Determination of trace metals in seawater by an automated flow injection ion chromatograph pretreatment system with ICPMS

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ABSTRACT

A novel flow injection ion chromatograph (FI-IC) system has been developed to fully automate pretreatment procedures for multi-elemental analysis of trace metals in seawater by inductively coupled plasma mass spectrometer (ICPMS). By combining 10-port, 2 position and 3-way valves in the FI-IC manifold, the system effectively increase sample throughput by simultaneously processing three seawater samples online for: sample loading, injection, buffering, preconcentration, matrix removal, metal elution, and sample collection. Forty-two seawater samples can be continuously processed without any manual handing. Each sample pretreatment takes about 10 min by consuming 25 mL of seawater and producing 5 mL of processed concentrated samples for multi-elemental offline analysis by ICPMS. The offline analysis improve analytical precision and significantly increase total numbers of isotopes determined by ICPMS, which include the metals Al, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Ti, V, and Zn. The blank value and detection limits of trace metals using the system with ICPMS analysis all range from 0.1 to 10 parts per trillion (ppt), except Al, Fe, and Zn. The accuracy of the pretreatment system was validated by measuring open-ocean and coastal reference seawater, NASS-5 and CASS-4. Using the system with ICPMS analysis, we have obtained reliable trace metal concentrations in the water columns of the South China Sea. Possessing the features of full automation, high throughput, low blank, and low reagent volume used, the system automates and simplifies rigorous and complicated pretreatment procedures for multi-elemental analysis of trace metals in seawater and effectively enhances analytical capacity for trace metal analysis in environmental and seawater samples.

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1. Introduction

Bioactive trace metals in seawater, including Cd, Co, Cu, Fe, Mn, Ni, and Zn, play important roles in influencing global biogeochemical cycles and oceanic ecosystem dynamics [1]. When the concentrations of the trace metals are depleted, the metals may become limiting and co-limiting factors for phytoplankton growth [2,3]. In contrast, when the concentrations of some bioactive trace metals are elevated, even to a few nanomol L^{-1}, the metals can become toxic to some marine phytoplankton. For example, cyanobacteria are sensitive to a few nanomolar dissolved Cu and Cd [4,5]. In addition, the relative concentrations of bioactive trace metals can strongly influence how marine phytoplankton interacts with trace metals. Trace metals with similar chemical properties can substitute for each other in enzymatic functions when the concentration of an essential metal is depleted in ambient seawater [6,7]. Contrarily, trace metals with relatively high concentrations

can have antagonistic effects on algal uptake of other trace metals with similar chemical properties [8,9]. Therefore, the concentration information of the whole suite of the trace metals in seawater is essential to fully understand trace metal biogeochemistry in the ocean and their toxicity to phytoplankton and other organisms in marine environment [10].

Analytical techniques for trace metal analysis in seawater have been greatly improved during past two decades, mainly due to sensitivity improvement of analytical instruments. In particular, ICPMS has evolved to be one of the most sensitive analytical techniques for multi-elemental analysis of trace metals. Using high resolution ICPMS coupled with sensitivity-enhanced desolvation apparatus, the detection limits for trace metals are down to sub-ppt or picomol L^{-1} levels in simple matrix solution. However, high salt content in seawater precludes direct analysis by ICPMS due to strong ionization suppression and severe interference caused by polyatomic isobaric interference by major salts in seawater. Thus, removing the salts in seawater samples without causing significant contamination is essential to trace metal analysis in seawater by ICPMS. Trace metal chelating resins is one of the most common techniques for preconcentrating trace metals and removing

the major salts in seawater. To avoid significant contamination, pretreatment processes to separate trace metals from salts in seawater generally involve rigorous preparative procedures. While using chelating resin techniques, the procedures include: sample loading, buffering, preconcentration, matrix removal, metal elution, and eluted sample collection. Highly experienced analytical personnel are required to operate rigorous preparative procedures to avoid contamination. When the procedures are processed manually or only partially automated, the pretreatment steps can be time consuming thus restrict analytical capacity for multi-trace metal analysis in seawater samples. With increasing needs for trace metal analysis in environmental and natural samples with seawater matrix, a fully automated and efficient pretreatment system is needed.

Some previous studies have successfully established multi-elemental analysis for trace metals in seawater by coupling flow injection manifold to ICPMS for direct online analysis [e.g., 11–13]. Although online analysis save time and elevate signal noise ratios between samples and blanks, analytical stability and precision from online analysis is not as steady as continuous signals obtained from offline analysis. For isotope composition analysis, it appears to be inappropriate to use online ICPMS analysis to obtain high precision results. In addition, total numbers of isotopes or elements analyzed by online setup may be restricted due to limited analysis time with transient signals. Instead, offline ICPMS analysis with online sample pretreatment allows us to precisely analyze multi-elements and isotope composition in seawater samples. Eluted samples collected by offline setup can also be used for multiple time analysis for isotopes and elements eluted.

Here we present a new online pretreatment system to fully automate pretreatment procedures for offline trace metal analysis in seawater by ICPMS. This system is composed of a new flow injection manifold, two commercial trace metal chelating columns, and two 10-port, 2 position and two 3-way valves in a commercial programmable ion chromatograph. The chelating column we use in the FI-IC system can retain more than 30 trace metals [14], which include Al, Cd, Co, Cr, Cu, Fe, In, Mn, Ni, Pb, Th, Ti, U, V, Y, Zn and all lanthanide metals at pH around 5.5. Forty-two seawater samples can be continuously processed without any manual handing. Reliable trace metal concentrations in natural seawater and environmental samples were obtained by using the pretreatment system with ICPMS analysis.

2. Experimental

2.1. Reagents and material

Polypropylene centrifuge vials with 50 and 15 mL were used to contain seawater samples and eluted samples, respectively. Superpure de-ionized water used to clean bottles and prepare all reagents was Element-grade purified water from Milli-Q water purification system. All of the polypropylene vials and seawater sample bottles were acid washed by filling with 10% reagent grade HCl solution for 3 days and rinsed with the Milli-Q water thoroughly then filled with 50% sub-boiling distilled HNO_3 for at least 2 day then rinsed thoroughly with the Milli-Q water in clean room right before use. The polypropylene reagent bottles used in the IC system are all with gas tight plastic connectors and caps (Schott, UK), which are positively pressurized with high purity nitrogen gas. The only two reagents used in the IC system include superpure $2 \, mol \, L^{-1}$ ammonia acetate buffer and superpure 2 N nitric acid. The buffer solution is prepared by mixing 116 mL superpure glacial acetic acid (Seastar, USA), 178 mL superpure grade pure ammonia solution (Seastar, USA), and 206 mL Milli-Q water together in a class 100 clean bench to form 0.5 L $4 \, mol \, L^{-1}$ buffer solution of pH 6.0 ± 0.1. The super

pure $2 \, mol \, L^{-1}$ nitric acid was prepared by diluting concentrated nitric acid (Seastar, Superpure) with the Milli-Q water. Standards for calibration curves were prepared by adding known amounts of trace metals into acidified chelated blank seawater. Seawater blanks were prepared by using natural surface seawater collected by Go-Flo bottles (Seabird, USA) from oligotrophic surface seawater in the South China Sea and stored in acid washed 20-L polypropylene bottles (Nalgene, USA). The seawater was filtered through an online closed system in clean room by acid-washed POLYCAP cartridge (Whatman, USA) with 0.2 μm pore size to remove particulate materials. The filtered seawater was UV oxidized under 1200 W for 20 min then was passed through a large quartz column (45 cm long × 5 cm wide) containing conditioned mesh 100–200 Chelex-100 resins (Biorad, USA) to remove trace metals. The pH of the standard solution in seawater was also adjusted to 1.0 by adding nitric acid. Seawater samples were acidified to solution with pH 1 by adding superpure nitric acid. Details about seawater samples collected from the South China Sea were presented in the study of [15,16].

2.2. Method development

2.2.1. Ion chromatograph system

An ion chromatograph with plastic tubings, high-pressure pumps, and time programmable function is required to construct the system (Fig. 1). Except for the Teflon tubing (1.0 mm ID) used for the autosampler, all other tubing used in the IC system are PEEK materials with three different internal diameter sizes of 0.25, 0.51, and 0.76 mm. The IC system we use (Dionex ICS 3000, USA) is equipped with a gradient pump and an isocratic high-pressure pump. High-pressure pumps maintain steady flow rates to accurately control the overall performance of the system, which also avoid possible leaking caused by back-pressure in chelating columns. The trace metal complexation column we used is a commercial chelating column specifically designed to concentrate cationic transition metals from high-ionic-strength matrices (Dionex MetPac CC-1, USA). The chelated elements can include: Al, Cd, Co, Cr, Cu, Fe, In, Mn, Ni, Pb, Th, Ti, U, V, Y, Zn, and all lanthanide metals. The dimension of the column is 4 mm × 50 mm and the chelating resins are composed of 18 μm diameter beads containing iminodiacetate functional groups.

Forty milliliters of acidified seawater samples (pH 1) were prepared in pre-acid washed 50-mL standard polypropylene centrifuge vials by adding suitable amount of superpure nitric acid. Sample loading in the sample loops is driven by a peristaltic pump with the flow rate of 15 mL/min. The internal volume of the sample loops may be changed, depending on preconcentration factor or trace metal concentrations level in the samples. Sample loops with less volume may be used to save loading time when trace metal concentrations are high in samples such as estuarine, coastal, or environmental samples. The isocratic pump of the IC system is used to drive ammonium acetate buffer under flow rate of 0.50 mL/min through a third chelating column (Dionex MetPac CC-1, USA), which was used to further remove trace metal impurity in the superpure buffer solution if any (Fig. 1). The super pure buffer is first mixed with seawater samples pushed out from sample loops by the other independent simple pump (SP2) to chelating columns under flow rate of 3.50 mL/min. The gradient pump is used to drive the Milli-Q water or $1 \, mol \, L^{-1}$ superpure nitric acid, which is obtained by mixing 50% of $2 \, mol \, L^{-1}$ superpure nitric acid with 50% of Milli-Q water. Using the chelating column, we observed that it took 2 min to obtain complete elution of chelated trace metals from the chelating columns with a 2 mL/min flow rate. Using the setup shown in Table 1 and Fig. 1, the elution time of the metals

Table 1

The flow chart of samples processed in the system at position A. The switch of the valves and the on and off of the pumps are controlled by the programmable ion chromatograph. S1, S2, and S3 stand for samples 1, 2, and 3 processed in the manifold. SL1 and SL2 stand for sample loops 1 and 2. C1 and C2 stand for chelating columns 1 and 2. MQ stands for element grade Milli-Q water.

| Time (min)	Autosampler probe	10-way valve 1 (10W_V1)		10-way valve 2 (10W_V2)		3-way valve 1	3-way valve 2	Peristaltic pump	Single pump 1	Single pump 2	Gradient pump
		SL1	SL2	C1	C2	3W_V1	3W_V2	PP	SP1	SP2	GP
0.00	Start taking sample	Start loading SL1 with S3	Start injecting S2 into C2	Start rinsing C1 with MQ	Start loading C2 with S2	To W3	Loading SL with S3	Loading S3	Start mixing S2 with buffer	Start injecting S2 to C2	Start rinsing C1 with MQ
4.00	Stop taking sample	Stop loading	Injecting S2 into C2	Rinsing C1 with MQ	Loading C2 with S2	To W3	Stop loading	Stop loading	Mixing S2 with buffer	Injecting S2 to C2	Rinsing C1 with MQ
6.00	Rinsing probe	S3 in SL1	Injecting S2 into C2	Rinsing C1 with MQ	Loading C2 with S2	To probe for rinsing	To probe for rinsing	Off	Mixing S2 with buffer	Injecting S2 to C2	Rinsing C1 and probe with MQ
7.00	Stop rinsing	S3 in SL1	Stop injecting	Rinsing C1 with MQ	Washing C2 with buffer	To W3	To SL	Off	Washing C2 with buffer	Stop injecting	rinsing C1 with MQ
7.10	Go to fraction vial	S3 in SL1	MQ in SL2	Start eluting C1 with acid	Stop buffer washing	To W3	To SL	Off	Stop washing	Off	Eluting C1 with acid
7.50	Start collecting	S3 in SL1	MQ in SL2	Eluting C1 with acid	S2 metals in C2	To probe for collecting	To probe for collecting	Off	Off	Off	Eluting C1 with acid
10.00	Stop collecting	S3 in SL1	MQ in SL2	Rinsing C1 with MQ	S2 metals in C2	To W3	To SL	Off	Off	Off	Switch to MQ
10.25	Stay on fraction vial	S3 in SL1	MQ in SL2	Rinsing C1 with MQ	S2 metals in C2	To W3	To SL	Off	Off	Off	Rinsing C1 with MQ
10.65	Move to next sample	S3 in SL1	MQ in SL2	MQ in C1	S2 metals in C2	To W3	To SL	Off	Off	Off	Stop rinsing
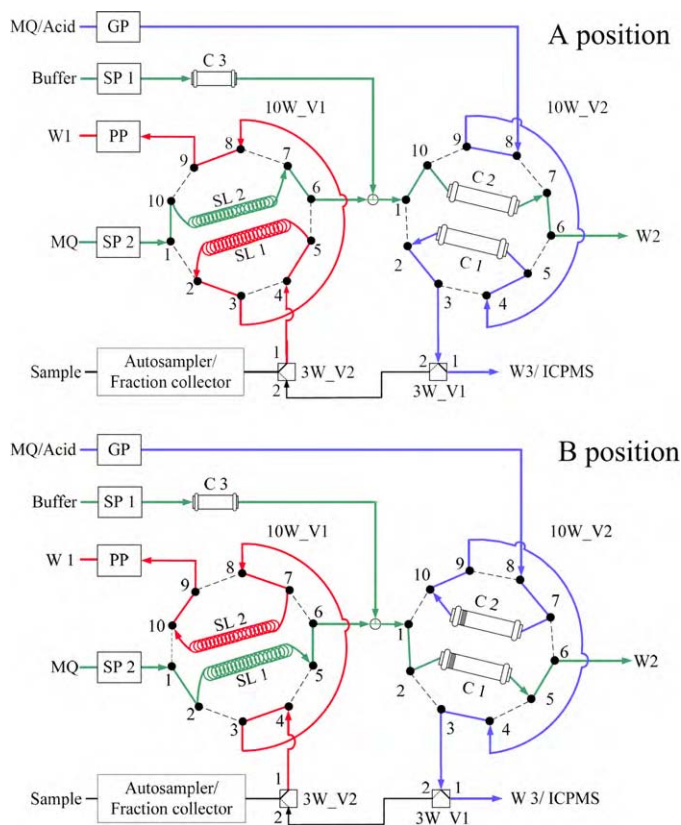
Fig. 1. The flow injection manifold of the FI-IC pretreatment system. The 10-port, 2 position or 3-way valves are represented as 10W_V1, 10W_V2, 3W_V1, and 3W_V2, respectively. GP, SP, and PP stand for gradient pump, single pump, and peristaltic pump, respectively. SL1 and SL2 stand for sample loops 1 and 2. C1, C2, and C3 represent chelating columns 1, 2, and 3. W1, W2, and W3 stand for wastes 1, 2, and 3. The output of W3 may be connected to ICPMS for online analysis. The solid and dashed lines between the numbers in the flow pathways of the two 10-port, 2 position valves stand for the open and closed positions. The solid lines stand for open flow pathways and the dashed lines stand for closed flow path pathways. At position A, SL1 and C2 are under loading mode and SL2 and C1 are under injection mode.

was set at 2.5 min so that we obtained 5.0 mL elution solution under the flow rate. The volume of 5.0 mL is sufficient to carry out multi-elemental analysis by ICPMS for more than 20 isotopes for multiple times. By taking up 25 mL of seawater in each sample in our setup, we preconcentrated trace metals in seawater by a factor of 5 in the setup. The preconcentration factor can be adjusted by increasing or decreasing the volume of sample loops. The seawater standards of calibration curves we prepared to quantify trace metal concentrations in samples were also pretreated by the IC system using exactly same procedures as seawater samples treated.

2.2.2. Flow injection manifold

The flow injection manifold processes three samples simultaneously by connecting two sample loops, two chelating columns, and an autosampler with two 10-port, 2 position valves and two 3-way valves in the programmable ion chromatograph (Fig. 1). For the position A shown in Fig. 1, both sample loop 1 and chelating column 2 are in loading mode and sample loop 2 and chelating column 1 are in injection mode. While the third sample, colored red, is loaded in sample loop 1 (SL1) of 10-port, 2 position valve 1 (10P_V1), the second sample, colored green, in sample loop 2 (SL2) is simultaneously pushed by Milli-Q water driven by single pump 2 (SP2) toward the second 10-port, 2 position valve (10P_V2) and mixes with the 2 N super pure ammonium acetate buffer before entering the second 10P_V2. The trace metals in the buffered seawater sam-
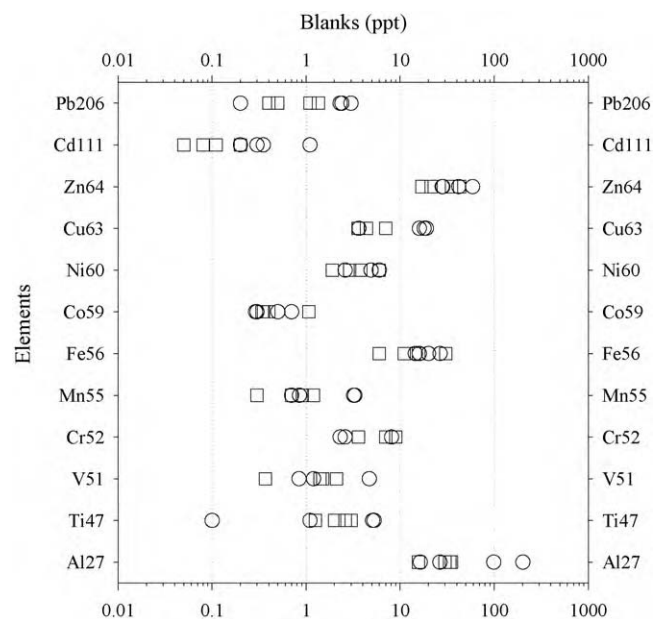

Fig. 2. The concentrations of the blanks for Al, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Ti, V, and Zn. The samples include acidified Element grade Milli-Q water (open square) or acidified chelated seawater (open circle) after passing through the FI-IC system. The concentrations were determined by dividing the signal (counts per second) of the blank samples with the slopes of calibration curves and without subtracting any other blank signals. Each point stands for the averaged concentrations of 6–12 replicates in each occasion.

ple 2 are then chelated in chelating column 2 (C2). At the same time, after chelating column 1 (C1) is rinsed with buffer and Milli-Q water sequentially, the chelated metals of the first sample, colored blue, is eluted out by 1 N nitric acid driven by the gradient pump (GP). After sample loading is finished in sample loop one, the two three way valves were turned from position 1 to position 2, switching the autosampler to become a sample collector for the eluted metal solution. Before collecting the eluted solution, the autosampler probe
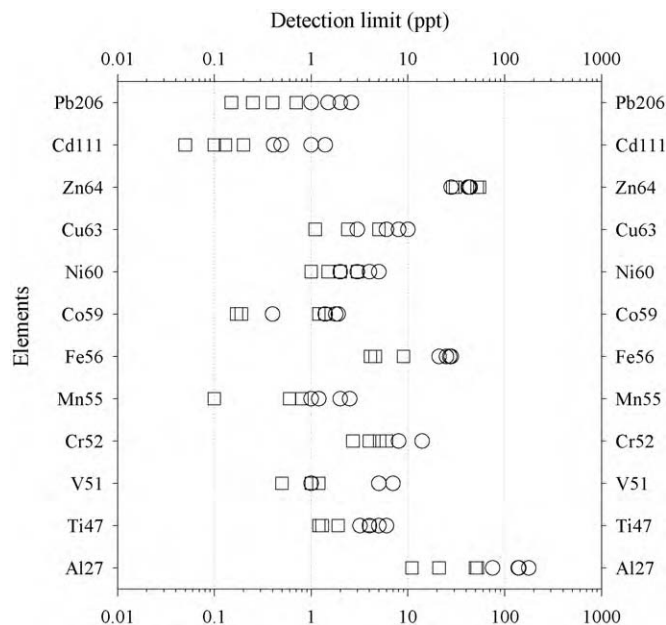

Fig. 3. The detection limits of Al, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Ti, V, and Zn. The samples include acidified Milli-Q water (open square) or acidified chelated seawater (open circle) after being processed by the FI-IC system. The detection limits are estimated by 3 times of the standard deviation of the blank value.
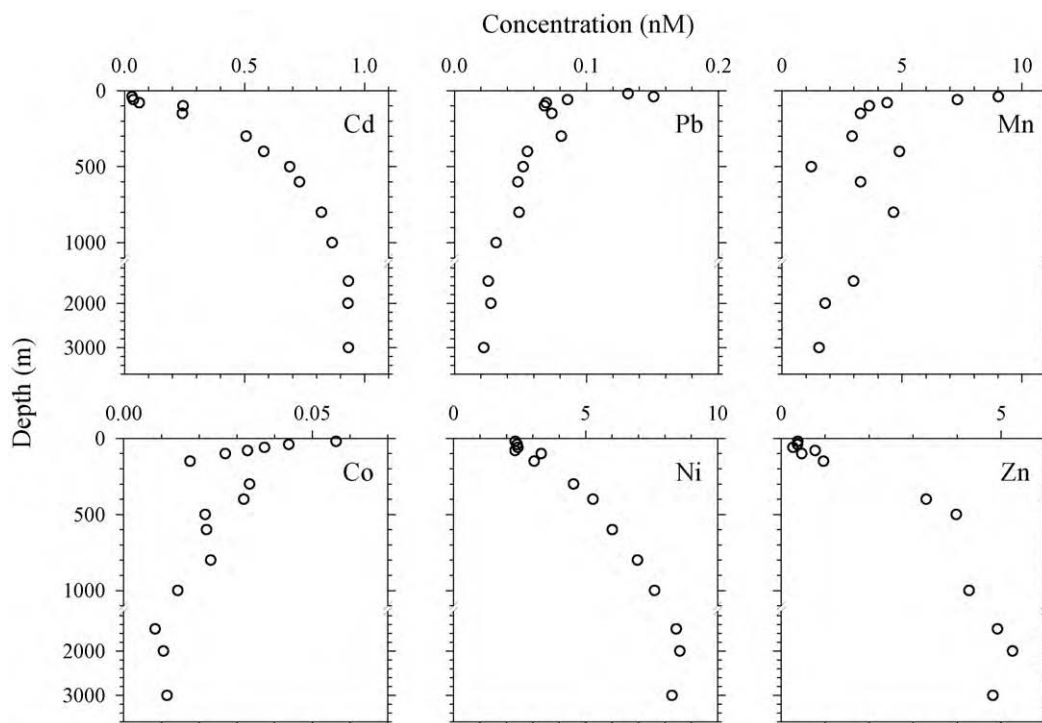
Fig. 4. Some trace metal profiles in oceanic water. The vertical profiles of some dissolved trace metals (Cd, Co, Mn, Ni, Pb, and Zn) in the water column of the South China Sea. The concentration unit stands for nanomole trace metal with per liter of seawater.

is automatically rinsed and washed by nitric acid and Milli-Q water sequentially (Table 1). By coupling the output of position 1 of the first 3-way valve to ICPMS directly, the offline system may become a FI-IC-ICPMS online system. The online setup is beyond the scope of this study. In the B position, both sample loop 2 and chelating column 1 are in loading mode and sample loop 1 and chelating column 2 are in injection mode. The timings for switching loading to injection modes for the valves and turning of the pumps on and off are programmed and controlled by the IC system. Detailed information is presented in Table 1.

2.2.3. ICPMS analysis

The eluted samples collected in polypropylene 15-mL vials would be ready for ICPMS analysis. We use sector field high resolution ICPMS (Element XR, Thermo, USA) with autosampler (ESI, SC-4, USA) coupled with PEEK standard probe (ESI Spectro AS-400) and desolvation apparatus. The pretreatment and desolvation apparatuses include an SC-FAST system (ESI) with a 1-mL sample loop, PFA ST nebulizer (ESI), Apex HF and Spiro TMD desolvation (ESI), 10-mm precision torch for an O-ring free removable injector (ESI), ESI 1.5-mm i.d. sapphire injector for Thermo-Finnigan Element, Ni sampler, and skimmer cones, under the conditions of 1200 W RF power and 16 L/min cooling gas. The plasma condition and the related mass spectrometer parameters were optimized for signal sensitivity and stability. Sensitivity of 1 ppb In is generally around 2 million counts per second under low resolution. The instrument precision for 1 ppb standard is generally between 1 and 2%. External and internal standards are both used to obtain accurate analysis. Sc, Y, and In were used as internal standards for trace metals analyzed. Two isotopes for elements with multiple natural isotopes were determined for the analysis to examine the influence of interference, including Ti 47, Ti 48, Cr 52, Cr 53, Fe 54, Fe 56, Ni 58, Ni 60, Cu 63, Cu 65, Zn 64, Zn 66, Cd 111, Cd 114, Pb 206, and Pb 208. All of the trace metals were analyzed under medium resolution except Cd and Pb, which were conducted under low resolution [15,16].

3. Results and discussion

3.1. Blank and detection limits

The determined isotopes for blank and detection limits include Al, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd, and Pb. After passing through the FI-IC system, the overall blank value and the detection limits with ICPMS analysis in pretreated acidified Milli-Q water and chelated seawater were presented in Figs. 2 and 3. The detection limits were estimated by using the equivalent concentrations of 3 times the standard deviation of replicated blanks in the Milli-Q water or seawater. The detection limits have been evaluated on different dates to obtain the possible range of the detection limits (Figs. 2 and 3). At least six blanks for each occasion were processed through the IC system and determined by ICPMS. Overall, although the blank value and detection limits of trace metals in Milli-Q water and chelated seawater varied from time to time, they generally ranged from 0.1 to 10 ppt (Figs. 2 and 3), except Zn, Fe and Al. The detection limits of Zn and Fe are a few tens of ppt for most occasions. The detection limits of Al generally ranged from a few tenth ppt to 200 ppt. Since the blank concentrations for the elements in the non-processed acidified Milli-Q water are almost all below 1 ppt and all below 5 ppt, the major source of the elevated blanks for Al, Fe, and Zn has to originate from the IC system itself during the pretreatment process. The detection limits of this pretreatment design for the three elements can be further improved when a chromatograph with lower blank value for Al, Fe, and Zn than the one we use is available. With the exception of Al, Fe, and Zn, the detection limits for most of trace metals determined in this study are at sub-ppt to low ppt or picomolar levels, which are sufficient to determine seawater samples from coastal to open-ocean regions for most bioactive trace metals. For Fe, Zn, and Al, their concentrations in the surface water of the open-ocean may be lower than the detection limits of this system.

Table 2
The comparison of measured concentrations with certified value in the CASS-4 and NASS-5 reference seawater.

Element	Measured isotope	NASS-5		CASS-4	
		Certified	This work	Certified	This work
Cr	52	110 ± 10	84 ± 18	144 ± 29	102 ± 7
Mn	55	919 ± 57	1097 ± 24	2780 ± 190	3205 ± 131
Fe	56	207 ± 35	179 ± 16	713 ± 58	688 ± 27
Co	59	11 ± 3	13.6 ± 0.7	26 ± 3	27 ± 1
Ni	60	253 ± 28	265 ± 14	314 ± 30	325 ± 16
Cu	63	297 ± 46	298 ± 14	592 ± 55	597 ± 21
Zn	64	103 ± 39	103 ± 36	381 ± 57	394 ± 48
Cd	111	23 ± 3	21.9 ± 1.99	26 ± 3	24.6 ± 3.7
Pb	206	8 ± 5	5.22 ± 0.81	9 ± 3	6.34 ± 1.17

3.2. Recovery and calibration curves

The quantification of trace metal concentrations in processed Milli-Q or seawater samples are carried out by adding known concentrations of trace metal mixed standards (High purity standard, USA) into acidified chelated seawater as explained in the method section. The concentration ranges of the calibration curves prepared were based on the certified concentrations of the NASS-5 and CASS-4 seawater reference materials (Table 2). The linear correlations for all other metals were all better than 0.999, except Al, Fe, and Zn, which are generally between 0.995 and 0.999. As expected, elevated blank values or intercepts were observed for Al, Fe, and Zn. The corresponding concentrations of these intercepts are considered to be the overall blank of sample pretreatment, which are subtracted while calculating sample concentrations.

The recovery of trace metals in seawater samples through the system was quantified by using non-processed standards. We first determine the pH and the concentrations of Ca and Mg in the eluted samples then prepared the non-processed standards by adjusting the pH and adding same amount of Ca and Mg as processed seawater samples contain. By using 1 ppb seawater samples as standards, the recovery of trace metals through the IC system were in the ranges of $103 \pm 5\%$ for all of the trace metals determined except Cu, which is around $85 \pm 5\%$. Since the calibration curves are also obtained from the standards processed through the IC system, the slightly higher or lower recovery would be generally cancelled out by calibration. The trace metal recovery of seawater samples by using the commercial chelating columns (Dionex MetPac CC1) at different pH were reported in details in the study [14].

3.3. Accuracy validation

To evaluate the accuracy of the pretreatment system on trace metal analysis in seawater, we determined trace metal concentrations in the reference seawater NASS-5 and CASS-4 (NRC, Canada). The reference seawaters were processed by our pretreatment system then determined by ICPMS. Except for the blank value of the standard, the precision of triplicate standards and SRM seawater samples were generally between 1 and 5%. The comparison of our analytical results with the certified averages is shown in Table 2. Overall, the measured concentrations are comparable for all of the known certified value. The slight difference for Cd and Pb between our results and the certified average value were statistically insignificant. The results indicate that the analytical accuracy of the pretreatment system is validated.

3.4. Application

The vertical profiles of some trace metals, determined using the pretreatment system with ICPMS, in the water column of the northern South China Sea were exhibited in Fig. 4. The systematic vertical profiles, which are consistent to our understanding about their concentration levels and vertical distributions, demonstrate that the pretreatment system provides accurate and precise data in oceanic water samples for multiple trace metals. Once the blank value is stable, we still obtain fairly reliable data for Fe, Zn, and Al, at least in the deeper waters. We have also obtained reliable data by using the system to process coastal seawater and seawater samples from marine aquariums, which are featured with elevated trace metal concentration. It appears that this pretreatment system is appropriate to be used for routine trace metal analysis in environmental samples, such as monitoring trace metal concentrations in estuarine and coastal waters, seawater cultures in laboratories, seawater in marine aquarium tanks, etc. In addition, the offline setup of this pretreatment system also allows using other trace metal detectors, such as graphite furnace atomic absorption spectrophotometer. The offline design of this system may potentially become a useful pretreatment tool to retrieve trace metals for isotope composition study in seawater matrix. The chemical separation pretreatment for isotope composition analysis is carried out manually and time consuming. We believe that the design of this pretreatment system can also be potentially applied to process other trace analytes in environmental samples with complex matrices by changing elution columns and elution reagents.

4. Conclusions

An automated and efficient new online pretreatment system for offline trace metal analysis in seawater by ICPMS has been established. This automated pretreatment system has been successfully applied to determine trace metal concentrations in natural seawater and environmental samples with seawater matrix. The reliable results have demonstrated that the system can obtain accurate concentrations in seawater samples and significantly enhance analytical capacity for multi-trace metal analysis in seawater samples.

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