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Accurate, precise and direct determination of dissolved phosphate and silicate in seawater by IEC SF-ICPMS

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ABSTRACT

A method is described for the accurate, precise and direct determination of dissolved phosphate and silicate in seawater using ion exclusion chromatography (IEC) for separation and sector field inductively coupled plasma mass spectrometry (SF-ICPMS) detection. Dissolved silicate was determined by isotope dilution and reverse isotope dilution IEC SF-ICPMS using a ^{29}Si spike. One point standard addition coupled with internal standardization of employing the same ^{29}Si spike was used to obtain dissolved phosphate concentration in seawater. Medium resolution was used for all measurements in order to resolve polyatomic interferences on Si and P isotopes. Concentrations of $1.686 \pm 0.008 \mu\text{M}$ and $30.20 \pm 0.09 \mu\text{M}$ (SD, $n=6$) with precisions of 0.47 and 0.31 % for the dissolved phosphate and silicate, respectively, were obtained in National Research Council of Canada (NRCC) seawater MOOS-3 using the proposed method, in good agreement with certified values of 1.60 ± 0.15 and $30.5 \pm 0.8 \mu\text{M}$ (U , $k=2$).

Seven- and ten- fold improvements in the precisions of dissolved phosphate and silicate using the proposed method were obtained as compared to that obtained using standard addition calibration alone. The reported method provides for a relatively rapid (10 minutes per run), simple and accurate on-line technique requiring no sample pre-treatment with high precisions of <0.5 % for dissolved phosphate and silicate, superior to these reported in previous studies. The detection limits (3σ) of 0.006 and 0.004 μM (0.06 as P and 0.14 ng g^{-1} as Si) for dissolved phosphate and silicate, respectively, with injection of 100 μl seawater were obtained, demonstrating the proposed technique is well suited to the determination of dissolved phosphate and silicate in seawater.

Keywords: One point standard addition with internal standardization, Isotope dilution, Inductively coupled plasma mass spectrometry, Ion exclusion chromatography

INTRODUCTION

The roles of micronutrients (i.e., nitrate, phosphate, and silicate) in seawater are of importance to the understanding of ocean circulation and ecological processes.¹⁻³ As a result, determinations of micronutrients in seawater are among the most commonly performed analyses in oceanographic research and survey work. Due to the demand of a seawater certified reference material (CRM) for nutrients for the validation of methodologies used for such analyses, National Research Council of Canada (NRCC) had released its first seawater CRM MOOS-1 for nutrients in 2002. Good agreement between two or more independent analysis methods is considered as an essential prerequisite for the certification of reference materials. Furthermore, methods with highest possible precision and accuracy for such measurements are required for the continue production of high quality CRMs. In this vein, to complement the well-known standard colorimetric methods⁴ for the determination of phosphate, silicate, nitrite and nitrate, alternative methodologies have been developed over the last decade. For example, Pagliano *et al.*⁵ recently reported a GC-MS method for the accurate and precise determination of nitrite and nitrate in seawater with relative combined uncertainties of 2.5 and 0.7 %, respectively, using exact matching double spike isotope dilution and derivatization with triethyloxonium tetrafluoroborate.

Up to date, apart from the standard colorimetric methods^{4, 6-9}, efforts were made to the development of new techniques for the determination of dissolved phosphate and silicate in seawater over the last decade. Two reports of the determination of dissolved phosphate in seawater based on di-isobutyl ketone extraction of reduced molybdoantimonylphosphoric acid from 500 mL samples with quantitation by inductively coupled plasma atomic emission spectrometry yielded a detection limit of 0.37 ng ml⁻¹ (0.01 µM) as P.¹⁰⁻¹¹ Dahllof and co-workers¹² also determined dissolved phosphate in seawater using anion exchange chromatography with conductivity detection, achieving a detection limit of 1 µM. More recently, Jońca *et al.*¹³ reported an electrochemical method for phosphate determination in seawater

based on the oxidation of molybdenum to form molybdates and protons, and subsequently to create phosphomolybdic complex electrochemically detectable by means of amperometry using a gold disk electrode and achieved a detection limit of $0.19\ \mu\text{M}$. Wang *et al.*¹⁴ reported an ion chromatography with cycling-column-switching method for phosphate and other anions determination in seawater and achieved a detection limit of $0.24\ \mu\text{M}$. For dissolved silicate, Rimmelin-Maury *et al.*¹⁵ reported a new method based on magnesium induced co-precipitation spectrophotometric method and achieved a detection limit of $0.003\ \mu\text{M}$ using 250 mL seawater.

Inductively coupled plasma mass spectrometry (ICPMS) is a sensitive technique for the determination of a wide range of metals and several nonmetals.¹⁶ The advantages of ICPMS as an elemental detector include low detection limits, large dynamic range, and multielement capability. Methods based on ion exclusion chromatography (IEC) and quadrupole ICPMS detection were thus developed in our previous studies for the quantification of dissolved phosphate¹⁷ and silicate² in seawater using standard additions calibration. Although elevated background signals on Si and P isotopes were reported in these studies due to polyatomic interferences using qICPMS, good detection limits of 0.06 and $0.08\ \mu\text{M}$, respectively, were still obtained for the dissolved phosphate and silicate based on injection of $100\ \mu\text{L}$ seawater with IEC qICPMS, superior to DLs obtained using standard colorimetric methods^{4, 6-9}. Polyatomic interferences on Si and P isotopes can be circumvented by either using medium resolution with a sector field (SF) ICPMS or qICPMS with reaction cell to resolve potential interferences. Moreover, if two interference-free isotopes of a given element can be found, isotope dilution ICPMS (ID ICPMS) can be considered, which generally provides superior accuracy and precision over other calibration strategies, including external calibration and standard additions, because a ratio, rather than an absolute intensity measurement, is used for the quantitation of analyte concentration.¹⁸⁻¹⁹ The objective of this study was to evaluate the application of isotope dilution and one

point standard addition with internal standardization using the same enriched ^{29}Si spike to IEC SF-ICPMS for the simultaneous, high accuracy and precision determination of dissolved silicate and phosphate in seawater. To the best of our knowledge, this is the first report of the application of isotope dilution calibration and one point standard addition with internal standardization for high accuracy and precision (RSDs <0.5%) determination of dissolved silicate and phosphate simultaneously in seawater.

EXPERIMENTAL SECTION

Instrumentation. An Agilent HPLC 1200 Series (Agilent Technologies Canada Inc., Mississauga, Ontario, Canada) with an ion exclusion column ICE-AS1 (9 mm id x 250 mm) from Thermo Fisher Scientific (Waltham, MA, USA) was used for the separation of analytes from the major ions in seawater. The coupling of LC to ICP-MS was accomplished by directing the eluent from the column to the nebuliser of the ICP-MS through a 1 m length of PEEK tubing (0.13 mm id, 1.59 mm od). The eluent was 0.01% HCl at a flow rate of 0.80 mL min^{-1} .

All measurements were made with a SF-ICPMS, Thermo Fisher Element2 (Bremen, Germany), equipped with a combination of cyclonic and Scott-type spray chambers. A PFA ST nebulizer ES-2040 (Elemental Scientific; Omaha, NE, USA) operating at 0.80 mL min^{-1} and medium resolution were used for all measurements. A plug-in quartz torch with a Quartz injector and a Pt guard electrode were used.

Reagents and Solutions. Hydrochloric acid was purified by subboiling distillation of reagent grade feedstock in a quartz still prior to use. Deionized water (DIW) was obtained from a Nanopure ion exchange reverse osmosis system (Barnstead/Thermolyne, Boston, MA, USA). High-purity sodium hydroxide (99.9995+ %) made by Fluka was purchased from Sigma-Aldrich (Oakville, ON, Canada). SRM 3186 Phosphate and SRM 3150 silicon stock solutions at 1.0002 ± 0.0017 and $10.458 \pm 0.032 \text{ mg g}^{-1}$ (U, 95% confidence interval) respectively, were purchased from National Institute of Standards and Technology (Gaithersburg, MD USA). Working standard solutions of 7400 ng g^{-1} (as P) and 45113 ng

g^{-1} (as Si) were prepared by serial dilutions of the respective stock in DIW. Isotopic enriched ^{29}Si in SiO_2 form (95%+ enrichment) was obtained from Trace Sciences International (Richmond Hill, ON, Canada). Stock solution of ^{29}Si ($500 \mu\text{g g}^{-1}$) was prepared by dissolution of the ^{29}Si enriched SiO_2 in 25 % NaOH solution according to the procedure described previously²¹⁻²², followed by dilution with DIW. A $100 \mu\text{g g}^{-1}$ ^{29}Si spike solution was prepared by dilution of the stock in DIW.

Nutrient-free seawater was purchased from Ocean Scientific International Ltd. (Surrey, UK). Seawater CRM MOOS-3 was obtained National Research Council Canada (Ottawa, ON, Canada) and was collected in the North Atlantic Ocean at a depth of 200 m, as described by Hioki *et al.*² and used for the validation of the proposed method.

Sample Preparation for the Determination of Dissolved Silicate by Isotope Dilution IEC SF-ICPMS. Samples were prepared in a class-10 or class-100 clean room environment. Six replicates of 15 g each of MOOS-3 seawater (namely MOOS 1-1 to 1-6) were accurately weighed into individual precleaned 25 mL polyethylene bottles. A suitable amount of the enriched ^{29}Si spike was then added to each bottle to achieve a near one ratio for $^{28}\text{Si}/^{29}\text{Si}$. Three sample blanks (namely BL 1-1 to 1-3) spiked with 15% of the amount of enriched ^{29}Si spike used for the samples were prepared along with the samples using a nutrient-free seawater. Prepared seawater samples were manually shaken for a few minutes and left on the bench for at least 24 hours in order to achieve isotopic equilibrium between the spike and the endogenous analyte in the seawater.

Calibration of the $103.00 \mu\text{g g}^{-1}$ ^{29}Si enriched spike was achieved by reverse isotope dilution. Four replicate reverse ID solutions (namely RSID 1-1 to 1-4) were prepared by accurately weighing 0.20 g of $103.00 \mu\text{g g}^{-1}$ ^{29}Si enriched spike into precleaned 25 mL PE plastic bottles. Aliquots of 0.40 g of 45113 ng g^{-1} natural abundance Si standard solution were added. The contents of each bottle were then diluted with 15 g DIW prior to IEC SF-ICPMS analysis.

Sample Preparation for the determination of Dissolved Phosphate by One Point Standard Addition Coupled with Internal Standardization IEC SF-ICPMS. Similarly, sample preparation for the determination of dissolved phosphate was undertaken in the same class-10 or class-100 clean room environment. To prepare P spiked samples (namely MOOS 1-1s to 1-6s), each 7.5 g of above ^{29}Si spiked MOOS-3 seawater samples (MOOS 1-1 to 1-6) was accurately weighed into individual precleaned 15 mL PE bottles. A suitable mass of 7400 ng g^{-1} (as P) dissolved phosphate standard was added to each of six P spiked samples, resulting in a spiked concentration of 1.5- to 2-fold to the endogenous phosphate concentration in seawater samples. The remaining 7.5 g each of six replicates of ^{29}Si spiked seawater samples (MOOS 1-1 to 1-6) served as the unspiked samples for phosphate determination. Similarly, for procedural blanks, spiked and unspiked solutions were prepared as above using three ^{29}Si spiked blanks (namely BL1-1 to 1-3 and BL 1-1s to 1-3s).

Measurement Procedure and Data Processing for IEC SF-ICPMS analysis. Optimization of the Element2 was performed as recommended by the manufacturer. The operating parameters of the SF-ICPMS and HPLC are given in Table 1. Medium resolution was used for all measurements in order to resolve polyatomic interferences on Si and P isotopes. The ^{29}Si spiked seawater samples, four reverse spike ID calibration solutions and six P spiked samples were analyzed on the same day. Samples were transferred into precleaned 1 mL polypropylene autosampler vials (Agilent Technologies Canada Inc., Mississauga, Ontario, Canada) for injections. The measurement sequence is presented in Table 2. A 100 μL of seawater was injected for IEC SF-ICPMS analysis. Data acquisition was manually triggered immediately after sample injection. ^{31}P , ^{28}Si and ^{29}Si were simultaneously monitored. A mass bias correction solution of a nature abundance 1000 ng g^{-1} Si standard was injected a few times during the sequence of analysis to permit mass bias correction on ratios. The mass bias correction was obtained by use of the theoretical natural abundance ratio of Si (assumed IUPAC abundance²³) divided by the

measured $^{28}\text{Si}/^{29}\text{Si}$ ratio. At the end of the chromatographic run, the acquired raw data were transferred to an off-line computer for further processing using in-house software, which yields both background-corrected peak height and peak area. Peak areas were used to generate $^{28}\text{Si}/^{29}\text{Si}$ and $^{31}\text{P}/^{29}\text{Si}$ ratios, from which the analyte concentrations in the seawater were calculated.

RESULTS AND DISCUSSION

As noted in previous studies^{2, 17} wherein a qICPMS was used, high background signals on ^{28}Si , ^{29}Si , ^{30}Si and ^{31}P isotopes were observed due to polyatomic interferences such $^{12}\text{C}^{16}\text{O}^+$, $^{14}\text{N}_2^+$, $^{28}\text{Si}^1\text{H}^+$, $^{13}\text{C}^{16}\text{O}^+$, $^{12}\text{C}^{16}\text{O}^1\text{H}^+$, $^{14}\text{N}^{15}\text{N}^+$, $^{14}\text{N}_2^1\text{H}^+$, $^{14}\text{N}^{16}\text{O}^+$, $^{13}\text{C}^{16}\text{O}^1\text{H}^+$, $^{14}\text{N}^{15}\text{N}^1\text{H}^+$ on Si isotopes and $^{14}\text{N}^{16}\text{O}^1\text{H}^+$, $^{15}\text{N}^{16}\text{O}^+$ on P isotope. To achieve accurate Si isotope ratio and P measurements, medium resolution was thus employed throughout all measurements in order to resolve these potential polyatomic interferences. As shown in Figure 1, good peak shapes for both phosphate and silicate were obtained for the MOOS-3 seawater by IEC SF-ICPMS. Slightly modified eluting conditions of 0.01% HCl as eluent at a flow rate of 0.80 mL min^{-1} were used in this study instead of original both higher HCl concentration and flow rate used in previous studies^{2, 17}, in consideration of the preservation of the stainless HPLC pump head and the proper range of flow rate of the nebulizer used in this study.

Quantitation of Dissolved Si in Seawater by Isotope Dilution IEC SF-ICPMS. As noted earlier, ID-MS technique is capable of generating high accuracy and precision results, providing the isotopic equilibrium is achieved between the added spike and the endogenous analyte in the sample, and as well as two interference free isotopes are available. To confirm interference free measurements of $^{28}\text{Si}/^{29}\text{Si}$ ratio in MOOS-3 seawater, natural MOOS-3 seawater was injected a few times for the IEC SF-ICPMS analysis under chosen experimental conditions. A value of 19.68 ± 0.17 (1 SD, $n=6$) mass bias corrected $^{28}\text{Si}/^{29}\text{Si}$ ratio was obtained in the natural MOOS-3 seawater, not significantly different from the expected natural abundance ratio of 19.685 based on IUPAC value²³. This confirms that no significant spectroscopic

interferences on either Si isotope arise from the seawater sample matrix, permitting accurate analytical results to be obtained. However, results would be biased if isotopic equilibrium between the added spike and the endogenous analyte in the sample was not achieved prior to the ratio measurements. This is usually attained relatively quickly in single-phase systems such as water.^{20, 24} Results for $^{28}\text{Si}/^{29}\text{Si}$ ratio obtained from one of ^{29}Si spiked MOOS-3 seawater measured on the second day, 7th day and 30th day later after sample preparation showed no significant differences. This observation confirms that isotopic equilibrium between the added spike and the endogenous analyte in the seawater sample can be achieved within 24 hours.

The following equation was used for the quantitation of dissolved silicate in seawater samples based on isotope dilution and reverse isotope dilution:

$$w_x = w_z \cdot \frac{m_y}{m_x} \cdot \frac{m_z}{m'_y} \cdot \frac{A_y - B_y \cdot K \cdot r}{B_{xz} \cdot K \cdot r - A_{xz}} \cdot \frac{B_{xz} \cdot K \cdot r' - A_{xz}}{A_y - B_y \cdot K \cdot r'} \cdot \frac{d}{A_r(\text{Si})} \quad (1)$$

where:

- w_x is the analyte concentration in the sample (μM);
- w_z is the analyte concentration as Si in natural abundance primary standard solution (ng g^{-1});
- m_y is the mass of ^{29}Si enriched spike solution used to prepare the mixture of sample and spike (g);
- m_x is the mass of sample used (g);
- m_z is the mass of natural abundance primary standard used (g) to prepare the mixture of spike and primary standard;
- m'_y is the mass of spike used to prepare the mixture of spike and primary standard (g);
- A_y is the abundance of the reference isotope (^{28}Si) in the spike;
- B_y is the abundance of the spike isotope (^{29}Si) in the spike;
- A_{xz} is the abundance of the reference isotope (^{28}Si) in the sample or primary standard;
- B_{xz} is the abundance of the spike isotope (^{29}Si) in the sample or primary standard;
- K is the mass bias correction factor obtained by using IUPAC value of $^{28}\text{Si}/^{29}\text{Si}$ divide by measured value;
- r is the measured reference/spike $^{28}\text{Si}/^{29}\text{Si}$ isotope ratio in the mixture solution of sample and spike;
- r' is the measured reference/spike $^{28}\text{Si}/^{29}\text{Si}$ isotope ratio in the mixture solution of spike and primary standard;
- d is the density of the seawater (g mL^{-1});
- $A_r(\text{Si})$ is the atomic weight of Si;

As clearly expressed by this equation, only $^{28}\text{Si}/^{29}\text{Si}$ isotope ratios in the spiked MOOS-3 and reverse ID

calibration solutions, and mass bias correction factor need to be determined to derive the final analyte concentration. In order to measure both dissolved phosphate and silicate simultaneously, phosphate spiked blanks (BL1-1s to 1-3s) and samples (MOOS 1-1s to 1-6s) were run along with samples prepared for the dissolved silicate, as show in Table 2 injection sequence. However, only $^{28}\text{Si}/^{29}\text{Si}$ isotope ratios measured in 1000 ng g⁻¹ Si standard, three blanks (BL1-1 to 1-3), MOOS-3 samples (MOOS 1-1 to 1-6) and four ID calibration solutions (RSID 1-1 to 1-4) were used for the calculation of dissolved silicate concentration. A value of 30.20±0.09 (1SD, n=6) with a relative standard deviation (RSD) of 0.31 % for dissolved silicate was obtained in MOOS-3 seawater, in good agreement with the certified value of 30.5±0.8 (*U*, k=2), confirming the accuracy of the proposed method. A detection limit of 0.004 μM (0.14 ng g⁻¹ as Si) was estimated for the dissolved silicate, based on three times the standard deviation of the measured analyte concentrations in three blanks normalized to 15 g subsamples used for MOOS-3 seawater and 100 μL injection volume, superior to these reported in previous studies^{2, 4, 6-7, 15}.

For comparison, subsequent experiments based on one point standard addition calibration were conducted for the dissolved silicate in MOOS-3 seawater. The dissolved silicate concentration in the sample based on one point standard addition was calculated using the following equation:

$$w_x = \left(\frac{I_{un} \cdot w_z \cdot m_{sp}}{I_{sp} \cdot m_f - I_{un} \cdot m_0} \right) \cdot \frac{d}{A_r(\text{Si})} \quad (2)$$

where:

- w_x is the analyte concentration in the sample (μM);
- w_z is the analyte concentration as Si in primary standard solution (ng g⁻¹);
- m_0 is the mass of seawater solution used to prepare the spiked sample (g);
- m_{sp} is the mass of Si standard solution used to prepare the spiked sample (g);
- m_f is the sum mass of mass of m_0 and m_{sp} (g);
- I_{un} is the measured intensity of the analyte isotope (^{28}Si) in the unspiked sample (cps);
- I_{sp} is the measured intensity of the analyte isotope (^{28}Si) in the spiked sample (cps);
- d is the density of the seawater (g mL⁻¹);
- $A_r(\text{Si})$ is the atomic weight of Si.

Values of 30.25±0.94 (1SD, n=6) and 30.23±0.46 (1SD, n=6) with RSDs of 3.1 and 1.5 % for dissolved

silicate in MOOS-3 seawater were obtained for the injection of unspiked sample and spiked sample in pairs and for the bracketing injection of unspiked sample-spiked sample-unspiked sample (as shown in Table 2), respectively. Clearly, bracketing measurements of unspiked sample-spiked sample-unspiked sample provided 2-fold improvement in precision, simply due to its better correction of instrument drift over time. As expected, 5- to 10-fold improvement in the precision of dissolved silicate was obtained using ID IEC SF-ICPMS method compared to standard addition methods, confirming the superiority of ID method.

Quantitation of Dissolved Phosphate in Seawater by IEC SF-ICPMS. Unfortunately phosphorus is a monoisotopic element and thus preventing the use of ID for the determination of dissolved phosphate in seawater. It is known that suppression of ion sensitivities by concomitant elements in the sample matrix and instrument drift can often occur with ICPMS detection. To improve measurement precision and accuracy, internal standard is often used with external calibration for the determination of trace elements by ICPMS²⁵⁻³⁰. To overcome matrix effect arising from seawater, previous¹⁷ qICPMS based study employed standard addition method for its quantification and reported a RSD of 2.4% for dissolved phosphate. A recent study³¹ has shown that better measurement precisions can be obtained by using a combination of standard addition and internal standardization for the determination of trace elements using ICPMS. Thus, one point standard addition with internal standardization of using ²⁹Si spike was applied for the determination of dissolved phosphate in MOOS-3 seawater.

The following equation was used to calculate dissolved phosphate concentration in the sample based on the one point standard addition with internal standardization of using ²⁹Si spike:

$$w_x = \frac{w_z \cdot m_{sp}}{m_0} \cdot \frac{R_{un}}{R_{sp} - R_{un}} \cdot \frac{m_x + m_y}{m_x} \cdot \frac{d}{A_r(P)} \quad (3)$$

where:

w_x is the analyte concentration in the sample (μM);

w_z is the analyte concentration as P in primary standard solution (ng g^{-1});

m_0 is the mass of seawater (already spiked with ²⁹Si) to prepare the P spiked sample (g);

m_{sp} is the mass of P standard solution used to prepare the P spiked sample (g);
 m_x is the mass of original seawater used to prepare the mixture of sample and enriched ^{29}Si spike (g);
 m_y is the mass of ^{29}Si enriched spike solution used to prepare the mixture of sample and enriched spike (g);
 R_{un} is the measured intensity ratio ($^{31}\text{P}/^{29}\text{Si}$) of analyte to internal standard in the unspiked sample;
 R_{sp} is the measured intensity ratio ($^{31}\text{P}/^{29}\text{Si}$) of analyte to internal standard in the spiked sample;
 d is the density of the seawater (g mL^{-1});
 $A_r(\text{P})$ is the atomic weight of P.

A value of 1.686 ± 0.008 (1SD, $n=6$) with a RSD of 0.46 % for dissolved phosphate in MOOS-3 seawater was obtained using the bracketing injection of unspiked sample-spiked sample-unspiked sample (shown in Table 2). The dissolved phosphate concentration measured using the proposed method is in good agreement with the certified value of 1.60 ± 0.15 (U, $k=2$), confirming the accuracy of the proposed method. A value of 1.687 ± 0.023 (1SD, $n=6$) with a poorer RSD of 1.35 % for dissolved phosphate in MOOS-3 seawater was obtained with injections of unspiked sample and spiked sample in pairs. For comparison, a value of 1.701 ± 0.057 (1SD, $n=6$) with a RSD of 3.35 % was obtained for the dissolved phosphate with use of one point standard addition alone based on ^{31}P intensities. Clearly, use of an internal standard, ^{29}Si in this case, significantly improves the measurement precision, about 2.5-fold for the dissolved phosphate. Furthermore, a close to 3-fold in measurement precision is evident with use of one point standard addition coupled with internal standardization using ^{29}Si spike and bracketing injections of unspiked sample-spiked sample-unspiked sample, resulting from a better correction of instrument drift over time using such approach. It is worth to note that internal standard other than ^{29}Si such as ^{28}Si or other element isotopes can be used providing they can be eluted out from the IEC near phosphate peak during the IEC SF-ICPMS analysis.

CONCLUSION

An accurate, precise and direct method is described for the determination of dissolved phosphate and silicate simultaneously in seawater using ID and one point standard addition coupled with internal

standardization IEC SF-ICPMS. The reported method provides for a relatively rapid (10 minutes per run), simple and accurate on-line technique requiring no sample pre-treatment with high precisions of <0.5 % for both dissolved phosphate and silicate, superior to that reported in previous studies^{2, 4, 6-17}. The method achieves sufficiently low DLs of 0.006 and 0.004 μM (0.06 and 0.14 ng g^{-1}) for dissolved phosphate and silicate, respectively, with injection of only 100 μl seawater, superior to that achieved using standard colorimetric methods or other techniques.^{2, 4, 6-17}. To the best of our knowledge this is the first report of the application of isotope dilution calibration and one point standard addition with internal standardization for high accuracy and precision (<0.5%) determination of dissolved silicate and phosphate simultaneously in seawater.

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Table 1. LC-ICPMS Operating Conditions

	Element2 ICP-MS
Rf power	1125 W
Plasma Ar gas flow rate	15.0 l min ⁻¹
Auxiliary Ar gas flow rate	1.0 l min ⁻¹
Nebulizer Ar gas flow rate	0.995 l min ⁻¹
Sampler cone orifice (nickel)	1.00 mm
Skimmer cone orifice (nickel)	0.88 mm
Lens voltage	Focus: -920 V; x deflection: -3.54 V; y deflection: 12.24 V; Shape: 102 V
Dead Time	13 ns
Resolution	4000 Medium resolution (mass offset and lock mass features used)
Data acquisition	E-scan, 100 % mass window, 0.001s settling time, 0.040s sample time, 10 samples per peak, 500 runs and 1 pass, 60% integration window
	Agilent HPLC 1200 Series
Column	ICE-AS1 (9 mm id x 250 mm)
Mobile phase A	0.01% HCl
Isocratic elution	100% A
Injection volume	100 µL

**Table 2. Injection Sequence for the Determination of Dissolved Phosphate and Silicate in Seawater
by IEC SF-ICPMS**

1, 1000 ng g ⁻¹ Si standard	18, MOOS 1-3
2, BL1-1	19, MOOS 1-3s
3, BL1-1s	20, MOOS 1-3
4, BL1-2	21, MOOS 1-4
5, BL1-2s	22, MOOS 1-4s
6, BL1-3	23, MOOS 1-4
7, BL1-3s	24, RSID 1-3
8, RSID 1-1	25, 1000 ng g ⁻¹ Si standard
9, 1000 ng g ⁻¹ Si standard	26, MOOS 1-5
10, MOOS 1-1	27, MOOS 1-5s
11, MOOS 1-1s	28, MOOS 1-5
12, MOOS 1-1	29, MOOS 1-6
13, MOOS 1-2	30, MOOS 1-6s
14, MOOS 1-2s	31, MOOS 1-6
15, MOOS 1-2	32, RS1-4
16 RSID 1-2	33, 1000 ng g ⁻¹ Si standard
17, 1000 ng g ⁻¹ Si standard

Figure 1. Chromatogram of an injection of 50 μL ^{29}Si spiked MOOS-3 seawater; ^{28}Si (solid black line), ^{29}Si (dash black line) and ^{31}P (solid grey line).