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High-accuracy determination of iron in seawater by isotope dilution multiple collector inductively coupled plasma mass spectrometry (ID-MC-ICP-MS) using nitrilotriacetic acid chelating resin for pre-concentration and matrix separation

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ABSTRACT

In the present paper we describe a robust and simple method to measure dissolved iron (DFe) concentrations in seawater down to <0.1 nmol L^{-1} level, by isotope dilution multiple collector inductively coupled plasma mass spectrometry (ID-MC-ICP-MS) using a ^{54}Fe spike and measuring the $^{57}Fe/^{54}Fe$ ratio. The method provides for a pre-concentration step (100:1) by micro-columns filled with the resin NTA Superflow of 50 mL seawater samples acidified to pH 1.9. NTA Superflow is demonstrated to quantitatively extract Fe from acidified seawater samples at this pH. Blanks are kept low (grand mean 0.045 ± 0.020 nmol L^{-1}, $n = 21$, 3× S.D. limit of detection per session 0.020–0.069 nmol L^{-1} range), as no buffer is required to adjust the sample pH for optimal extraction, and no other reagents are needed than ultrapure nitric acid, 12 mM H_2O_2, and acidified (pH 1.9) ultra-high purity (UHP) water. We measured SAFe (sampling and analysis of Fe) reference seawater samples Surface-1 (0.097 ± 0.043 nmol L^{-1}) and Deep-2 (0.91 ± 0.17 nmol L^{-1}) and obtained results that were in excellent agreement with their DFe consensus values: 0.118 ± 0.028 nmol L^{-1} ($n = 7$) for Surface-1 and 0.932 ± 0.059 nmol L^{-1} ($n = 9$) for Deep-2. We also present a vertical DFe profile from the western Weddell Sea collected during the Ice Station Polarstern (ISPOL) ice drift experiment (ANT XXII-2, RV *Polarstern*) in November 2004–January 2005. The profile shows near-surface DFe concentrations of ~0.6 nmol L^{-1} and bottom water enrichment up to 23 nmol L^{-1} DFe.

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1. Introduction

Iron (Fe) in the oceans is of great interest to marine biogeochemists and ecosystem modelers for its role in the oceanic carbon cycle as a regulating factor of marine primary productivity [1]. However, despite the recognized importance of Fe, the global observational database of dissolved Fe concentrations in the oceans is still very limited [2]. To conduct Fe biogeochemical research it is crucial to measure Fe accurately and precisely on a routine basis. Unfortunately, Fe is notoriously difficult to measure in ocean waters due to a high risk of sample contamination in combination with its low concentrations at the nmol L^{-1} level, even as low as 0.05 nmol L^{-1} [2]. Potential sources of random contamination include the inevitable rust from the research vessel, airborne particles (e.g. from ship exhaust), sampling gear, lab ware, lab environment, and sample manipulations (e.g. during filtration and analysis). The past three decades great efforts have been undertaken to improve the analytical quality of iron concentration data. The risk of contamination has come under control by the use of clean sampling systems, clean filtration techniques, portable clean air labs, plastic lab ware, thorough lab ware cleaning procedures, ultraclean reagents, etc. [3].

On the instrumental side, analytical methods have shifted in recent years from techniques involving large shore-based equipment such as electrothermal atomic absorption spectrometry (ET-AAS) or inductively coupled plasma mass spectrometry (ICP-MS), towards portable shipboard techniques such as cathodic stripping voltammetry (CSV) or flow injection analysis (FIA) with chemiluminescence or photometric detection [4]. The difficulties associated with most of these applications lie in the necessity of pre-concentrating the iron from the sample and removing the heavy salt matrix that could generate interferences during the measurements. These separation techniques include solvent extraction or solid phase extraction in batch or in-line applications, with sample sizes that can range from 500 mL to just a few mL.

Several international intercalibration efforts during the last 25 years have led to a greater understanding of the sampling and analytical issues that determine data quality. Progress has been made in data quality assurance in terms of improved accuracy, precision and reproducibility. To illustrate this progress, the first trace metal intercomparison ICES-4 in 1978 on North Atlantic seawater with 65 participating laboratories was unsuccessful for Fe [5]. During the IOC1990 intercalibration exercise in the East-Atlantic, two laboratories reported vertical dissolved Fe profiles that exhibited oceanographically consistent concentrations in the range of 0.1 to 2 nmol L^{-1} although problems of random sample contamination and systematic analytical off-set were encountered [6]. More recent shipboard intercomparisons in 1998 (MERLIM98) between two laboratories [7] and in 2000 (IRONAGES) between four laboratories [8], both along transects in the Atlantic Ocean, arrived at much better agreement between the involved laboratories. A second IRONAGES intercomparison exercise involving a single bulk sample of Atlantic Ocean surface water collected during the IRONAGES cruise, was conducted from 2000 to 2002 by 24 laboratories and yielded an average consensus value of 0.59 ± 0.21 nmol L^{-1} [9]. However, problems related to different sensitivities to different physicochemical species of Fe, blank quantification and inaccurate system calibration were reported [8,9], explaining the relatively large error. A three-laboratory blind intercomparison exercise conducted in 2003 using the same IRONAGES bulk seawater sample produced excellent agreement between the three laboratories (0.54 ± 0.03 nmol L^{-1}) as well as with the IRONAGES consensus value [10]. As a follow up to these exercises, the SAFe cruise in the Pacific Ocean (30°N, 140°W) in 2004 with participants from 18 laboratories, has led to the development of low Fe 'consensus' reference materials (Surface-1: 0.097 ± 0.043 nmol L^{-1} and Deep-2: 0.91 ± 0.17 nmol L^{-1} Fe), which come as a welcome addition to the existing 'low iron' seawater reference material NASS-5 (3.71 ± 0.63 nmol L^{-1} Fe) [11]. At present, still more progress in clean sampling and analytical techniques can be expected from the intercalibration exercises that are underway as part of the GEOTRACES international program, which aims at the global study of the biogeochemical cycles of trace elements and their isotopes [12].

The quality assurance of routine analytical measurements depends on traceability to the SI, which can be achieved by using certified reference materials (CRM's), comparing with primary methods, or the method itself having the potential to be a primary method. The Consultative Committee for Amount of Substance (CCQM, *Comité Consultatif pour la Quantité de Matière*) developed a definition for a primary method of measurement as a method having the highest metrological qualities, whose operation is completely described and understood, for which a complete uncertainty statement can be written down in terms of SI units [13]. The CCQM distinguishes within this definition the primary direct method, which measures the value of an unknown without reference to a standard of the same quantity, and the primary ratio method, which measures the value of a ratio of an unknown to a standard of the same quantity and whose operation must be completely described by a measurement equation [13]. Methods with empirical measurement equations, i.e. depending on calibration with one or more standards, are not primary methods because they do not meet the requirement of having full measurement equations in the sense of being fully described and understood in terms of SI units [13]. They can be called secondary methods, because they can only attain traceability to the SI when validated by a primary method of measurement or primary standard [13,14]. This classification of measurement methods is not intended to give a superior status to some methods or to devaluate others that have demonstrated capability to produce high-quality data (e.g. during SAFe [11]), but to provide a reference of a methods' ability to be traceably linked to the SI.

The CCQM has identified isotope dilution mass spectrometry (IDMS) as a potential primary ratio method [13]. Isotope dilution is based on the addition of a precisely known amount of a highly enriched isotope to a sample, so that the isotopic composition of the target element in the sample is modified. By measuring the modified isotopic composition of the target element, the mass fraction of this element in the sample can be calculated. Concerning the measurement of Fe in seawater, these IDMS methods consist to date of single step or double step magnesium hydroxide co-precipitation

as pre-concentration technique [10,15–18]. Isotope dilution ICP-MS can be seen as another contributor to the field of high-quality iron data in oceanography, but can also serve to certify CRM's, validate standard methods, determine reference values in inter-laboratory comparisons, or resolve disagreements between other methods [14].

In this paper we describe a robust and simple method to measure Fe in seawater accurately and precisely down to the 0.1 nmol L^{-1} level, using isotope dilution in combination with multiple collector inductively coupled plasma mass spectrometry (ID-MC-ICP-MS). The method includes a pre-concentration step by a commercially available chelating resin with nitrilotriacetic acid (NTA) functional groups [17], NTA Superflow (Qiagen). NTA Superflow was used previously for the analysis of Fe in seawater in flow injection applications utilizing detection by either ICP-MS [19] or chemiluminescence on board ship [20], yielding high-quality data. The advantage of NTA Superflow over $Mg(OH)_2$ co-precipitation, in combination with isotope dilution ICP-MS, is that there is no introduction of large amounts of Mg salts into the instrument that could create mass bias drift of the mass spectrometer due to buildup of salt residue inside the instrument. Isotope dilution in the form of adding a high-purity mono-isotopic ^{54}Fe spike, warrants accuracy of the results. Incomplete Fe extraction, signal suppression and instrumental sensitivity fluctuations are accounted for (provided that there is isotopic equilibrium), because these affect all isotopes (natural and spiked) and therefore should not affect the isotopic ratios of the spiked sample. Multi-collector ICP-MS has the advantage of simultaneous detection of the different masses leading to improved precision. However, the Faraday detectors are less sensitive as compared with classical single detector double focusing magnetic sector ICP-MS instruments. This is compensated for by using a high pre-concentration factor (100×), and by working in low resolution ($R \sim 500$, highest instrumental sensitivity mode), combined with a desolvating sample introduction system to enhance sensitivity, as well as greatly reducing isobaric argon-based interferences on the measured Fe masses.

Finally, to demonstrate the feasibility of the method, we present results for the SAFe (Sampling and Analysis of Fe) seawater reference materials [11] as well as a vertical dissolved Fe profile sampled in the western Weddell Sea during the Ice Station Polarstern (ISPOL) ice drift experiment (ANT XXII-2, RV *Polarstern*) in November 2004–January 2005.

2. Experimental

2.1. Reagents

The following reagents were used or prepared: Liquinox detergent from Alconox (White Plains, NY, USA) was used in a 1% dilution. Hydrogen peroxide 30% (H_2O_2, Merck suprapur) was diluted to 12 mM and prepared fresh daily. Triple sub-boiled 14 M nitric acid (HNO_3, Merck Reagent Grade) was prepared with a Teflon PTFE (polytetrafluoroethylene) subboiling distillation still from Berghof (BSP929, Eningen, Germany) and collected into a Teflon FEP (fluorinated ethylene propylene) bottle. From this a 1 M HNO_3 dilution was made in a Teflon FEP bottle. Ultra-high purity (UHP) water for rinsing and dilutions was drawn from a Millipore Element (18.2 MΩcm) water purification apparatus, fed from a Millipore Elix reverse osmosis filtration apparatus. Acidified UHP water (0.014 M HNO_3, pH 1.9) was made by adding 1 mL of sub-boiled 14 M HNO_3 to 1 L of UHP water in a Nalgene HDPE (high density polyethylene) bottle.

The ^{54}Fe spike was obtained from Isoflex (Russia) in its metallic form, of which 50 mg was precisely weighed on a Sartorius 4 digit analytical balance in a Savillex Teflon PFA (perfluoroalkoxy) screw-cap beaker and dissolved in 2 mL concentrated sub-boiled nitric acid while heated at 125 °C on a hot plate. Upon cooling the solution was gravimetrically diluted to 100 mL in a clean Teflon PFA bottle to yield a stock solution of 500 mg ^{54}Fe kg^{-1} in 0.28 M HNO_3. From this stock, 100 mL of a work solution of 500 μg kg^{-1} in 0.28 M HNO_3 was gravimetrically prepared in a LDPE (low density polyethylene) bottle. Concentration and isotopic abundance of the ^{54}Fe spike work solution was verified by inverse isotope dilution using the international natural Fe isotopic standard IRMM-014 [21]. Inverse isotope dilution is a technique by which a pure solution containing the enriched isotope is spiked with a precisely known amount of a standard with a precisely known natural isotopic composition. The calculation of the concentration is similar to normal isotope dilution. Inverse ID yielded a concentration of the work solution of 501.4 ± 5.0 μg kg^{-1} and a composition of 0.1471 ± 0.0023% ^{57}Fe, 0.327 ± 0.093% ^{56}Fe and 99.523 ± 0.093% ^{54}Fe was calculated. From these abundances, an atomic weight for the ^{54}Fe spike was derived of 53.951 ± 0.071 amu. The manufacturer's certificate of analysis mentions abundances of 0.02% ^{57}Fe, 0.13% ^{56}Fe and 99.85% ^{54}Fe with no reported uncertainties. The difference with the abundances in the work solution may stem from a small contamination by the dilute HNO_3. Based on the measured abundances, the work solution has a $^{57}Fe/^{54}Fe$ of 0.001478 ± 0.000023 (R.S.D. = 1.6%) and a $^{56}Fe/^{54}Fe$ of 0.00327 ± 0.00093 (R.S.D. = 28.5%). The above-mentioned uncertainties were estimated by similar error propagation calculations as will be explained in Section 3.1.

Although all care must be taken to prevent contamination during the whole analytical process, gradual slow contamination of the spike work solution can be a source of systematic error (as for any IDMS method). It would however be detectable as a measurable change in the isotopic composition relative to IRMM-014, based on the monitoring at the beginning of an analytical session (see further). It does not necessarily disqualify the data as long as the systematic difference is small, within the uncertainty envelope. Of course the work solution has then to be refreshed or recalibrated. Flagrant contamination has never occurred in our experience.

The natural Fe isotopic reference material IRMM-014 was obtained from the Institute of Reference Materials and Measurements (IRMM) in Geel (Belgium) as metallic wires. One wire of 20 mg was precisely weighed on a Sartorius 4 digit analytical balance in a Savillex Teflon PFA beaker and dissolved in 2 mL concentrated sub-boiled nitric acid while heated at 125 °C on a hot plate. Upon cooling the solution was gravimetrically diluted to 40 mL in a clean Teflon FEP bottle to yield a stock solution of 500 mg kg^{-1} Fe in 0.7 M HNO_3. From this

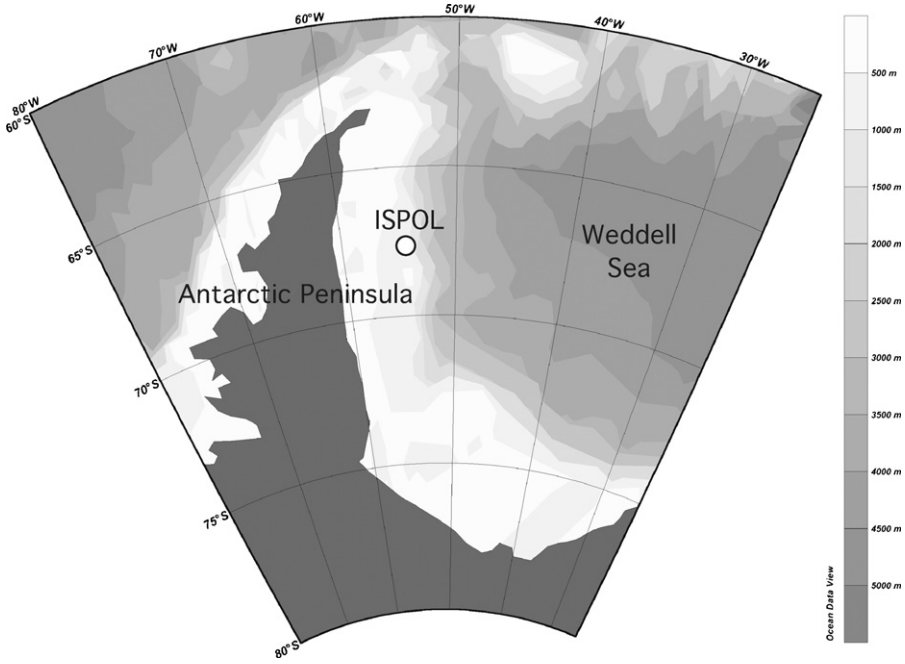

Fig. 1 – Map of the Antarctic Peninsula and the adjacent western Weddell Sea with the location of Ice Station Polarstern (ISPOL) on January 1, 2005 when a vertical profile of DFe was sampled. The map was generated with Ocean Data View, courtesy Schlitzer, R., Ocean Data View, http://odv.awi.de, 2008.

stock, 100 mL of a work solution of 500 μg kg^{-1} in 0.28 M HNO_3 was gravimetrically prepared in a LDPE bottle. The IRMM-014 has a $^{57}Fe/^{54}Fe$ of 0.3626 ± 0.0019 (R.S.D. = 0.52%), a $^{56}Fe/^{54}Fe$ of 15.699 ± 0.067 (R.S.D. = 0.43%) [21]. The IRMM-014 atomic weight is 55.845 ± 0.002 amu [22].

2.2. *Clean procedures*

All cleaning and sample manipulations were carried out in a class 100 clean air laboratory, with personnel wearing Tyvek clean room coveralls, plastic clogs and Nitrile gloves. All plastic lab ware was first cleaned by overnight soaking in a detergent bath (1% Liquinox) followed by abundant rinsing with UHP water. Teflon PFA beakers (Savillex, Minnetonka, MN, USA) and Teflon FEP reagent bottles (Nalgene) were acid cleaned for 24 h in 6 M HCl at 125 °C on a hotplate and three times rinsed with UHP water. The containers were then acid cleaned for 24 h with 7 M HNO_3 at 125 °C on a hotplate, five times rinsed with UHP water and air-dried inside a class 100 laminar flowhood. Low density polyethylene (LDPE) materials (Nalgene, Kartell) were cleaned with 6 M HCl at 60 °C in a water bath. Polypropylene centrifuge tubes of 50 mL (Falcon) and a polycarbonate filtration device (Sartorius) were cleaned in a 1 M HCl bath for 1 week at room temperature followed by abundant rinsing with UHP water. Polycarbonate membrane filters of 47 mm diameter and 0.2 μm pore size were likewise soaked in 1 M HCl for 1 week, abundantly rinsed with UHP water and stored in UHP water. NTA Superflow resin was cleaned three times by carefully centrifuging an amount of the resin slurry in UHP water in a Falcon tube, upon which the supernatant was discarded each time. The resin was then soaked in 0.5 M HNO_3 for 1 week at room temperature followed by three rinses with UHP water. The resin was then stored in 0.5 M HNO_3 and kept in the dark at +4 °C when not used.

2.3. *Sampling procedures*

During Ice Station Polarstern (ISPOL, cruise ANT/XXII-2 between November 27, 2004 until January 2, 2005) in the western Weddell Sea [23], a water column profile was sampled at station PS67/06-142 on January 1, 2005 at position 67°22′ S, 55°25′ W (Fig. 1). The station was situated on the continental slope of the Antarctic Peninsula at a water depth of 1380 m. Water samples were taken using 10 L General Oceanics Niskin samplers with stainless steel internal springs, which were hung on an epoxy-coated rosette frame with a Sea-Bird 911+ CTD thermosalinograph. The rosette was deployed from a standard stainless steel co-axial cable. As this was the 142nd deployment of the CTD rosette during this cruise, the Niskin bottles were deemed sufficiently rinsed for trace metal sampling. Prior to deployment of the rosette, the Niskins and their internal springs were visually inspected for cleanliness and corrosion stains. Niskin bottles were rinsed during the down-cast and closed during the up-cast. Upon recovery on deck, sub-samples for measurement of total dissolved Fe (DFe = filtered) were immediately taken from each Niskin in 250 mL LDPE bottles (Kartell). In a class 100 clean air van, the samples were filtered using polycarbonate filtration devices (Sartorius) with Teflex O-rings (Eriks, the Netherlands) and 47 mm diameter 0.2 μm pore size polycarbonate membrane filters (Nuclepore). Gentle vacuum (<0.5 bar) was applied with a Masterflex hand pump. The samples were acidified to pH 1.9 with 250 μL concentrated sub-boiled HNO_3 to 250 mL of sample. DFe was analyzed by IDMS nearly 2.5 years later.

2.4. Iron pre-concentration and matrix separation by NTA Superflow resin

For pre-concentration and matrix separation NTA Superflow resin (Qiagen Inc., Netherlands) in Bio-Rad Poly-Prep columns was used. The NTA Superflow resin has the great advantage of being capable to quantitatively extract Fe from acidified (as low as pH 1.7) and oxidized (hydrogen peroxide addition) seawater samples, while rejecting other trace metals (except Cu) and sea salts [19]. At this low pH, complexes of Fe with natural organic ligands can be considered dissociated, thus greatly reducing the possibility of competition for Fe binding between these natural ligands and the resin functional groups. Blanks can be kept low, as micro-columns were used, no buffer is needed to adjust sample pH to optimal extraction pH, and no other reagents are needed than ultrapure HNO_3, 12 mM H_2O_2, and acidified (pH 1.9) UHP water.

Bio-Rad Poly-Prep columns were packed with NTA Superflow resin (300–400 μL, column height 5–6 mm, diameter 8 mm, column reservoir 10 mL). The resin and the column reservoir were rinsed with one aliquot of 10 mL 1 M HNO_3 and three aliquots of 2 mL 1 M HNO_3 followed by conditioning with two aliquots of 2 mL UHP water acidified to pH 1.9. In the meanwhile, 50 mL acidified seawater samples were prepared in 50 mL Falcon centrifuge tubes, and 50 μL of a 12 mM H_2O_2 solution and 25.0 μL of a 500 μg kg^{-1} ^{54}Fe spike (0.25 μg ^{54}Fe L^{-1} or 4.6 nmol ^{54}Fe L^{-1} addition) were added. The sample containers were then weighed on a top load balance (0.1 g precision). After an equilibration/reaction time of 15 min, the seawater was passed through the resin by gravity flow. The resin was subsequently rinsed with three aliquots of 2 mL acidified UHP to rinse off remaining sea salts. The Fe was eluted with three aliquots of 2 mL 1 M HNO_3 into a PFA Savillex screw-cap vial. The samples were dried down overnight on a hotplate at 125 °C inside a class 100 clean air fume cabinet. Prior to analyses the samples were re-dissolved in 500 μL 0.05 M HNO_3. This was done for three reasons: (1) 1 M HNO_3 would exhibit a much higher $^{40}Ar^{14}N$ interference on mass 54; (2) to drive off chlorides that could interfere on mass 54 as $^{37}Cl^{16}O^{1}H$ and on mass 53 (Cr correction) as $^{37}Cl^{16}O$; (3) to obtain a sufficiently large pre-concentration factor (100×) for high enough precision on the measurement.

Concerning the abovementioned isotope equilibration time, a survey of the existing IDMS literature about Fe in seawater mentions equilibration times ranging from 5 min to 12 h [10,15–18], all at room temperature (Table 1). We did not conduct tests to verify correctness of our chosen equilibration time. However, equilibration time was tested by [15] on unfiltered samples acidified for 4 years at pH 1.5, with durations between 10 min and 3 weeks at room temperature, as well as at a temperature of 50 °C for 72 h, and no differences in result were observed. We surmise from this that after a sufficiently long acidification at pH 1.9 and a peroxide oxidation step, as in this study, spiked ^{54}Fe is rapidly equilibrated with the dissolved Fe because all Fe is oxidized to Fe(III) and natural organic ligands are dissociated [15]. Any colloidal Fe <0.2 μm that may not have dissolved at pH 1.9, may not have equilibrated fully. It will probably be retained by the resin anyway and upon elution with 1 M HNO_3 still dissolve rapidly and equilibrate.

Table 1 – Comparison of IDMS methods for Fe in seawater

Method	Instrument	Resolution	Spike	Equilibration time	Sample volume (mL)	Pre-concentration factor	Blank (pM)	LOD (pM)	Reference
NTA Superflow pre-concentration ID-MC-ICP-MS	Nu Plasma	Low	^{54}Fe	15 min	50	100	31–58	20–69	This study
Single $Mg(OH)_2$ co-precipitation ID-MC-ICP-MS	GV Isoprobe	Low	^{54}Fe	Not reported	1.3	6–8	80–170	90	[18]
Single $Mg(OH)_2$ co-precipitation ID-ICP-MS	ThermoFinnigan MAT Element	Medium	^{57}Fe	10 min	1.4	14	121	162	[15]
Single $Mg(OH)_2$ co-precipitation ID-ICP-MS	ThermoFinnigan MAT Element2	Medium	^{57}Fe	Overnight	15–30	7.5–15	113	100	[17]
Single $Mg(OH)_2$ co-precipitation ID-ICP-MS	ThermoFinnigan MAT Element	Medium	^{57}Fe	12 h	5	5	30	60	[10]
Double $Mg(OH)_2$ co-precipitation ID-ICP-MS	ThermoFinnigan MAT Element	Medium	^{57}Fe	10 min	14	140	45	50–60	[15]
Double $Mg(OH)_2$ co-precipitation ID-ICP-MS	ThermoFinnigan MAT Element2	Medium	^{57}Fe	5 min	50	500	16	2	[16]

On the basis of runs with twelve parallel columns, with each run taking about 2 h, three runs could be carried out daily, so a maximum of 36 samples were processed per day. Each day columns were freshly packed. The resin is recycled and stored until reuse in 0.5 M HNO_3 at +4 °C. Based on observed ion beam intensity we have no indication of deterioration of resin efficiency over a 1-year period.

2.5. *Mass spectrometry*

Isotope dilution measurements were carried out on a Nu Plasma MC-ICP-MS (Nu Instruments, Wrexham, UK). The Nu Plasma is a double focusing magnetic sector instrument with 12 Faraday collectors in fixed positions. The ion beams of the masses of interest are aimed into the collectors by variable dispersion ion optics ('zoom lens'). All collectors have a $10^{11}\,\Omega$ resistor allowing a signal range from 0 to 10 V. The instrument is operated in low resolution ($R \sim 500$) for highest sensitivity.

For this study, the mass spectrometer was used in combination with an Aridus desolvating sample inlet system (Cetac Technologies, Omaha, NE, USA) to achieve dry plasma conditions. The Aridus was upgraded with a Teflon PFA spraychamber with a PFA microconcentric nebulizer for a solution uptake of $100\,\mu L\,min^{-1}$ (Elemental Scientific, Omaha, NE, USA). The Aridus was operated at a spraychamber temperature of 105 °C, a membrane temperature of 160 °C and an argon sweep gas flow of around $3.9\,L\,min^{-1}$. The introduction into the plasma of a dry sample aerosol by the removal of water (desolvation) reduces argide interferences by >99% [24]. Interferences of $^{40}Ar^{14}N^+$ on mass 54, $^{40}Ar^{16}O^+$ on mass 56 and $^{40}Ar^{16}O^1H^+$ on mass 57 have typical intensities of 25 ± 3 mV, 122 ± 50 mV and 0.5 ± 0.3 mV, respectively (mean of three analytical sessions), at an average sensitivity of 80–100 V ppm^{-1} total ion beam. One analysis consists of 14×10 s integration to measure simultaneously ^{57}Fe (H6), ^{56}Fe (H4), ^{54}Fe (L3) and ^{53}Cr (L5). The monitoring of ^{53}Cr serves to correct for potential ^{54}Cr isobaric interference on mass 54 using a $^{54}Cr/^{53}Cr$ ratio of 0.2489 [25]. ^{53}Cr intensities are typically around 0.5 mV, usually do not exceed 1 mV and do not significantly alter the measured isotopic ratios. An analysis, including signal rise, peak centering and measurement, takes nearly 4 min, in which time nearly 0.5 mL of sample are consumed. Between analytical runs, rinsing is carried out with 0.5 M HNO_3 (3 min) and 0.05 M HNO_3 (3 min). An argon interference baseline measurement with 30 s integration time prior to each analytical run is done in 0.05 M HNO_3, which is subtracted on-line during the ensuing analytical run. Blank measurement, sample measurement and rinsing sequence take about 10–11 min, so 5–6 measurements per hour can be carried out.

After plasma ignition the mass spectrometer is allowed to warm up for 1 h, before optimization of the instrumental settings. The analytical session begins by running in triplicate $25\,\mu g\,L^{-1}$ solutions in 0.05 M HNO_3 of IRMM-014 and the ^{54}Fe spike, to assess the mass bias of the mass spectrometer and to verify the purity of the spike. Also a standard solution mix of 1:1 ^{54}Fe spike and IRMM-014, both at a concentration of $25\,\mu g\,L^{-1}$ is being measured in triplicate, which is afterwards used as bracketing standard during subsequent sample measurements (every five measurements) to correct for drift in the instrumental mass bias behavior due to the deposition of residual sample matrix (sea salts, organics bled from the resin) on the mass spectrometer's cones. These solutions yield ion beam signals of approximately 2 V at masses 54 (spike) or 56 (IRMM-014), or at both masses (bracketing standard). This is followed by measurement of the procedural blanks first and then the samples.

3. Results and discussion

3.1. *Design and uncertainty budgeting of the isotope dilution method*

Iron has four stable natural isotopes: ^{58}Fe (0.28%), ^{57}Fe (2.12%), ^{56}Fe (91.75%) and ^{54}Fe (5.85%) [25]. In principle, the highest enriched spike of the least abundant natural isotope should be chosen. However, the choice of the indicator isotope in isotope dilution ICP-MS depends on the availability and cost of the spike, its purity, as well as relative contribution of occurring isobaric interferences. For Fe, the preferred indicator isotope would then be ^{58}Fe, but this isotope is more expensive than ^{57}Fe or ^{54}Fe spikes and cannot be measured in the Faraday cup configuration of our mass spectrometer.

As $^{40}Ar^{14}N$ interference to the signal on mass 54 constitutes the largest relative interference contribution in a natural (unspiked) sample (Fig. 2A), we chose to use a ^{54}Fe spike as to greatly reduce the relative contribution of this interference to the signal at mass 54 in a spiked sample. This is shown in Fig. 2B displaying the relative contributions of $^{40}Ar^{16}O^1H$, $^{40}Ar^{16}O$ and $^{40}Ar^{14}N$ interferences to the ion beams at masses 57, 56 and 54 when spiking with ^{54}Fe, as a function of the final Fe concentration (varying amount of natural Fe and fixed amount of spiked Fe) in the sample after pre-concentration. In addition, ^{54}Fe is available in a higher purity than ^{57}Fe.

Although ^{56}Fe is the naturally most abundant isotope, the relative $^{40}Ar^{16}O$ contribution at low natural Fe concentrations becomes dominant (Fig. 2B) with increased uncertainty on the ratio $^{56}Fe/^{54}Fe$. This is because the error in the interference baseline measurement impedes the precise calculation of the ^{56}Fe presence in the signal at mass 56 at low natural Fe concentrations ($<\sim 0.5\,nmol\,L^{-1}$). In the end, the $^{57}Fe/^{54}Fe$ ratio has the lowest combined interference contributions (Fig. 2B) and the lowest uncertainty at low ratios (Fig. 3A). Fig. 3A shows the internal relative standard error (R.S.E.) on the $^{57}Fe/^{54}Fe$ and $^{56}Fe/^{54}Fe$ ratios for a singular sample measurement (i.e. standard deviation of 14 integrations of 10 s, divided by the square root of the number of integrations), for samples analyzed during this study. Internal R.S.E.'s increase with smaller ratios, which can be attributed to worsened counting statistics, but internal uncertainties on $^{57}Fe/^{54}Fe$ are at small ratios always better than those of $^{56}Fe/^{54}Fe$.

The standard deviation on a reported concentration is a function of all the uncertainties in the variables used to calculate the concentration (Eq. (3) further below), but depends mostly on the internal standard error on the measured ratio in the spiked sample (R_{mix}) and this ratio's error propagation factor f_R [26]. The error propagation factor f_R defines how the uncertainty in the R_{mix} measurement propagates into the uncertainty on the concentration. It is calculated by the fol-

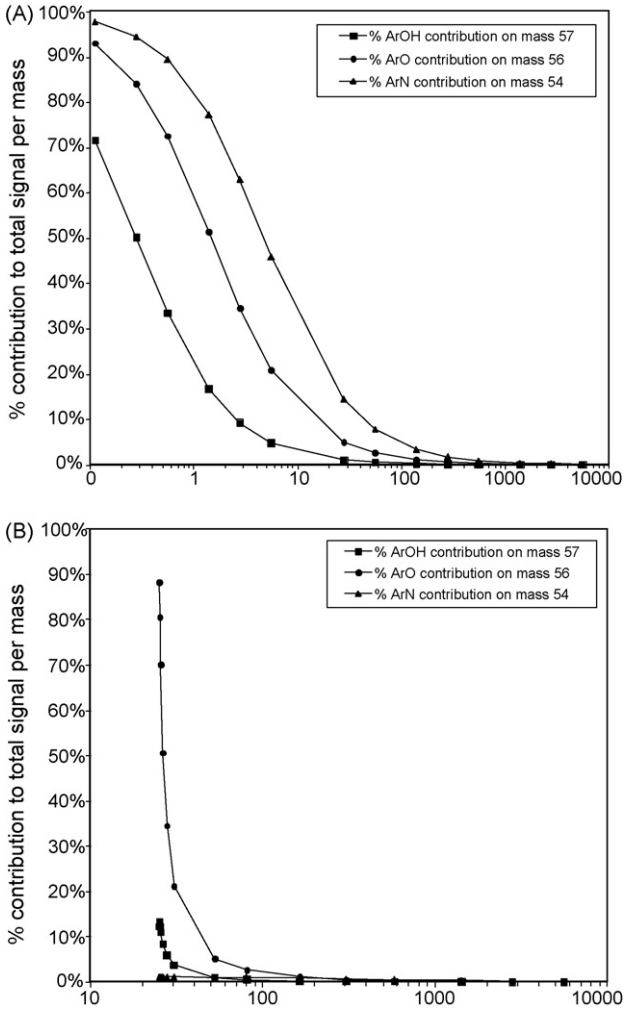

Fig. 2 – (A) Percentage contribution of argon-based interferences to the signals at masses 54, 56 and 57 with increasing natural Fe concentration ($\mu g\,L^{-1}$) in an unspiked sample after 100× pre-concentration. The calculations are based on measured argon-based interferences and typical sensitivities of the instrument (see text). (B) Percentage contribution of argon-based interferences to the signals at masses 54, 56 and 57, with increasing natural Fe concentrations for a sample spiked with 4.6 nmol L^{-1} ^{54}Fe (0.25 $\mu g\,L^{-1}$), after 100× pre-concentration (final concentration ^{54}Fe 25 $\mu g\,L^{-1}$ plus a varying amount of natural Fe). The calculations are based on measured argon-based interferences and typical sensitivities of the instrument (see text).

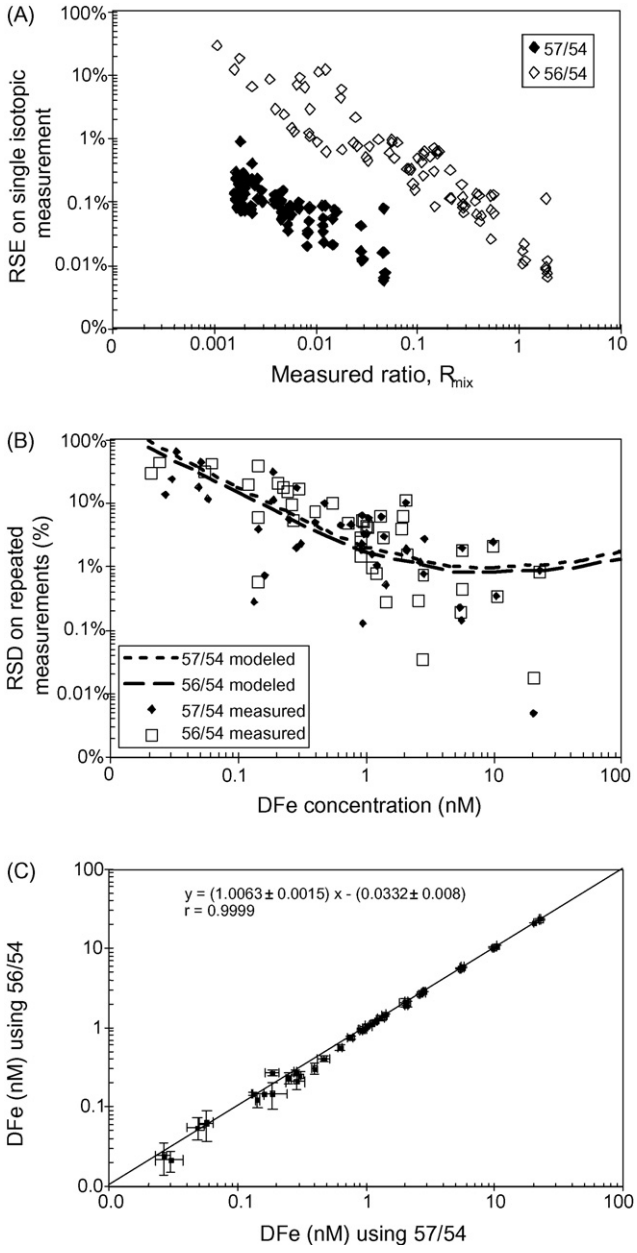

Fig. 3 – (A) Internal relative standard error (single isotopic measurement) versus measured ratio R_{mix} in samples analyzed during this study. (B) External relative standard deviation (replicate isotopic measurements) versus increasing sample concentration in samples analyzed during this study. Dotted line: External relative standard deviation versus increasing sample concentration modeled for the $^{57}Fe/^{54}Fe$ ratio. Dashed line: External standard deviation versus increasing sample concentration modeled for the $^{56}Fe/^{54}Fe$ ratio. (C) Linear regression of Fe concentrations in the same samples, either measured using the $^{57}Fe/^{54}Fe$ ratio, or the $^{56}Fe/^{54}Fe$ ratio.

lowing equation [26]:

$$f_R = \frac{[(^{57\,or\,56}Fe/^{54}Fe)_{natural} - (^{57\,or\,56}Fe/^{54}Fe)_{spike}]R_{mix}}{[R_{mix} - (^{57\,or\,56}Fe/^{54}Fe)_{natural}]\,[(^{57\,or\,56}Fe/^{54}Fe)_{spike} - R_{mix}]} \quad (1)$$

The error propagation factor increases when R_{mix} approaches the isotopic ratio of the spike R_{spike} (over-spiking), or the natural isotopic ratio of the sample $R_{natural}$ (underspiking) [27]. At minimal f_R (~1) the optimal isotopic

Table 2 – Model to predict R_{mix} and error propagation factor (f_R) in function of sample-to-spike ratio

Natural Fe concentration in seawater (nmol/L)	Sample-to-spike ratio	Fe-54 spike[a]			
		57/54[b]		56/54[c]	
		Predicted R_{mix}	f_R	Predicted R_{mix}	f_R
0.02	0.0043	0.00157	17.2	0.0072	1.8
0.05	0.011	0.00171	7.5	0.0132	1.3
0.1	0.021	0.00193	4.3	0.0231	1.2
0.25	0.054	0.00261	2.3	0.0529	1.1
0.5	0.11	0.00374	1.7	0.1021	1.0
1	0.21	0.00597	1.3	0.1998	1.0
5	1.1	0.02289	1.1	0.9389	1.1
10	2.1	0.04190	1.2	1.7692	1.1
25	5.4	0.08797	1.3	3.7802	1.3
50	11	0.14098	1.6	6.0911	1.6
100	21	0.20262	2.3	8.7743	2.3
250	54	0.27518	4.2	11.9279	4.2
500	107	0.31259	7.4	13.5516	7.3
1000	215	0.33541	13.7	14.5414	13.7

[a] Assuming an addition of 4.6 nmol/L ^{54}Fe to a sample of 50 mL.
[b] Assuming a 57/54 ratio in the spike of 0.001478 (calculated from abundances in the spike measured by inverse isotope dilution) and a natural 57/54 ratio of 0.3626 (IRMM-014).
[c] Assuming a 56/54 ratio in the spike of 0.00327 (calculated from abundances in the spike measured by inverse isotope dilution) and a natural 56/54 ratio of 15.699 (IRMM-014).

ratio of the spiked sample (R_{opt}) is reached. R_{opt} can be calculated by the following equation [26]:

$$R_{opt} = \sqrt{(^{57 \text{ or } 56}Fe/^{54}Fe)_{natural}(^{57 \text{ or } 56}Fe/^{54}Fe)_{spike}} \quad (2)$$

For ^{57}Fe/^{54}Fe R_{opt} would be 0.023 and for ^{56}Fe/^{54}Fe 0.23. Based on the evolution of the error propagation factor f_R in function of the sample-to-spike molar ratio, which changes with the concentration of natural Fe in the seawater sample, ^{56}Fe/^{54}Fe would be the preferred measured ratio over ^{57}Fe/^{54}Fe (Fig. 4, Table 2). However, as explained above, the relatively high ^{40}Ar^{16}O contribution to the signal at mass 56 would impede the precise measurement of ^{56}Fe/^{54}Fe at low Fe concentrations.

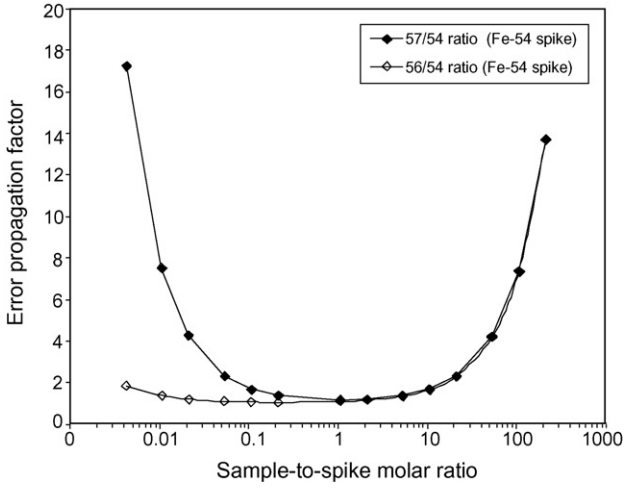

Fig. 4 – Dependency of the error propagation factor on the sample-to-spike ratio.

Concentrations in samples and blanks were calculated as follows [28]:

$$C_{sample} = \frac{(V_{spike}\rho_{spike}C_{spike}M_{natural}A_{spike})}{(m_{sample}/\rho_{SW}M_{spike}A_{sample})} \times \frac{(R_{spike} - R_{mix})}{(R_{mix} - R_{natural})} \times 1000 \quad (3)$$

with C_{sample}, concentration Fe in sample (nmol L^{-1}); C_{spike}, concentration spike, 501.4 μg kg^{-1}; ρ_{spike}, density spike, 1008 kg m^{-3}; ρ_{SW}, density seawater, 1025 kg m^{-3}; V_{spike}, volume spike, 0.0250 mL; m_{sample}, mass sample, 50.0 g; A_{spike}, atomic abundance indicator isotope (^{54}Fe) in spike, 99.52%; A_{sample}, atomic abundance indicator isotope (^{54}Fe) in unspiked sample, 5.85%; $M_{natural}$, atomic weight natural Fe, 55.845 [22]; M_{spike}, atomic weight spike, 53.951; R_{spike}, measured ^{57}Fe/^{54}Fe spike; R_{mix}, measured ^{57}Fe/^{54}Fe spiked sample; $R_{natural}$, natural ^{57}Fe/^{54}Fe in the sample.

The range of natural variations in $R_{natural}$, ~7‰ (i.e. 0.7%) in δ^{57}Fe relative to IRMM-014 [24], is about as large as the analytical error of the $R_{natural}$ measurement, 0.67% (see Section 3.3). As most of the natural variations are within ~2‰ [24], it is safe to assume for all samples the $R_{natural}$ of IRMM-014. This would not create any analytical offsets.

Fig. 3B shows the external relative standard deviation (R.S.D.) for replicate measurements of sample concentrations in the samples analyzed during this study, using ^{57}Fe/^{54}Fe or ^{56}Fe/^{54}Fe for R_{mix}. From this result it must be concluded that the choice of measured ratio appears less important and that the evolution of standard deviation with increasing concentrations as measured by either ^{57}Fe/^{54}Fe or ^{56}Fe/^{54}Fe is overlapping. This can be explained by the fact that the final standard deviation on a reported concentration is a function of all the uncertainties in the variables used in Eq. (3) but depends mostly on the internal standard error on the measured ratio in the spiked sample and this ratio's error propagation factor

Table 3 – Variables in the isotope dilution calculation and their uncertainties

Variable	Unit	Value	S.D.	R.S.D.
V_{spike}	μL	25	0.1	0.40%
m_{sample}	g	50	0.1	0.20%
Conc. spike	μg/kg	501.4	1	0.20%
$M_{natural}$	g/mol	55.845	0.002	0.0036%
M_{spike}	g/mol	53.951	0.071	0.13%
A_{spike}	%	99.523	0.093	0.093%
A_{sample}	%	5.845	0.020	0.34%
R_{spike} 57/54		0.001645	0.000064	3.9%
R_{spike} 56/54		0.0032	0.0023	71.9%
R_{mix} 57/54[a]		Variable		$y = 1E-05x^{-0.7475}$, $R^2 = 0.67$
R_{mix} 56/54[a]		Variable		$y = 0.0003x^{-0.9595}$, $R^2 = 0.86$
$R_{natural}$ 57/54		0.4041	0.0027	0.61%
$R_{natural}$ 56/54		16.892	0.077	0.49%

[a] The relation between R.S.D. and R_{mix} was derived from Fig. 3A.

f_R [26]. At small ratios, the $^{57}Fe/^{54}Fe$ R_{mix} ratio can be measured more precisely but has a higher f_R while the $^{56}Fe/^{54}Fe$ R_{mix} ratio has a larger uncertainty but a lower f_R. The uncertainty was budgeted according to [26] using the parameters and their uncertainties as shown in Table 3:

$$\sigma_{C_{sample}} = \sqrt{\sigma^2_{R_{natural}} + \sigma^2_{m_{sample}} + \sigma^2_{C_{spike}} + \sigma^2_{A_{spike}} + \sigma^2_{A_{sample}}} + \frac{\sqrt{\sigma^2_{R_{spike}} + f_R^2\,\sigma^2_{R_{mix}}}}{(R_{spike} - R_{mix})} + \frac{\sqrt{\sigma^2_{R_{natural}} + f_R^2\,\sigma^2_{R_{mix}}}}{(R_{mix} - R_{natural})} \quad (4)$$

The error in R_{mix}, $\sigma_{R_{mix}}$, depends on the value of R_{mix} as can be seen from Fig. 3A and which function can be found in Table 3.

The modeled evolution of relative standard deviation versus sample concentration is given in Table 4 and by the dotted ($^{57}Fe/^{54}Fe$) and dashed ($^{56}Fe/^{54}Fe$) lines in Fig. 3B, which are nearly indistinguishable. The real standard deviations obtained from replicate sample analyses, nicely follow the modeled trend. This finally results in concentrations calculated by $^{57}Fe/^{54}Fe$ or $^{56}Fe/^{54}Fe$ being rather equivalent in terms of accuracy and precision (Fig. 3C). However, all concentrations reported in the present paper are based on the measurement of the $^{57}Fe/^{54}Fe$ ratio. $^{56}Fe/^{54}Fe$ based concentrations are calculated nonetheless to check the internal consistency of the results (data not shown). For the replicate sample concentration measurements carried out in the frame of the underlying work, and calculated with the $^{57}Fe/^{54}Fe$ ratio, we report typical average relative standard deviations of 30% (DFe ≤ 0.1 nmol L^{-1}), 6% (DFe = 0.1–1 nmol L^{-1}), 3% (DFe = 1–5 nmol L^{-1}), 1% (DFe = 5–10 nmol L^{-1}), 0.5% (DFe = 10–20 nmol L^{-1}).

3.2. *Column calibration and resin efficiency*

To determine the minimal volume of elution acid in order to obtain full recovery, 50 mL acidified clean Antarctic seawater from the Weddell Sea (with 0.45 nmol L^{-1} natural Fe) was enriched with 5.09 nmol L^{-1} IRMM-014 Fe, loaded on NTA Superflow resin and eluted with 1 M HNO_3 and collected into Savillex Teflon PFA vials in fractions of 2 mL. Most of the Fe (92%) was eluted in the first fraction of 2 mL, while blank levels were obtained in the third fraction of 2 mL. To ensure the highest recovery, also for samples with a Fe concentration higher than was tested here, the elution volume was set at 6 mL.

The efficiency of the resin was investigated by standard addition to clean Antarctic seawater from the Weddell Sea

Table 4 – Uncertainty budget of the concentration in function of sample concentration

Concentration (nM)	Estimated R.S.D. (57/54) (%)	S.D.	Estimated R.S.D. (56/54) (%)	S.D.
0.02	92.5	0.018	71.3	0.014
0.05	34.6	0.017	28.4	0.014
0.1	17.2	0.017	14.2	0.014
0.25	7.0	0.017	5.8	0.015
0.5	3.7	0.018	3.1	0.016
1	2.2	0.022	1.9	0.019
5	1.4	0.071	1.3	0.066
10	1.4	0.140	1.3	0.131
25	1.5	0.37	1.4	0.34
50	1.6	0.80	1.4	0.72
100	1.9	1.9	1.7	1.7
250	3.1	7.7	2.5	6.2
500	5.1	26	4.0	20
1000	9.4	94	7.3	73

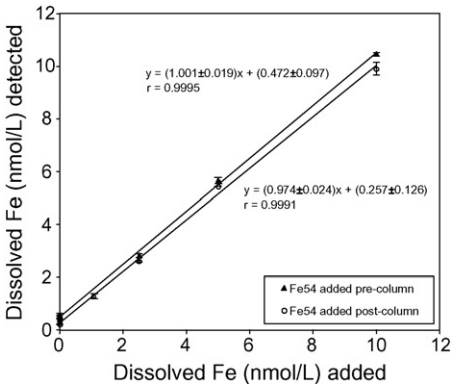

Fig. 5 – Linear regressions between added Fe and measured Fe in seawater samples, which were spiked with ^{54}Fe either after or before the separation procedure, to determine the efficiency of the procedure and verify the accuracy of the procedure.

(0.45 nmol L^{-1}), of increasing amounts of the natural Fe standard IRMM-014, spanning a concentration range between 1 and 10 nmol L^{-1}. These sample-standard mixtures were subsequently submitted to the separation/pre-concentration procedure as described in Section 2.4 with the ^{54}Fe spike added to the seawater samples before separation (pre-column) or with ^{54}Fe spike added to the eluate after separation (post-column). By post-column spiking with ^{54}Fe it is possible to verify the yield of the chromatographic separation by comparing the known amount of added Fe with the measured amount of Fe retained by the column and subsequently eluted. Contrary to that, pre-column spiking with ^{54}Fe will take into account any column yield artifacts and will thus give the original Fe concentration in the sample. Comparing the original Fe concentrations in the sample-standard mixtures as determined by pre-column spiking, with the known amount of added Fe, will provide a check if the whole procedure including the calculations would arrive at 100% accuracy for the whole range of investigated Fe concentrations. The results as illustrated in Fig. 5, indicated that across the investigated concentration range the resin retains overall 97.4 ± 2.4% of the Fe present in the sample. The method as a whole is 100.1 ± 1.9% accurately detecting Fe.

3.3. *Instrumental mass bias and matrix effects due to residual sea salt*

Each analytical session is started with triplicate measurement of $R_{natural}$ (IRMM-014), the bracketing standard and R_{spike} in concentrations of 25 μg L^{-1}, to account for mass bias changes from one session to another and to verify the isotopic purity of the spike. The bracketing standard is being measured every five sample measurements to correct for drift in the instrumental mass bias behavior. The average measured isotopic ratios for 11 analytical sessions are $^{57}Fe/^{54}Fe = 0.001645 \pm 0.000064$ (R.S.D. = 3.9%) for R_{spike}, $^{57}Fe/^{54}Fe = 0.4041 \pm 0.027$ (R.S.D. = 0.67%) for $R_{natural}$. For $^{56}Fe/^{54}Fe$ this is 0.0032 ± 0.0023 (R.S.D. = 72%) for R_{spike} and 16.892 ± 0.077 (R.S.D. = 0.45%) for $R_{natural}$. The bracketing standard had an average isotopic composition of $^{57}Fe/^{54}Fe = 0.02390 \pm 0.00012$ (R.S.D. = 0.49%) and $^{56}Fe/^{54}Fe = 0.9375 \pm 0.0049$ (R.S.D. = 0.53%). Comparing $R_{natural}$ with the true ratios for IRMM-014 (see above Section 2.1) a typical MC-ICP-MS instrumental mass bias of 3.8% amu^{-1} was deduced. Correction for this mass bias yields true ratios for the spike of $^{57}Fe/^{54}Fe = 0.001476$ and $^{56}Fe/^{54}Fe = 0.0030$, which is within error indistinguishable from the calculated ratios in Section 2.2. We assume that as the mass biases for IRMM-014 standard and spike are similar, this would also be the case for sample-spike blends. Hence a mass bias correction was deemed not necessary and using the uncorrected measured ratios should suffice in combination with standard-sample bracketing.

However, upon dry evaporation of the samples after column separation, a tiny deposit of residual sample matrix or organics bled from the resin could sometimes be discerned in the evaporation beakers. For a typical seawater sample we estimated a major cation concentration in the measurement solution of about 1 mg L^{-1} of Mg, 8 mg L^{-1} of Na and 0.3 mg L^{-1} of Ca and K. This residual salinity of 0.001% is much lower than the 0.05% reported by [17] for $Mg(OH)_2$ co-precipitation, but could still produce signal suppression and changes in mass bias behavior that could produce off-sets in the reported concentrations [29]. Therefore a test was carried out in which stripped Fe-free seawater was spiked with 2 nmol L^{-1} IRMM-014 Fe, and several sample replicates were subjected to column rinsing with different amounts of UHP water or acidified UHP water. This should cause the presence of different amounts of residual salt in the eluates and thus different effects on mass

Table 5 – UHP water rinsing test with seawater containing 2 nM DFe

mL rinse	Signal suppression (%)	DFe (nM)	No blank correction		
			Average	S.D.	R.S.D. (%)
UHP					
3	57	2.120	2.077	0.037	1.8
5	61	2.056			
10	44	2.056			
UHP, pH 1.9					
3	73	2.082	2.085	0.038	1.8
5	57	2.049			
10	0	2.125			

bias. The results are summarized in Table 5. The determined concentrations are as to be expected and remain impervious to any matrix residue effect. From this we surmise that residual matrix constituents are not causing a detectable mass bias anomaly that could create erroneous results. Given also the good agreement of our results for SAFe reference seawater with the assigned consensus values (see Section 3.6), we conclude that there is no need to apply a mass bias correction for matrix effects, contrary to findings by [29]. We do however correct for mass bias drift of the instrument by measuring at regular intervals a bracketing standard.

3.4. *Acidification time of seawater samples*

Determination of total DFe requires that Fe bound to organic or inorganic colloids and natural organic ligands, is quantitatively released in the dissolved phase for detection. For a Pacific seawater sample (0.75 nmol L^{-1} DFe) from 1000 m depth and acidified to pH 1.7, 2 h of acidification were minimally required prior to DFe measurement [20]. We conducted a similar experiment with an unacidified under-ice seawater sample collected during ISPOL and determined a minimal acidification of 3 h at pH 1.9 (Fig. 6) before a constant level of 0.40 nmol L^{-1} DFe was reached. It must be noted that acidification time of seawater samples for total DFe analysis likely depends on the speciation of DFe in the sample. As this speciation is *a priori* unknown, seawater samples for total DFe determination should be stored longer than the reported minimal times, especially if refractory colloids of biogenic or terrigenous origin could be present. For those samples that are likely to contain high DFe and colloids, the same acidification time should be applied as for total dissolvable (unfiltered) Fe, i.e. several months. This time can however be shortened considerably by briefly microwave heating samples [20,30].

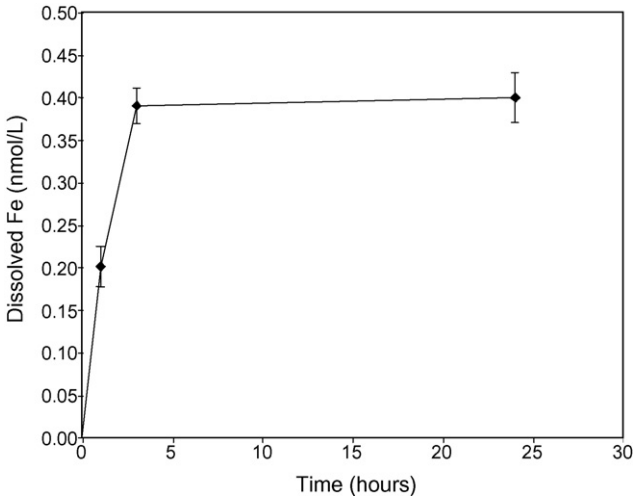

Fig. 6 – Dissolved Fe concentrations (nmol L^{-1}) in seawater acidified to pH 1.9 monitored during 24 h.

3.5. *Blanks and limit of detection (LOD)*

The reagents used in this determination comprise concentrated 14 M HNO_3, 12 mM H_2O_2 and UHP water. Reagent blanks were prepared by dry-evaporating 5 mL of each of these reagents in duplicate and measuring their concentrations by isotope dilution. Results are summarized in Table 6, with concentrated HNO_3 containing 0.4 nmol L^{-1} Fe, while the Fe contents of 12 mM H_2O_2 and UHP water were below the LOD (here taken as ~0.05 nmol L^{-1}). The use of these reagents as well as solutions made up from them (acidified UHP water, 1 M HNO_3, 0.05 M HNO_3) would potentially

Table 6 – Reagent blanks and their contribution to the procedural blank for a 50 mL sample

Reagent	Fe (nmol/L)	Fe (nmol)	Calculated procedural blank (nmol/L)
HNO_3 14 M	0.402		
H_2O_2 12 mM	<DL (0.05)		
UHP	<DL (0.05)		
HNO_3 14 M, 50 μL		0.000020	
H_2O_2 12 mM, 50 μL		0.000003	
HNO_3 0.014 M (UHP pH 1.9), 10 mL		0.000302	0.018
HNO_3 1 M, 6 mL		0.000366	
HNO_3 0.05 M, 500 μL		0.000025	

Table 7 – Procedural and 'field' blanks

Date dd/mm/yyyy	Blank type	Fe (nM)	S.D.	DL	*n*	Grand mean	S.D.	*n*
19/03/2007	Reagents, no column pass	0.030	0.007	0.022	3	0.026	0.013	9
13/02/2008	Reagents, no column pass	0.020	0.016	0.049	2			
21/03/2008	Reagents, no column pass	0.027	0.022	0.066	2			
10/04/2008	Reagents, no column pass	0.024	0.017	0.052	2			
19/03/2007	Reagents with column pass	0.027	0.004	0.011	3	0.024	0.007	6
20/03/2008	Reagents with column pass	0.022	0.009	0.027	3			
18/04/2007	Stripped SW, reagents, column	0.033	0.021	0.064	6	0.045	0.020	21
19/04/2007	stripped SW, reagents, column	0.058	0.007	0.020	5			
19/04/2007	Stripped SW, reagents, column	0.049	0.009	0.026	2			
19/06/2007	Stripped SW, reagents, column	0.051	0.023	0.069	5			
20/03/2008	Stripped SW, reagents, column	0.031	0.020	0.060	3			

Table 8 – SAFe seawater reference materials

Date dd/mm/yyyy	Sample	Bottle #	Fe (nM)	Avg. Fe (nM)	S.D.	n	Grand mean	S.D.	Assigned value
19/04/2007	D1	87	0.684 0.719 0.662 0.764 0.718 0.715	0.710	0.035	6	0.710	0.035	
19/06/2007	D2	239	0.0590 0.905	0.928	0.032	2	0.932	0.059	0.91 ± 0.17
19/06/2007	D2	268	0.893 0.894	0.893	0.001	2			
19/06/2007	D2	418	0.862 0.886	0.912	0.067	3			
26/05/2008			0.988						
19/06/2007	D2	449	1.048 0.961	1.004	0.061	2			
19/06/2007	S1	126	0.114	0.114		1	0.118	0.028	0.097 ± 0.043
19/06/2007	S1	249	0.120	0.120		1			
19/06/2007	S1	405	0.109 0.111	0.105	0.008	3			
26/05/2008			0.096						
19/06/2007	S1	434	0.095 0.179	0.137	0.059	2			

result in a calculated blank of 0.018 nmol L^{-1} (Table 6). We then ran procedural blanks by passing across the resin acidified UHP water and 1 M HNO_3 (with 50 μL 14 M HNO_3 and 50 μL 12 μM H_2O_2 added to the Savillex beakers after elution), yielding 0.026 ± 0.013 nmol L^{-1} ($n = 5$) (Table 7). A similar procedural blank, now without column pass of the aforementioned reagents but transferring them directly into a Savillex beaker, yielded 0.024 ± 0.007 nmol L^{-1} ($n = 5$) (Table 7). This points at the Bio-Rad columns and the NTA resin not contributing to the blank. The difference of ~0.007 nmol L^{-1} between the calculated blank and the procedural blanks lies within the uncertainty envelope of the measurements, but could be due to increased sample manipulation involved with procedural blank estimation.

'Field' blanks, i.e. procedural blanks incorporating the use of typical matrix with zero analyte concentration, which are deemed to give a more realistic quantification of the analytical blank [17], were estimated at a grand mean of 0.045 ± 0.020 nmol L^{-1} ($n = 21$) (Table 7). For this, seawater samples had been stripped from their Fe content using NTA Superflow. The field blank's grand mean is ~0.019 nmol L^{-1} higher than the procedural blank. It is not entirely clear where this comes from, but it may be a result of some residual Fe in the stripped seawater and/or contamination from extra sample handling and lab ware when seawater is treated.

Despite the large uncertainties, we may estimate the following contributions to the field blank: reagents 41% (0.018 nmol L^{-1}), resin 0%, and sample handling and lab ware 59% (0.027 nmol L^{-1}).

The limit of detection (LOD, 3× S.D. of the mean field blank) varied per session between 0.020 and 0.069 nmol L^{-1}.

3.6. SAFe seawater reference materials

During the 2004 SAFe intercalibration exercise [11] in the Pacific Ocean at 30° N, 140° W, clean seawater was collected from the sea surface and from 1000 m depth. To the oceanographic community the following seawater samples are now available, with the following assigned consensus values for DFe: Surface-1 (0.097 ± 0.043 nmol L^{-1}), Deep-1 (stability problems, informative value of ~0.7 nmol L^{-1}, useful for method development and training), and Deep-2 (0.91 ± 0.17 nmol L^{-1}). We analyzed 1 bottle of Deep-1, 4 bottles of Deep-2 and 4 bottles of Surface-1, the results are summarized in Table 8. Our grand mean DFe values for Deep-1 (0.710 ± 0.035 nmol L^{-1}, $n = 6$), Deep-2 (0.932 ± 0.059 nmol L^{-1}, $n = 9$) and Surface-1 (0.118 ± 0.028 nmol L^{-1}, $n = 7$) are in full agreement with the assigned consensus values.

3.7. Dissolved Fe in the Western Weddell Sea

A vertical profile of DFe at station PS67/06-142 during Ice Station Polarstern (ISPOL), as measured by the ID-MC-ICP-MS procedure described here, is shown in Fig. 7. The concentration data are listed in Table 9. The smoothness of the profile and the absence of outliers even at sub-nanomolar level, suggest that contamination during sampling did not occur, which lends confidence to the use of a well-rinsed regular Niskin/CTD rosette sampling system to provide reliable Fe data, as was pre-

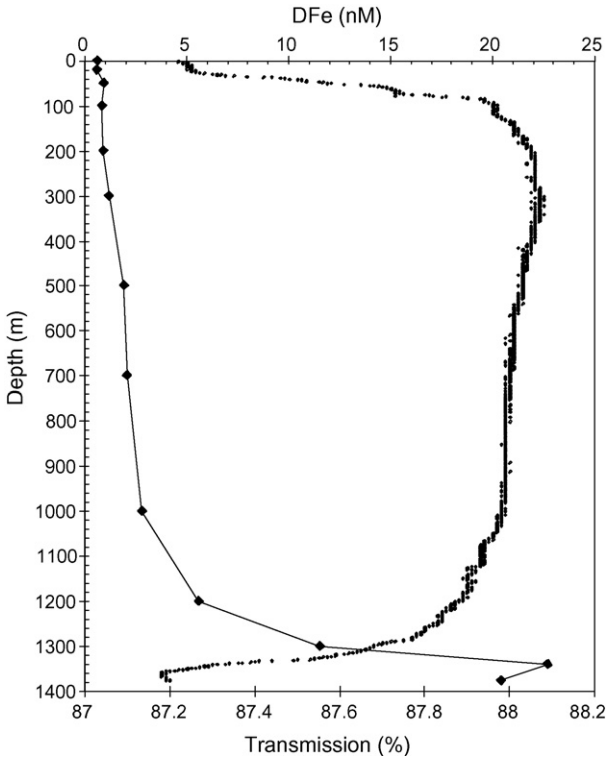

Fig. 7 – Vertical profiles of total dissolved Fe (nmol L^{-1}, black diamonds) measured by ID-MC-ICP-MS and transmission (black dots) in the western Weddell Sea (Antarctica) at Ice Station Polarstern (ISPOL, ANT XXII/2, station PS67/06-142) on January 1, 2005 at 67°22′ S, 55°25′ W. Transmission is determined by the beam attenuation and can be defined as light loss in a narrow collimated light beam as measured by the CTD's transmissiometer, due to absorption by dissolved materials and particulates and due to scattering by particulates.

viously shown by [31]. Concentrations of DFe are ~0.6 nmol L^{-1} in the surface mixed layer (30 m), ~0.9 nmol L^{-1} right below the surface mixed layer and throughout the thermocline until 200 m, followed by an increase to 2–3 nmol L^{-1} between 500 and 1000 m. Below 1200 m DFe is strongly enhanced to a maximum of ~23 nmol L^{-1} near the seafloor at 1386 m. The upper water column values are in concert with an average surface DFe in the Weddell Sea of 1.06 ± 0.46 nmol L^{-1} ($n = 14$) from recent work [32]. The mixed layer DFe minimum may be due to biological uptake by the presence of phytoplankton as evidenced by a minimum in surface beam attenuation (Fig. 7) and a chlorophyll *a* maximum up to 0.5 μg L^{-1} (not shown).

Identically shaped total dissolvable Fe (TD-Fe) profiles with ~1.3 nmol L^{-1} in the upper water column until ~25 nmol L^{-1} in the bottom water, have been reported for similar water depths on the continental shelf of the southern Weddell Sea [33]. The high values near the seafloor indicate a sediment source of DFe in bottom waters, either derived by diffusion across the sediment–water interface of high DFe from reducing pore waters, or by infusion of these pore waters by sediment resuspension [34]. The transmission profile (Fig. 7) indicated the presence of a nepheloid layer in the lowermost 250 m, likely due to resuspended sediment particles. Continental shelf slopes are known to be dynamic hydrographic environments where breaking internal tidal waves and slope circulation act to resuspend the sediment and enhance DFe concentrations in bottom waters [35]. Most of the reduced Fe would rapidly re-oxidize in the overlying seawater and adsorb to suspended particles, form colloids or precipitate. A part of this colloidal Fe may then pass through a 0.2 μm membrane filter and become detectable as DFe.

Table 9 – DFe profile ISPOL Western Weddell Sea by ID-MC-ICP-MS

Depth (bottom 1380 m)	DFe (nmol/L)	S.D.	R.S.D. (%)	*n*
0	0.583	0.028	4.8	6
−20	0.563			1
−50	0.892	0.059	6.6	2
−100	0.799			1
−200	0.877	0.022	2.5	2
−300	1.17	0.013	1.1	2
−500	1.85			1
−700	2.03	0.039	1.9	2
−1000	2.78	0.022	0.8	2
−1200	5.55	0.008	0.1	2
−1300	11.50			1
−1340	22.68	0.200	0.9	2
−1376	20.40	0.001	0.0	2

4. Conclusions

A procedure was presented to accurately measure dissolved Fe in seawater based on multiple collector inductively coupled mass spectrometry combined with isotope dilution and pre-concentration/matrix separation. Iron pre-concentration and matrix separation of acidified seawater samples spiked with ^{54}Fe was achieved through micro-columns filled with NTA Superflow resin. It was demonstrated that under the conditions described here, the resin is quantitatively binding Fe in seawater at pH 1.9. Blanks (procedural and field blanks) are low and reproducible. We analyzed reference seawater from the SAFe cruise, and our results are in agreement with the assigned consensus values. Comparison of the analytical numbers of merit for the existing IDMS methods to measure iron in seawater, shows that the method we propose here is compatible with these techniques, in terms of sample use, pre-concentration factor, blanks and LOD's (Table 1).

With the proposed method we measured a vertical profile of DFe on the shelf slope of the Antarctic Peninsula in the western Weddell Sea. Our results show DFe ranging from sub-nanomolar surface values of ~0.6 nmol L^{-1} to high near-bottom concentrations of ~23 nmol L^{-1}, reflecting enrichment due to sedimentary input.

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