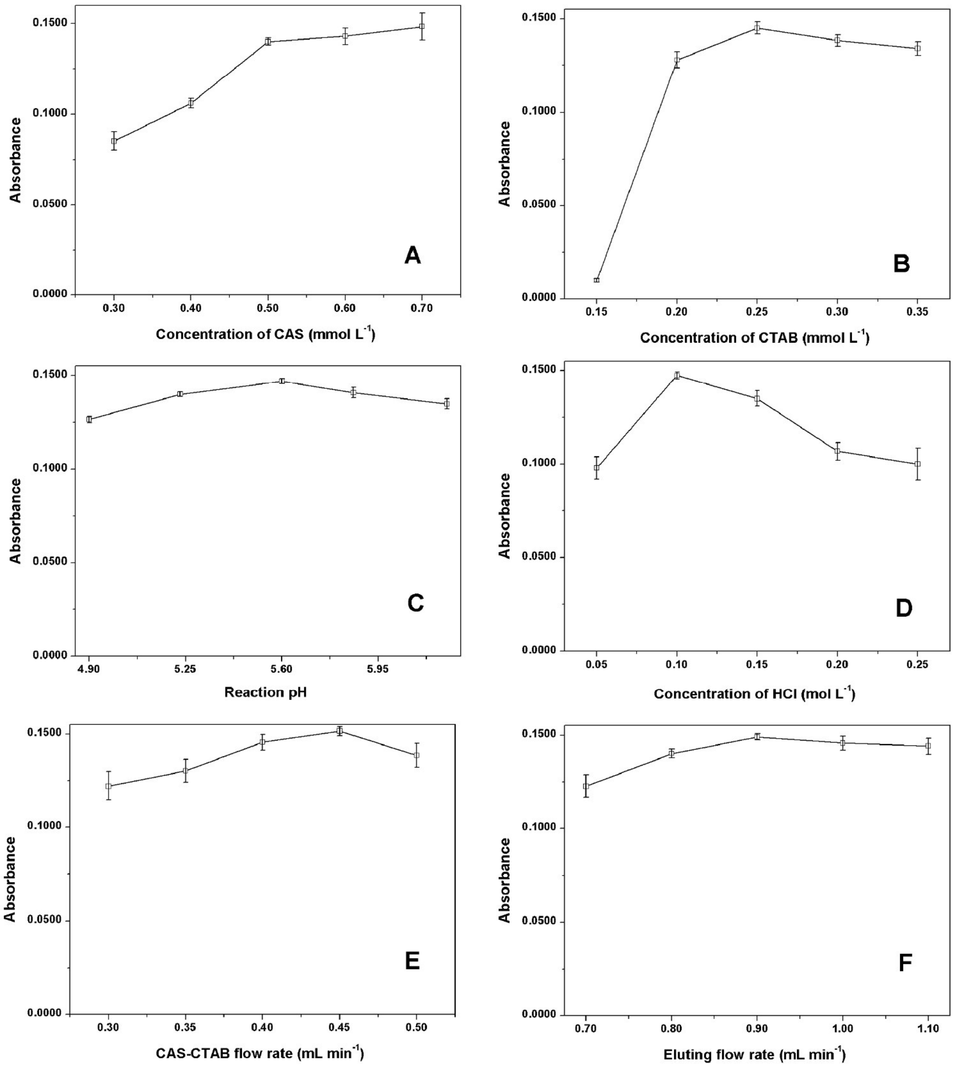


Fig. 2 Absorption spectra of dAl-CAS-CTAB complex solutions with various CTAB concentrations (concentration of dAl, 1000 nmol·L-1; concentration of CAS, 0.25 mmol·L-1; pH 5.6)
289x202mm (150 x 150 DPI)



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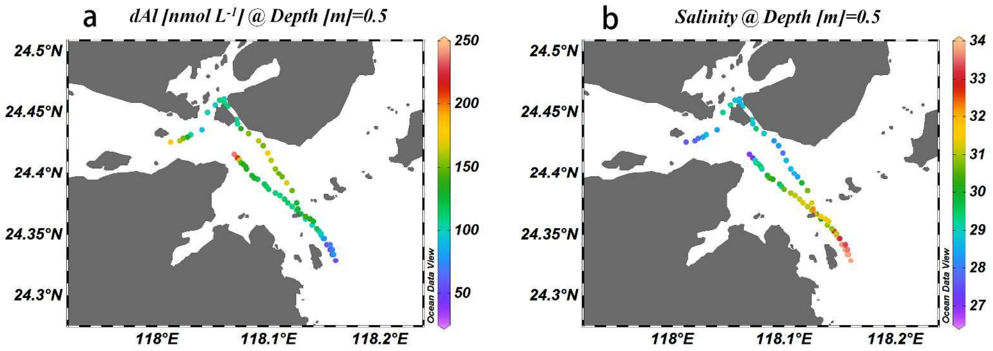

Fig. 4 Distribution of dAl (a) and salinity (b) in the Jiulongjiang Estuary
(The figure was created using the Ocean Data View software)
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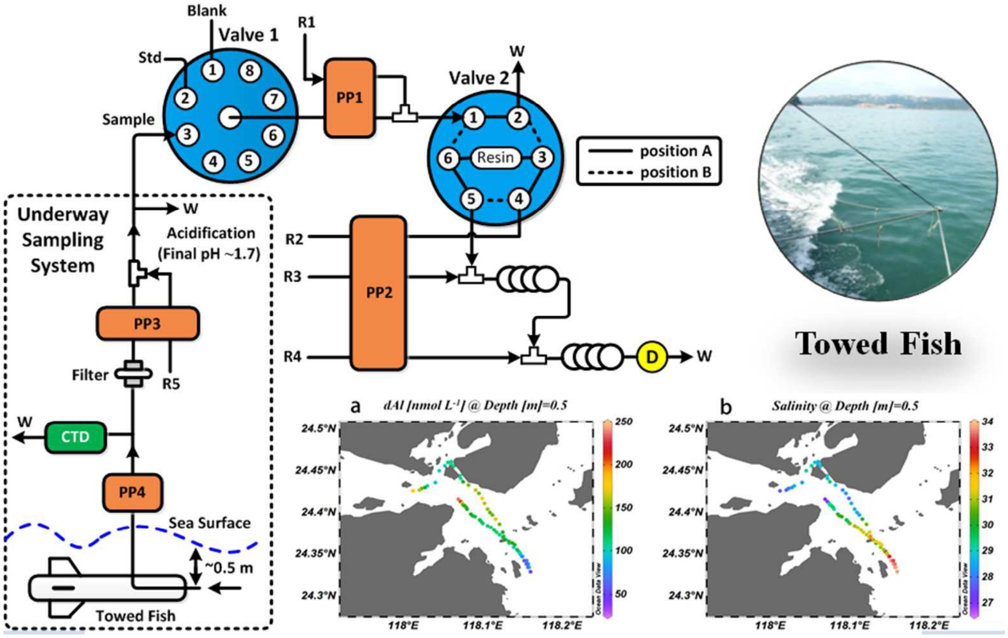

329x209mm (72 x 72 DPI)