Available online at www.sciencedirect.com
ScienceDirect
Analytica Chimica Acta xxx (2007) xxx–xxx
ANALYTICA CHIMICA ACTA
www.elsevier.com/locate/aca

A new method for nanomolar determination of silicic acid in seawater

Peggy Rimmelin-Maury *, Thierry Moutin, Bernard Quéguiner

Laboratoire d'Océanographie et de Biogéochimie, Université de la Méditerranée, Centre d'Océanographie de Marseille (OSU), Unité Mixte de Recherche 6535-CNRS, Campus de Luminy-Case 901, 163 Avenue de Luminy, F-13288 Marseille Cedex 09, France

Received 9 October 2006; received in revised form 14 December 2006; accepted 19 January 2007

Abstract

A novel method is proposed to determine concentrations of silicic acid in seawater in the nanomolar range of 3–500 nM. It preconcentrates silicic acid through a "Magnesium Induced Co-precipitation" (MAGIC) step before a classical spectrophotometric measurement. The detection limit (3 ± 2 nM) is improved by a factor 10 in comparison to the conventional colorimetric methods. The best precision obtained to date is ± 2 nM for a natural sample of 69 nM Si. No interference of phosphate was observed by contrast to previous methods. This simple method offers a simple, sensitive and accurate tool for silicic acid determination in depleted seawater, where its availability remains unknown.

Keywords: Magnesium Induced Co-precipitation; Spectrophotochemical analysis; Silicic acid; Seawater; Mediterranean sea

1. Introduction

The availability of silicic acid ($Si(OH)_4$) can control directly the distribution, abundance and growth of diatoms and they have a major impact on silicon and carbon cycles in the world ocean [1–3]. Its concentration is over 0.75 μM in a vast majority of the surface ocean. However, it has been known for many years that the surface water is seasonally or chronically depleted of silicic acid to submicromolar levels (<0.1 to 0.6 μM) over areas of the tropical, subtropical ocean [4–6] or more recently, in the Mediterranean Sea [7,8]. Accurate silicic acid concentration is also a prerequisite for a precise calculation of Si-fluxes (production and dissolution) and subsequently for a good understanding of the silicon cycle, especially in low silicic acid regions (e.g. HNLSiLC – high nutrients low silicic acid low chlorophyll – regions such as the Sub-Antarctic Zone [9]).The reference technic for silicic acid determination in seawater (S&P method) is the colorimetric silicomolybdenum blue method developped by Mullin and Riley [10] and adapted by Strickland and Parson [11].

It is based on the reaction of silicic acid ($Si(OH)_4$) with molybdic acid (or ammonium molybdate) at pH 1.5–2 to form the yellow isomer beta silicomolybdate $(SiMo_{12}O_{40})^{4-}$. Following, molybdate is reduced by a 1-amino-2-naphthol-4-sulfonic acid in silicomolybdenum blue to increase spectrophotometric sensitivity. This allows determination of silicic acid concentration at a detection limit of >60 nM with a precision of ±50 nM in the 0.1–0.3 to 140 μM [11,12]. The method determines a fraction referred to as soluble reactive silicate (SRSi). This fraction is composed by monosilicic acid (the chemical form of dissolved Si taken up by marine diatoms [13]) and by disilicic acid. Both are characterized by their rapid reaction with molybdic acid while more polymeric forms and colloids are non reactive [14]. However, in the seawater physicochemical conditions, silicic acid is mainly monomeric.

Thus improving sensitivity and precision for monomeric silicic acid is required to determine silicic acid bioavailability in the low silicic acid regions of the World Ocean.

Several methods have been proposed to quantify nanomolar silicic acid in freshwater but a single technique can be applied to seawater. It was proposed by Brzezinski and Nelson [15] and relies on extraction of silicomolybdic acid in *n*-butanol followed by the classical silico molybdenum blue analysis. It allows a linear spectrophotometric answer between 5 and 50 nM with a precision of 2.5 nM. However the solvent extraction technic was

* Corresponding author. Tel.: +33 4 91 82 91 07; fax: +33 4 91 82 19 91.
E-mail address: rimmelin@com.univmed.fr (P. Rimmelin-Maury).

0003-2670/$ – see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.aca.2007.01.055

somewhat cumbersome so that it has been seldom applied itherto at sea.

In this paper, we propose a quantitative "Magnesium Induced Co-precipitation" (MAGIC) procedure [16] to determine nanomolar concentrations of silicic acid in seawater with the objectives of gaining robustness, simplicity and onboard applicability.

A MAGIC method has been already proposed for isotopic silicate determination in micromolar samples [17]. However, our procedure (MAGIC) relies upon the adaptation for nanomolar silicic acid determination of the MAGIC technique, recently improved by Rimmelin and Moutin [18] for phosphate. It consists in preconcentrating silicic acid 12.5 times through a magnesium hydroxide precipitation followed, after resolubilization, by the classic colorimetric analysis [11]. Repeatability, sensitivity, and precision were tested on seawater previously depleted in silicic acid through diatom culturing. The proposed method was validated by comparing the concentration measured with the conventional colorimetric method, in silicic acid enriched seawaters and also in natural samples collected during the spring and summer 2006 in the Bay of Marseille.

2. Experimental

2.1. Instrumentation

A SIGMA^{TM} (4–15) centrifuge allowed centrifuging simultaneously four 300 mL samples at 1500 xg. A CECIL^{TM} 1011 spectrophotometer (range of measurement from 0.001 to 2; S.D. = 0.001) equipped with a 8 mL – volume – 10 cm-path length – borosilicate cell (Starna Gmbh^{TM}) was used to measure absorbance at room temperature (~20–25 °C). A hand-made support was adapted to position precisely the cylindrical cell. The zero procedure was conducted on the cell filled with ultrapurified water.

2.2. Preparation of reagent

All reagents were prepared with pro analysis Merck^{TM} Reagent Grade chemicals and with Milli-Q^{TM} high purity demineralised water (DW). All ustensils were washed with 10% hydrochloric acid and rinsed 3 times with DW.

Reagent 1: 1 M NaOH solution (40 g L^{-1}) (ref. 1.06495.1000; Si < 0.0005%; PO4 < 0.0001%). Storage of this solution is not recommended.
Reagent 2: 0.25 M HCl solution (ref. 1.00317.1000). The reagent can be stored at room temperature.
Reagent 3: The molybdic reagent was prepared by dissolving 4 g of $(NH_4)_6Mo_7O_{24}{\cdot}H_2O$ in 300 mL ED. 12 mL concentrated HCl (ref. 1.00317.1000) are added and the final volume was made up to 500 mL with DW.
Reagent 4: The reducing reagent was prepared daily by mixing in the volumetric ratio of 1/0.6/0.6/0.8 three stock solutions of: metholsulfite solution (6 g Na_2SO_3 dissolved in 400 mL DW, addition of 10 g $C_{14}H_{20}N_2O_6S$ and fitting the volume to 500 mL with DW), oxalic acid solution (50 g L^{-1}), sulfuric acid (50% volumique) and DW.

2.3. MAGIC procedure

A minimum of 0.75 L sample was filtered through a 0.2 μm polycarbonate membrane using a Nalgene^{TM} filtration apparatus. The sample was then divided into three aliquots and poured into 250 mL pre-gauged polycarbonate centrifuged bottles. After the addition of 3.5 mL of Reagent 1, two vigorous homogenizations were successively conducted for 5 min. The three bottles were then centrifuged for 10 min at 1500 × g followed by a smooth deceleration and the supernatant was discarded. The precipitate was then solubilized in 13 mL Reagent 2 under vigorous homogenization. Volume of MAGIC extract was made up to 20 mL with 3 mL DW. This corresponds to a 12.5 times pre-concentration.

10 mL of this MAGIC concentrate were pipetted in polyethylene scintillation vials for turbidity blank determination, while the remaining 10 mL were treated for colorimetry.

The colorimetric procedure was performed by adding 4 mL of Reagent 3 and, after 10 min reaction, by adding 6 mL Reagent 4. After two hours the absorbance was measured at 810 nm with a 10 cm-path length cell.

The turbidity blank was prepared by adding 10 mL of DW. The absorbance was also measured at 810 nm and subtracted from the silicic acid absorbance.

A reagent blank was determined and subtracted. It was prepared by mixing 1.75 mL Reagent 1, 7.4 mL Reagent 2 (to have an adequat pH for colorimetry) and 0.850 mL DW (to adjust the volume), 4 mL Reagent 3 and 6 mL Reagent 4.

2.4. S&P colorimetric blue procedure

The manual colorimetric method conducted on 10 mL sample was similar to the Mullin and Riley [10] adapted by Strickland et Parsons [11]. In 3 among 4 replicates 4 mL of Reagent 3 and 6 mL of Reagent 4 were added. After 2 h, the absorbance was measured at 810 nm. The fourth replicate was used to measure the turbidity blank after fitting the volume with 10 mL DW. The reagent blank was prepared by adding 4 mL of Reagent 3 and 6 mL of Reagent 4 to 10 mL DW.

2.5. Calibration procedure of the MAGIC and the S&P methods

The MAGIC calibration was conducted for each new batch of reagent. 10 mL of 0.500 mM $Si(OH)_4$ (0.53035 g $Na_2SiO_3{\cdot}5H_2O$, PROLABO, ref. 28.092.290 in 1 L DW) was diluted to 100 mL to prepare the daily 50 μM working solution. Different volumes of the working solution were directly added in the centrifuge pre-gauged polycarbonate bottles to prepare standards (from 0.05 to 0.8 mL for 10 nM to 160 nM standards). The volume was adjusted to 250 mL by adding pre-filtered (0.2 μm) seawater. We recommend to calibrate routinely with the seawater of the study site.

Please cite this article in press as: P. Rimmelin-Maury et al., A new method for nanomolar determination of silicic acid in seawater, Anal. Chim. Acta (2007), doi:10.1016/j.aca.2007.01.055

However, our laboratory test of calibration was specifically conducted with silicic acid depleted seawater in order to perform a calibration curve in a range as low as possible. It was previously depleted to between 60 and 160 nM, after several weeks of *Cylindrotheca clostridium sp*. inoculation. The standards were then treated as described on paragraph 2.3. A second type of calibration was tested by using a MAGIC supernatant instead of seawater. This allowed to verify the calibration coefficient in the absence of silicic acid.

The S&P calibration was conducted with standards prepared by adding different volumes of the 50 μM silicic acid solution in polyethylene scintillation vials (from 0.2 to 1 mL for 1 to 5 μM standards). A pre-filtered seawater was used to fit the volume to 10 mL. The standards were then treated as previously described (see Section 2.4).

2.6. Interfering ions

Because of their similar chemical properties, the phosphate and arsenate are the major potential interferents. They are quantitatively pre-concentrated and form molybdic heteropoly acid like silicic acid ions [16,18]. While arsenate is ubiquitous in marine waters with a concentration of 10–40 nM [16,19], phosphate concentrations are usually lower than 400 nM in the Mediterranean seawater [7]. The potential interference was verified by comparing absorbances measured with and without addition of 0.5 μM arsenate or 5 μM phosphate (an equivalent of ∼40 nM and ∼400 nM before preconcentration, respectively). Enrichment were undertaken by direct addition in a MAGIC concentrate of 0.5 mL of a 10 μM arsenic acid solution ($Na_2HAsO_4{\cdot}7H_2O$) or 0.1 mL of a 500 μM phosphate solution (0.06805 g KH_2PO_4 in 1 L DW).

2.7. Storage

Three storage technics were tested: poisoning with mercuric chloride (at 4 mg $HgCl_2\,L^{-1}$ per sample (Ref. 1.04417.0100), freezing (at −20 °C followed by ambient temperature thawing) and refrigeration of the precipitate (4 °C). Triplicate MAGIC measurements were compared after a storage time of 0, 1, and 3 weeks.

2.8. Validation

Validation was carried out through cross comparison of the MAGIC and the S&P methods between 50 to 1500 nM. The first data set corresponded to 12 silicic acid standards and the second to 20 samples collected during spring and summer 2006 in the Gulf of Marseille. For both standards and samples, 0.8 L was filtered and stirred before subsampling into three replicates of 250 mL and four replicates of 10 mL for the MAGIC and the S&P analysis respectively.

2.9. Statistics

All statistics were performed according to Skoog et al. [20].

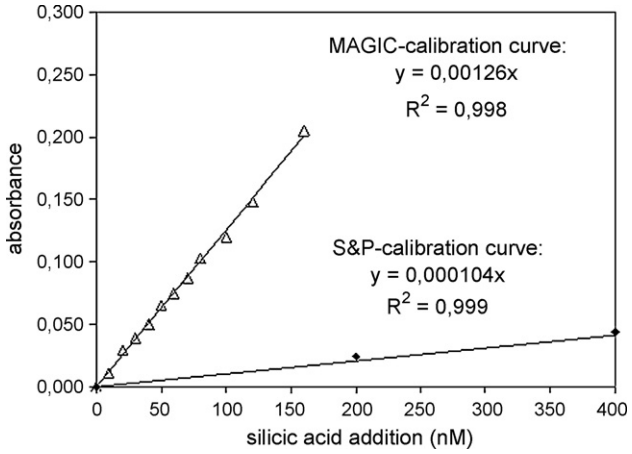

Fig. 1. Typical calibration curves of MAGIC and S&P method.

3. Results and discussion

3.1. Performance

3.1.1. Linearity and sensitivity

Calibration curves were established routinely by running procedural silicic acid standards. Recorded absorbance versus concentration ranging between 10 to 160 nM showed a highly significant linear relationship (Fig. 1). The MAGIC curves exhibited an average slope (mean = 0.00121 μa nM^{-1}; CV = 6.3%; $n = 6$) 11-fold higher than the S&P one (mean = 0.000113 μa nM^{-1}; CV = 4%; $n = 9$). The mean calibration slopes of the S&P method times the concentration factor was statistically different from the MAGIC method one (95% CI). A calibration curve prepared by adding silicic acid directly in a MAGIC concentrate confirmed this matrix effect of -15% and the complete recovery of silicic acid together. It is caused likely by the high ionic strengh in the MAGIC concentrate [18] which is known to favour the conversion of some of the beta acid to the less absorbent alpha form [21]. However the matrix effect is lower than the 30% of salt effect observed for the solvent extract method of Brzezinski and Nelson [15].

The coefficient of variation of the calibration coefficient amounted to 6.4% and involved a systematic error on the concentration calculation.

3.1.2. Reproducibility, detection limit and precision

Efficiency of the MAGIC treatment varied depending on the amount of 1 M NaOH added in the sample. The MAGIC procedure used a volume ratio of 1.4% (close to the mean addition preconized by Karl and Tien, [16]). A lower addition would decrease significantly the reproducibility while a higher addition would increase the reagent blank. Analyses of 8 replicates of a coastal prefiltered seawater (silicic acid depleted by diatom culturing) gave an average absorbance of 0.0833 with a S.D. of 0.0027. This corresponded to a silicic acid concentration of 69 nM with a CV of 3% which was 10 times lower than the S&P one (Table 1). Results demonstrate the good reproducibility of the MAGIC method at low concentration, even in the presence of suspended matter.

Please cite this article in press as: P. Rimmelin-Maury et al., A new method for nanomolar determination of silicic acid in seawater, Anal. Chim. Acta (2007), doi:10.1016/j.aca.2007.01.055

Table 1
Reproducibility and detection limit of the MAGIC and S&P methods

	Absorbance			Equivalent (nM) concentration	
	Average	S.D.[a]	n[b]	Average	S.D.[a]
Natural prefiltrated seawater treated with MAGIC method	0.0833	0.0027	8	68.8	2.3
MAGIC blank (Reagents 1, 2, 3, 4)	0.0110	0.0013	8	9.1	1.1
MAGIC turbidity blank (Reagents 1, 2, 4)	0.0076	0.0012	8	6.3	1.0
MAGIC detection limit (IC 95%)	0.0034		3	2.8	
Natural prefiltrated seawater treated with SSP method	0.0073	0.0022	8	68.6	19.3
S&P method reagent blank (reagents 3 an d 4)	0.0003	0.0005	8	2.5	4.0
S&P method turbidity blank	0.0001	0.0003	8	1.1	3.0
S&P detection limit (IC95%)	0.0013		3	11.5	

[a] S.D. is the standard deviation.
[b] n is the number of measurements.

The MAGIC reagent blank showed a silicic acid contamination equivalent to 9.1 nM, S.D. = 1.1 (Table 1). The contamination does not come from reagent 3 and 4 since the S&P reagent blank (Table 1) is not significantly different from zero. It likely comes from reagent 1 and 2. Decreasing this blank value is difficult because the chemicals used have the highest quality available (www.Sigmaaldrich.com). A minor part of the Si contamination might also come from the solvent. Sabarudin et al. [22] reported that highest ultrapurified waters can show a silicic acid concentration of up to 40 nM (an equivalent contamination of 7 nM of the sample). However, such a blank value is acceptable for subnanomolar analysis. The turbidity blank of some coastal waters induced also an overestimation of 6.3 nM on the average with a S.D. = 1.0, even after 0.2 μm filtration (Table 1). Both blanks were in the same magnitude order and controlled the MAGIC sensitivity for nanomolar measurement.

The detection limit was calculated by taking into account the S.D. of the turbidity (measured with coastal samples) and reagent blank measurement and was equivalent to 2.8 nM (IC95%). However optimal conditions are expected in oligotrophic region ocean waters where suspended matter levels are low by definition.

Precision is defined by the reproducibility of the analytical process. It exhibited generally a S.D. < 0.004 for sample triplicates absorbance (in the range 10–1000 nM) and a S.D. of 0.0025 for the reagent + turbidity blanks absorbance (Table 1). By considering also an error of 6.3% on the calibration coefficient, we calculated a relative total S.D. from 57 to 10% for concentration ranging between 10–160 nM, respectively (Table 2). Note that the variability of the calibration coefficient implies a proportional error on concentration which matched the S&P method one (50 nM) for concentrations over 500 nM. Accuracy of the MAGIC method appeared subsequently optimal for low nanomolar concentrations.

3.1.3. Interfering ions and storage

No significant increase of absorbance was found for an equivalent addition of 40 nM arsenate or 400 nM phosphate. The oxalic acid, known to decompose the molybdophosphoric complex, minimize phosphate interference even in the MAGIC medium. This differs from the sensitive method by solvent extraction which shows an interference for phosphate concentrations over 50 nM [15].

3.1.4. Storage

Freezing and precipitate refrigeration of the precipitate of a sample of 140 nM decreased the absorbance by 31% per week of conservation (Table 3). Number of investigators have reported decrease of silicic acid recoveries after freezing [23]. This is due to polymer formation of silicic acid after exclusion from the solid ice and concentration in the liquid phase. Polymers are known to be non-reactive in the S&P method [11,24]. The polymerization of silicic acid depends upon sample storage time, sample salinity and concentration of silicic acid [25,26]. An improvement of

Table 2
Accuracy of the MAGIC and S&P methods

	Average	S.D.[a]	CV%	n[b]
MAGIC method				
Calibration coefficient (μa nM^{-1})	0.00121	0.00008	6.3	6
Accuracy IC95% (nM)	10	5.8	58	3[c]
Accuracy IC95% (nM)	160	15.3	10	3[c]
S&P method				
Calibration coefficient (μa nM^{-1})	0.000113	0.000005	4.0	9
Accuracy IC95% (nM)	50	48	96	3[c]
Accuracy IC95% (nM)	160	58	36	3[c]

[a] S.D. is the standard deviation.
[b] n is the number of measurements.
[c] Number of replicate considered for the calculation.

Please cite this article in press as: P. Rimmelin-Maury et al., A new method for nanomolar determination of silicic acid in seawater, Anal. Chim. Acta (2007), doi:10.1016/j.aca.2007.01.055

Table 3
MAGIC recovery after 0, 1 and 3 weeks storage

Time (week)	Sample recovery (%)			
	Freezing	Precipitate refrigeration	Poisoning	
			Sample of 1400 nM	Sample of 460 nM
0	100	100	100	100
1	68	69	88	100
3	37	43	74	101

freezing storage may be obtained by optimal thawing technique which may allow partial or total depolymerization [26].

By contrast, poisoning (at 4 mg $HgCl_2$ L^{-1} of sample) showed a slight decrease of absorbance by 13% for a sample of 1400 nM (Table 3). This can be acceptable although a poison blank correction of 7 nM should be applied. Although mercuric chloride is not often applied to poison nutrient seawater samples, several authors reported its use as a suitable storage method for silicic acid [27–29]. The origin of the decrease of silicic recovery remains unknown. However, no significant decrease was observed for a sample of 460 nM after two months preservation. Poisoning is then considered as the best way of silicic acid signal conservation for seawater of low silicic acid concentration.

3.1.5. Validation: cross methodology comparison

A linear and significant correlation ($y = 0.96 \times x$, $r^2 = 0.99$) was established in the 50–1500 nM range value between the MAGIC and the S&P-SRSi measurements (Fig. 2). The slope was not significantly different from 1 if we consider a 50 nM error on S&P-SRSi determination. This result validates the MAGIC method for silicic acid determination in submicromolar concentration. A slight underestimation was observed in a seawater of 1430 nM (−11%). The origin of this result has not been identified yet. One hypothesis is a high concentration of phosphate which would compete for brucite adsorption so that an incomplete silicate adsorption would happend. The limit of adsorption capacity of brucite has been evoked by Reynolds et al. [30] in sample of micromolar range of concentration and would be solved by an increasing addition of sodium hydroxyde. This underline that our method is a valid and usefull tool for submicromolar to nanomolar measurement while the standard S&P method remains an adequat method for micromolar determination.

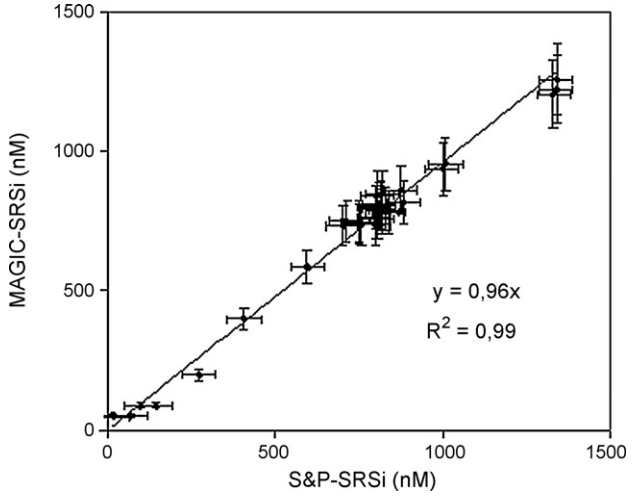

Fig. 2. Soluble reactive silicic acid measurement with MAGIC and S&P methodology.

4. Conclusion

The silicic acid measurement in seawater has been significantly improved owing to the development of the MAGIC technic. A 12.5 times preconcentration of the silicic acid through a magnesium induced precipitation enables a 10-fold improvement of precision and detection limit by comparison to the conventional methods. Laboratory investigations showed a low matrix effect and also the absence of phosphate and arsenate interferences by contrast to the previous sensitive method. The MAGIC method was validated in nano- to submicromolar concentration by comparing with the classical S&P method. This new method shows the great advantage to be easyly performed onboard at a nanomolar level. It would allow to determine accurate silicic acid concentrations in oceanic environments where it remains unknown. This new method could be also directly integrated to the more recent method for ^{30}Si measurement so that silicic acid availability, production, and dissolution would be determined simultaneously with a precision never observed before for low silicic acid regions.

Acknowledgements

We would like to thank the technicians of the COM-observatory service, Michel Lafont, Jean-Luc Fuda and Béatriz Bécker, and also Marie Sinoire, Véronique Barthaux, and Karine Leblanc for their help in sample collection and diatom cultures. The crew of the NO Antedon (CNRS-INSU) provided the seagoing support for our sampling. This is a contribution of the BIOSOPE and BOUM project of the LEFE-CYBER program. This research was funded by the Centre National de la Recherche Scientifique (CNRS), the Institut des Sciences de l'Univers (INSU), the Centre National d'Etudes Spatiales (CNES), the European Space Agency (ESA), The National Aeronautics and Space Administration (NASA) and the Natural Sciences and Engineering Research Council of Canada (NSERC).

Please cite this article in press as: P. Rimmelin-Maury et al., A new method for nanomolar determination of silicic acid in seawater, Anal. Chim. Acta (2007), doi:10.1016/j.aca.2007.01.055

References

[1] D.M. Nelson, P. Tréguer, M.A. Brzezinski, A. Leynaert, B. Quéguiner, Global Biogeochem. Cycles 9 (1995) 359.
[2] M.A. Brzezinski, D.M. Nelson, DSR II 43 (1996) 437.
[3] O. Ragueneau, P. Tréguer, A. Leynaert, R.F. Anderson, M.A. Brzezinski, D.J. DeMaster, R.C. Dugdale, J. Dymond, G. Fischer, R. François, Global Planet. Change 26 (4) (2000) 317.
[4] J. Marra, R.R. Bidigare, T.D. Dickley, DSR 37 (1990) 127.
[5] M.A. Brzezinski, D.M. Nelson, Deep Sea Res. 36 (1989) 1003.
[6] M.A. Brzezinski, D.M. Nelson, Deep Sea Res. I 42 (1995) 1215.
[7] J.-C. Marty, J. Chiavérini, M.-D. Pizay, B. Avril, Deep Sea Res. II 49 (2002) 1965.
[8] K. Leblanc, B. Quéguiner, N. Garcia, P. Rimmelin, P. Raimbault, Oceanol. Acta 26 (2003) 339.
[9] K. Leblanc, C.E. Hare, P.W. Boyd, K.W. Bruland, B. Sohst, S. Pickmere, M.C. Lohan, K. Buck, M. Ellwood, D.A. Hutchins, Deep Sea Res. 52 (10) (2005) 1842.
[10] J.B. Mullin, J.P. Riley, Anal. Chim. Acta 12 (1955) 162.
[11] J.D.H. Strickland, T.R. Parson, Bull. Fish. Res. Board Can. 167 (1972) 65.
[12] A. Aminot, M. Chaussepied. CNEXO Ed. Brest, 1983, p. 135.
[13] Y. Del Amo, M.A. Brzezinski, J. Phycol. 35 (1999) 1162.
[14] M.B. Ali, B. Hamrouni, S. Bouguecha, M. Dhahli, Desalination (2004) 273.
[15] M.A. Brzezinski, D.M. Nelson, Mar. Chem. 19 (1986) 139.
[16] D.M. Karl, G. Tien, Limnol. Oceanogr. 37 (1992) 105.
[17] M.A. Brzezinski, J.L. Jones, K.D. Bidle, F. Azam, Limnol. Oceanogr. 48 (5) (2003) 1846.
[18] P. Rimmelin, T. Moutin, Anal. Chim. Acta 548 (1–2) (2005) 174.
[19] O.A. Meinrat, Limnol. Oceanogr. 24 (1979) 440.
[20] D.A. Skoog, D.M. West, F.J. Holler, sixth ed., Saunders College Publishing–Harcourt Brace College Publishers, Chicago, 1993.
[21] J.D.H. Strickland, J. Am. Soc. 74 (1952) 872.
[22] A. Sabarudin, M. Oshima, S. Motomizu, Anal. Chim. Acta 532 (2005) 27.
[23] J.E. Dore, T. Houlihan, T. Hebel, D.V. Tien, G. Tupas, D.M. Karl, Mar. Chem. 53 (1996) 173.
[24] R.Y. Ning, Desalination 151 (2002) 67.
[25] R. Alvarez, D. Sparks, Nature 318 (1985) 649.
[26] J.-Z. Zhang, P.B. Ortner, Water Res. 32 (8) (1998) 2553.
[27] D.S. Kirkwood, Mar. Chem. 38 (1992) 151.
[28] K. Kremling, A. Wenck, Meeresforschung 31 (1986) 69.
[29] G. Kattner, Mar. Chem. 67 (1999) 61.
[30] B.C. Reynolds, M. Frank, A.N. Halliday, Earth Planet. Sci. Lett. 244 (2006) 431.

Please cite this article in press as: P. Rimmelin-Maury et al., A new method for nanomolar determination of silicic acid in seawater, Anal. Chim. Acta (2007), doi:10.1016/j.aca.2007.01.055