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Publisher's version / Version de l'éditeur:

<https://doi.org/10.1039/b104634a>

Journal of Analytical Atomic Spectrometry, 16, 11, pp. 1302-1306, 2001

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On-line determination of dissolved phosphate in sea-water by ion-exclusion chromatography inductively coupled plasma mass spectrometry†

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Received 29th May 2001, Accepted 22nd August 2001

First published as an Advance Article on the web 5th October 2001

Direct determination of dissolved phosphate in sea-water by ion-exclusion chromatography in combination with inductively coupled plasma mass spectrometry is described. This method was developed as an independent, complementary approach to the standard colorimetric procedure used for the determination of dissolved phosphate in a proposed sea-water reference material. The developed on-line method is rapid, simple and accurate, requiring no sample pre-treatment. One determination can be completed in 6 min. The detection limit (3σ), estimated at $0.06 \mu\text{M}$ (2.0 ng ml^{-1} as P) with injection of only $100 \mu\text{l}$ of sea-water, is superior to the $0.15 \mu\text{M}$ achieved using colorimetry. The dissolved phosphate concentration in sea-water of $1.69 \pm 0.04 \mu\text{M}$ measured by a standard additions technique using the proposed method is in good agreement with the $1.71 \pm 0.04 \mu\text{M}$ determined using a classic colorimetric approach.

Introduction

The roles of micronutrients (*i.e.*, nitrate, phosphate and dissolved silica) in sea-water are of importance to the understanding of ecological processes. Determinations of micronutrients in sea-water are among the most commonly performed analyses in oceanographic research and survey work. The accuracy of such analyses cannot be directly verified if a certified reference material (CRM) is not available for quality assurance. The National Research Council of Canada (NRCC) has undertaken a project, in collaboration with the Bedford Institute of Oceanography (BIO) of the Canadian Department of Fisheries and Oceans, to address the need for a sea-water CRM for nitrate, phosphate and dissolved silica micronutrients.

Good agreement between two or more independent analysis methods is considered an essential prerequisite for the certification of reference materials. One of the project objectives is to develop alternative methods to complement the well-known standard colorimetric methods. Hioki *et al.* refined a method for the direct determination of nitrate in sea-water by ion chromatography with UV absorbance detection.¹ The determination of dissolved silica in sea-water using ion-exclusion chromatography (IEC) with inductively coupled plasma mass spectrometry (ICP-MS) has also been reported.² In this study, a method is described for the direct determination of dissolved phosphate in sea-water using a combination of IEC with ICP-MS without any pre-treatment of the sea-water samples.

Phosphate in natural, waste and industrial waters has been determined by a variety of techniques.^{3–13} The two most commonly used colorimetric methods for phosphate determination rely on either the yellow coloured vanadomolybdate method for relatively high phosphate concentrations or the molybdenum blue procedure for relatively low phosphate concentrations.^{3–5} Barciela Alonso and Prego⁶ determined phosphate in river waters by capillary electrophoresis, reporting a detection limit of $0.60 \mu\text{M}$. Simonet *et al.*⁷ recently

published a technique for phosphate determination in urine by sequential injection analysis based on the inhibitory action of phosphate on the crystallisation of calcium carbonate. A detection limit of 10 ng ml^{-1} ($0.3 \mu\text{M}$) was achieved. Ledo de Medina *et al.*⁸ determined phosphate in estuarine water using ion chromatography and reported a detection limit of 1 ng ml^{-1} ($0.03 \mu\text{M}$).

There are few publications addressing the determination of phosphate in sea-water. Two reports of the determination of dissolved phosphate in sea-water based on diisobutyl 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} ($0.01 \mu\text{M}$) as P.^{9,10} Dahllof *et al.* also determined dissolved phosphate in sea-water using anion-exchange chromatography with conductivity detection, achieving a detection limit of $1 \mu\text{M}$.

Dissolved phosphorus is believed to exist as orthophosphate in sea-water.¹⁴ At pH 8.0, about 1% of the orthophosphate is present as H_2PO_4^- , 87% as HPO_4^{2-} and 12% as PO_4^{3-} . Phosphoric acid is a weakly dissociated inorganic acid having dissociation constants of $K_1 = 2.35 \times 10^{-3}$, $K_2 = 8.8 \times 10^{-7}$ and $K_3 = 1.37 \times 10^{-7}$ at 20°C in 3.3% salinity sea-water. It can therefore be separated from strong acids such as HCl, HNO_3 and H_2SO_4 by ion-exclusion chromatography using a simple eluent such as deionized water (DW) and dilute HCl.¹⁵ These eluents are ideal for ICP-MS analysis. In the present work, advantage was taken of the high sensitivity and selectivity of ICP-MS as a detector for on-line determination of phosphate separated from major sea-water ions by IEC. To the best of our knowledge, this is the first reported use of either ICP-MS or IEC for the direct determination of dissolved phosphate in sea-water.

Experimental

Apparatus

A Model AGP-1 advanced gradient pump (Dionex, Sunnyvale, CA) was used for IEC. Samples were injected onto the column

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using a microinjection valve from a Dionex Model LCM liquid chromatography module, equipped with an injection loop of 100 μl nominal volume. A Dionex IonPac ICE-AS1 ion-exclusion column (9 mm id $\times$ 250 mm) having a capacity of 27 mequiv was used for separation of phosphate from the major ions in sea-water. The eluent was 50 mM HCl at a flow rate of 1.20 ml min^{-1} . The effluent from the column was directed to the ICP-MS nebulizer through a 0.3 m length of PEEK tubing (0.254 mm id, 1.59 mm od).

All measurements were made with a PerkinElmer SCIEX (Concord, Ontario, Canada) Elan 6000 ICP-MS equipped with a Rytan cross-flow nebulizer. A quartz torch with an alumina sample injector tube was used. The double pass Rytan spray chamber was mounted outside the torch box and maintained at room temperature. The operating conditions used for measuring P^+ at m/z 31 and PO^+ at m/z 47 in separate runs are given in Table 1.

Reagents and solutions

Hydrochloric acid and nitric acid were purified by sub-boiling distillation of reagent grade feedstocks in a quartz still prior to use. Deionized water (DW) was obtained from a Nanopure ion-exchange reverse osmosis system (Barnstead/Thermolyne, Boston, MA, USA). Reagent grade Na_2HPO_4 was purchased from Anachemia Science (Montreal, Quebec, Canada). A 1000 $\mu\text{g ml}^{-1}$ (as P) stock solution of Na_2HPO_4 was prepared by dissolving Na_2HPO_4 in DW. A 10 $\mu\text{g ml}^{-1}$ (as P) working standard was then prepared by dilution of 1000 $\mu\text{g ml}^{-1}$ in DW. Isotopically enriched sodium bicarbonate (99.4 at% ^{13}C) was purchased from Isotec Inc. (Miamisburg, OH, USA). A 2.0 μM phosphate standard in 3.05% NaCl solution was purchased from Wako Pure Chemical Industries Ltd. (Richmond, VA, USA).

Nutrient-free sea-water was purchased from Ocean Scientific International Ltd. (Surrey, UK). A sea-water sample was collected in the North Atlantic Ocean at a depth of 200 m, as described by Hioki *et al.*²

Procedure

Prior to chromatographic analysis, the ICP-MS instrument was optimized daily for nebulizer gas flow, lens voltage and rf power to achieve the best signal-to-background ratio for P^+ at m/z 31 and PO^+ at m/z 47 using a 15 μM phosphate standard solution and DW at a 1.0 ml min^{-1} flow rate. Typical operating conditions for P^+ and PO^+ are summarized in Table 1. The optimum conditions for achieving the best separation and shortest retention time by IEC were also investigated for various eluent concentrations and flow rates.

For sea-water analysis, an aliquot of about 0.5 ml was used to flush and fill the 100 μl injection loop. Data acquisition was manually triggered immediately after sample injection. Raw data were processed off line using in-house software which

yields both peak height and peak area. Quantitation was based on calibration by the method of standard additions.

Results and discussion

Optimization

Phosphorus is a monoisotopic element having a high ionization energy (10.49 eV). Under normal hot plasma conditions with a quadrupole ICP-MS, the high background arises principally from $^{14}\text{N}^{16}\text{OH}$ at m/z 31, which degrades the detection power for this element. An alternative means of determining phosphorus was explored by monitoring PO^+ under cold plasma conditions at m/z 47. Cold plasma conditions were optimised for PO^+ through a study of the influence of nebulizer gas flow, lens voltage and rf power on intensity from a 15 μM phosphate standard solution and DW. Optimum conditions for P^+ at m/z 31 were established using a similar approach. A signal-to-background ratio of 125 was obtained for PO^+ at m/z 47 under optimum conditions compared to that of 30 obtained under optimum conditions for P^+ at m/z 31 (optimum conditions for detection of both analytes are shown in Table 1). A detection limit of 0.04 μM , based on a 100 μl sample injection volume, was estimated under optimum operating conditions for PO^+ . This was slightly better than a value of 0.06 μM obtained under optimum conditions for P^+ . Both detection limits, obtained under optimum conditions for P^+ and PO^+ , are superior to 0.15 μM achieved by a classic molybdenum blue colorimetric method. As a consequence, both conditions were tested in the present study for determination of phosphate in sea-water.

The retention time for phosphate in sea-water spiked at a concentration of 3.0 μM was not appreciably altered by use of hydrochloric acid eluent over a concentration range from 25 to 200 mM. Addition of acid to the eluent suppresses dissociation of phosphoric acid, and significantly improves the peak shape. The broadest peak width and shortest peak height were observed when DW was used as the eluent. When the acid concentration was increased beyond 50 mM, no further improvement in peak height was observed. As such, 50 mM HCl was selected as the eluent for subsequent experiments. The maximum manufacturer-specified flow rate for the Dionex IonPac ICE-AS1 ion-exclusion column is 1.5 ml min^{-1} . Flow rates from 0.80 to 1.4 ml min^{-1} were thus investigated in an effort to obtain the best separation and shortest retention time possible. Retention times for phosphate in sea-water decreased from 430 to 260 s as the flow rate increased from 0.80 to 1.4 ml min^{-1} . The signal-to-background ratio (peak height in counts s^{-1} divided by background height in counts s^{-1}) improved from 2.7 to 3.3 as the flow rate increased from 0.80 to 1.20 ml min^{-1} , but dropped to 3.0 as the flow rate increased to 1.40 ml min^{-1} . Retention time for phosphate decreased slightly from 290 s at a flow rate of 1.20 ml min^{-1} to 260 s at 1.40 ml min^{-1} . A flow rate of 1.20 ml min^{-1} was therefore chosen for further study as result of its effects on both retention time and signal-to-background ratio.

Interferences

The chromatogram of a 6.2 μM phosphate standard in DW, run under the experimental conditions chosen for PO^+ at m/z 47, contained a single peak at 290 s. Under the same conditions, the chromatogram from North Atlantic sea-water, which has a dissolved phosphate concentration of about 1.7 μM , generated two additional peaks at 235 s and 590 s, as shown in Fig. 1b. Responses from the two m/z 47 peaks at 235 s and 590 s in sea-water were independent of any phosphate spiked into the sample, indicating that they arise from species other than phosphorus. Since carbonic acid is a weak inorganic acid, it may exhibit some retention on an ion-exclusion column.

Table 1 ICP-MS operating conditions

	P^+	PO^+
Rf power	1000 W	850 W
Plasma Ar gas flow rate	15.0 l min^{-1}	15.0 l min^{-1}
Auxiliary Ar gas flow rate	1.0 l min^{-1}	1.0 l min^{-1}
Nebulizer Ar gas flow rate	0.700 l min^{-1}	0.875 l min^{-1}
Sampler cone (nickel)	1.00 mm	1.00 mm
Skimmer cone (nickel)	0.88 mm	0.88 mm
Lens voltage	6.75 V	3.0 V
Scanning mode	Peak hopping	Peak hopping
Points per peak	1	1
Dwell time	100 ms	100 ms
Sweeps per reading	1	1
Readings per replicate	3500	6500
Number of replicates	1	1

Fig. 1 Chromatograms obtained under optimum operating conditions for PO^+ . a: 6.2 μM phosphate standard solution. b: North Atlantic sea-water.

The chromatogram from the North Atlantic sea-water at m/z 13 contained a single peak at 590 s, indicating some retention of carbonic acid on this IEC-AS1 column, but it was temporally well separated from that of phosphate at 290 s as shown in Fig. 1b. The possibility that this peak corresponded to $^{12}\text{C}^{16}\text{O}^{18}\text{OH}$ and $^{13}\text{C}^{16}\text{O}^{18}\text{O}$ was tested by acquiring chromatograms of 2 mM NaHCO_3 and 2 mM $\text{NaH}^{13}\text{CO}_3$ solutions in DW. Chromatograms at 590 s for m/z 45, 46, 47 and 48 for 2 mM NaHCO_3 (a concentration that is approximately the sum of carbonate and bicarbonate species in sea-water) shown in Fig. 2b had features similar to chromatograms obtained with sea-water shown in Fig. 2a. This suggests that the peak observed at 590 s for m/z 47 in sea-water arises from carbon-containing polyatomic species. The chromatograms of 2 mM $\text{NaH}^{13}\text{CO}_3$ solution had peaks at m/z 46 and 48 at 590 s in addition to the peaks at m/z 47 and 45 shown in Fig. 2c. If the peak at m/z 47 was due to $^{12}\text{C}^{35}\text{Cl}$ in sea-water, then no peak should be detected at m/z 47, but a peak at m/z 48 ($^{13}\text{C}^{35}\text{Cl}$) should be observed when running a $\text{NaH}^{13}\text{CO}_3$ (contains 99.4 % ^{13}C) solution. The peak observed at 590 s for m/z 45 in $\text{NaH}^{13}\text{CO}_3$ solution could only be contributed by $^{13}\text{C}^{16}\text{O}^{16}\text{O}$, and the smaller peak at m/z 46 by $^{13}\text{C}^{16}\text{O}^{16}\text{OH}$. Furthermore, the chromatogram for sea-water at 590 s for m/z 45 also contained a small peak, probably arising from $^{12}\text{C}^{16}\text{O}^{16}\text{OH}$.

Since nitric, hydrochloric and sulfuric acids are strong inorganic acids, they are not retained on an ion-exclusion column and elute within the exclusion volume. Under the conditions used to detect PO^+ , a single peak at 235 s was registered when monitoring m/z 34, 37 and 23, indicating that a good separation from sulfate, chloride and sodium (and, by inference, other major sea-water ions) had been achieved. Potential interfering polyatomic species at m/z 47, which can be expected to arise from direct injection of sea-water, include $^{32}\text{S}^{14}\text{NH}$, $^{33}\text{S}^{14}\text{N}$, $^{14}\text{N}^{16}\text{O}^{16}\text{OH}$, $^{30}\text{Si}^{16}\text{OH}$, $^{13}\text{C}^{16}\text{O}^{18}\text{O}$, $^{12}\text{C}^{16}\text{O}^{18}\text{OH}$ and $^{12}\text{C}^{35}\text{Cl}$. With the higher nebulizer gas flow and lower rf power used for PO^+ detection, a higher percentage of oxides and hydroxides is expected to arise. The possibility that the peak observed at 235 s for m/z 47 in sea-water corresponded to $^{32}\text{S}^{14}\text{NH}$ and $^{33}\text{S}^{14}\text{N}$ was tested by obtaining chromatograms for solutions containing 0.03 M Na_2SO_4 , 0.3 M Na_2SO_4 and 300 μM HNO_3 . No peak occurred at 235 s for m/z 47 with a 300 μM HNO_3 solution (a concentration approximately five times the sum of nitrogen

Fig. 2 Chromatograms obtained under optimum operating conditions for PO^+ . a: North Atlantic sea-water. b: 2 mM NaHCO_3 solution. c: 2 mM $\text{NaH}^{13}\text{CO}_3$ solution.

gas, nitrate and nitrite species in the sea-water). This indicates that no significant $^{14}\text{N}^{16}\text{O}^{16}\text{OH}$ interference arises from the sea-water matrix under these experimental conditions. The m/z 47 chromatogram of a 0.03 M Na_2SO_4 solution (approximately the sulfate concentration in sea-water) contained a peak at 235 s, the height of which was in the same proportion as the peak obtained for unspiked sea-water shown in Fig. 3b. This suggests that the peak at 235 s for m/z 47 in sea-water arises from sulfur-containing polyatomic species. A much higher peak at 235 s was generated when 0.3 M Na_2SO_4 solution was used, further confirming this hypothesis [reagent grade Na_2SO_4 also evidently contained some phosphate (peak at 290 s)]. All observations indicate that the peak obtained at 235 s for m/z 47 in sea-water corresponds to polyatomic species of $^{32}\text{S}^{14}\text{NH}$ and $^{33}\text{S}^{14}\text{N}$ rather than $^{14}\text{N}^{16}\text{O}^{16}\text{OH}$.

Preliminary studies found that the retention time for silicic acid was the same as for phosphate at 290 s. An investigation to determine if $^{30}\text{Si}^{16}\text{OH}$ posted significant interference on PO^+ at m/z 47 was conducted. Chromatograms of nutrient-free sea-water and nutrient-free sea-water spiked with Si at a concentration of 200 μM (approximately eight times higher than the Si concentration in the North Atlantic sea-water studied here) were obtained. No peak at 290 s for m/z 47 was generated in nutrient free sea-water, but one appeared for the Si-spiked nutrient-free sea-water with an intensity similar to the peak observed for the North Atlantic sea-water. These observations indicate that PO^+ at m/z 47 is subject to $^{30}\text{Si}^{16}\text{OH}$ interference. The North Atlantic sea-water had a dissolved silicate concentration of about 25 μM , which could result in a 7–8% apparent enhancement of the phosphate concentration in this sample when quantitated *via* measurement of PO^+ (see analytical results section).

The chromatogram of the North Atlantic sample for m/z 31 shown in Fig. 4a contained a single peak at 290 s, identical to the DW phosphate standard solution. Under the optimal experimental conditions for detection of P^+ at m/z 31, a good

Fig. 3 Chromatograms obtained under optimum operating conditions for PO^+ . a: North Atlantic sea-water. b: 0.03 M Na_2SO_4 solution. c: 0.3 M Na_2SO_4 solution.

separation of phosphate from major sea-water ions and carbonate was also obtained (indicated by the peak observed at 235 s for m/z 37 and the peak at 590 s for m/z 13). Potential interfering polyatomic species at m/z 31, which could be expected to arise from direct injection of sea-water, include $^{15}\text{N}^{16}\text{O}$, $^{14}\text{N}^{16}\text{OH}$, $^{13}\text{C}^{18}\text{O}$, $^{12}\text{C}^{18}\text{OH}$ and ^{30}SiH . No peaks were detected at 235 and 590 s for m/z 31 for the North Atlantic sea-water sample, indicating that no significant polyatomic interference arising from $^{15}\text{N}^{16}\text{O}$, $^{14}\text{N}^{16}\text{OH}$, $^{13}\text{C}^{18}\text{O}$ and

Fig. 4 Chromatograms obtained under optimum operating conditions for P^+ . a: North Atlantic sea-water. b: 6.2 μM phosphate standard solution.

$^{12}\text{C}^{18}\text{OH}$ occurs in the sea-water matrix under the plasma operating conditions selected for P^+ . It was also important to investigate whether ^{30}SiH produced a significant interference on ^{31}P , since silicic acid has the same retention time as phosphate under the selected experimental conditions used with this IEC-AS1 column. This investigation was similar to the earlier one for PO^+ at m/z 47 in which chromatograms were obtained for the nutrient-free sea-water and the nutrient-free sea-water spiked to a Si concentration of 200 μM . Chromatograms of the Si-spiked nutrient-free sea-water were identical to those obtained for the nutrient free sea-water for m/z 31, suggesting that ^{30}SiH does not cause significant interference on ^{31}P under the experimental conditions selected. All results indicated that the phosphate peak at 290 s obtained for m/z 31 for the North Atlantic sea-water is not subject to interference by species arising from nitrate, carbonate, silica and other ions present in the sea-water matrix. However, it should be noted that a steady state elevation of the baseline remained, due to constant diffusion of nitrogen into the plasma, forming $^{15}\text{N}^{16}\text{O}$ and $^{14}\text{N}^{16}\text{OH}$ at m/z 31.

Analytical results

The North Atlantic sea-water used for this study contained a dissolved phosphate concentration of about 1.7 μM . An initial analysis of this sample was undertaken by the method of standard additions. The linearity of the calibration curves was tested under optimum plasma conditions for both P^+ and PO^+ . Additions of approximately 1- and 2-fold of the dissolved phosphate concentration in the sample were made and the peak area at 290 s was used for quantitation. The correlation coefficients of the standard additions calibration curves for P^+ and PO^+ in the concentration range of 0–6 μM were 0.999 90 and 0.999 94, respectively.

The final analysis of the sea-water sample was performed on six separate bottles using the optimum experimental conditions determined for P^+ at m/z 31 with one standard addition, since PO^+ at m/z 47 suffered from $^{30}\text{Si}^{16}\text{OH}$ interference. Each spiked sample was prepared by adding approximately the same concentration of dissolved phosphate, as initial estimates indicated. A mean concentration of 1.69 ± 0.04 (one standard deviation at $n=6$) μM was obtained based on peak area quantitation at 290 s for m/z 31. A phosphate concentration of 1.81 ± 0.02 μM was determined when quantitating *via* PO^+ intensities at m/z 47. This was 7% higher than the concentrations derived from P^+ intensities, a consequence of the $^{30}\text{Si}^{16}\text{OH}$ interference on PO^+ at m/z 47 noted earlier. The result of 1.69 ± 0.04 μM obtained under optimum conditions for P^+ by the IEC-ICP-MS method was in good agreement with the result of 1.71 ± 0.04 μM (mean and one standard deviation, $n=6$) obtained using a classic molybdenum blue colorimetric method. Since no sea-water CRM for micro-nutrients is available, a phosphate standard having a concentration of 2.0 μM in 3.05% NaCl solution (from Wako Pure Chemical Industries Ltd.) was used to further evaluate the accuracy of this IEC-ICP-MS method. A concentration of 1.99 ± 0.03 μM (mean and one standard deviation at $n=3$) was found in this standard solution, in good agreement with the reference value.

Conclusion

The IEC-ICP-MS method developed here provides for an alternative methodology to the standard colorimetric method for the determination of dissolved phosphate in sea-water. The reported method provides for a rapid (6 min per run), simple and accurate on-line technique requiring no sample pre-treatment. The method achieves a sufficiently low detection limit (0.06 μM) that only a small sample volume is needed and

the simple eluent (50 mM HCl) is compatible with ICP-MS operation.

Acknowledgements

The authors thank A. Hioki of the National Institute of Materials and Chemical Research, Ibaraki, Japan for his initial study on dissolved phosphate in sea-water by ICP-MS and V. Clancy for providing colorimetric phosphate data.

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