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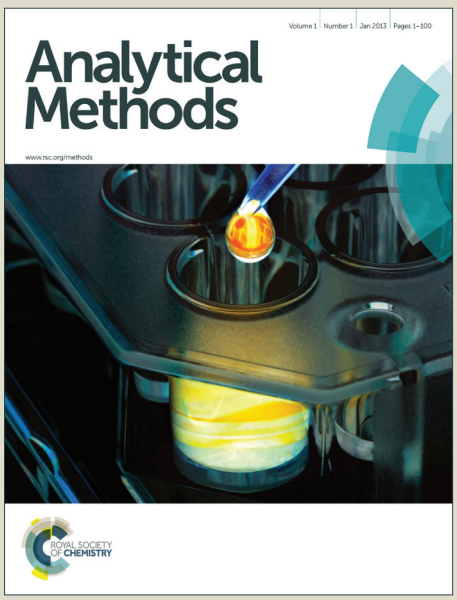

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Advances in the offline trace metal extraction of Mn, Co, Ni, Cu, Cd, and Pb from open ocean seawater samples with determination by Sector Field ICP-MS analysis

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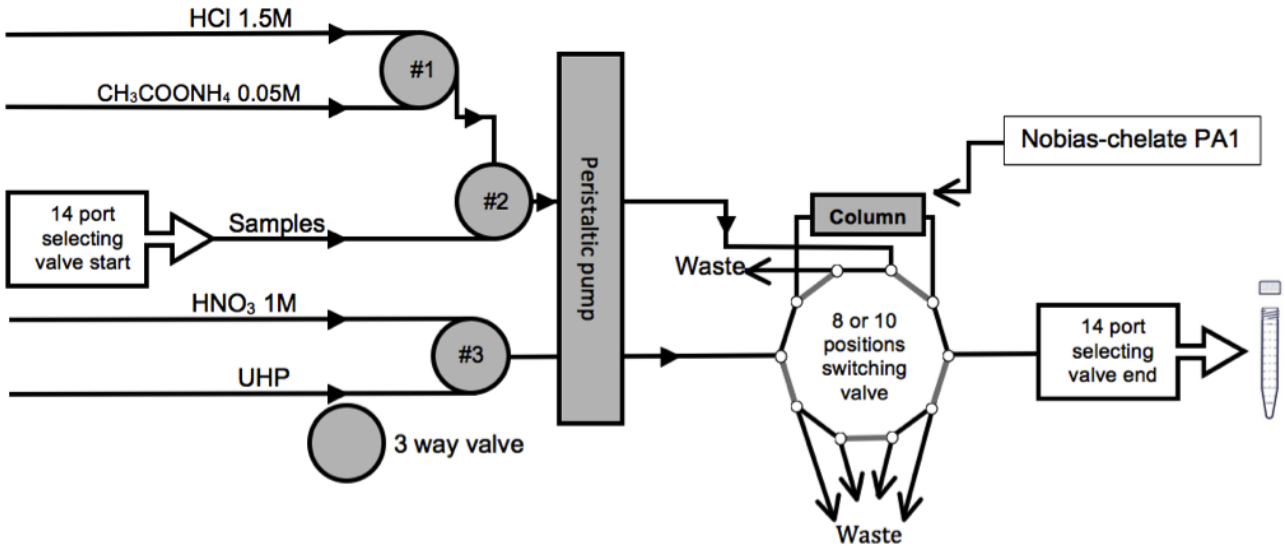

Fig. 1 Schematic of a simplified, automated, low cost, portable, off-line extraction manifold coupled to SF-ICP-MS for the determination of dissolved trace element concentrations (Mn, Co, Ni, Cu, Cd and Pb) in seawater.

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Trace metals are fundamental components of various biochemical reactions for phytoplankton. They serve as micronutrients and therefore play a key role in marine biogeochemical cycles. International programs such as GEOTRACES require fast, sensitive and reliable methods for the simultaneous analysis of multiple trace elements in seawater. This paper reports the development of a simplified, automated, low cost, portable, off-line extraction method with high sample throughput. The extraction uses the chelating resin Nobias-chelate PA1 offering an extraction factor of 18 from 27 mL of seawater. This solid phase extraction has been coupled to Sector Field-Inductively Coupled Plasma-Mass Spectrometry (SF-ICP-MS) for analysing dissolved manganese Mn (dMn), cobalt (dCo), nickel (dNi), copper (dCu), cadmium (dCd) and lead (dPb). An optimum pH of 6.2 was selected allowing quantitative recovery of most elements of interest, offering stable Cu and minimum Molybdenum (Mo) recoveries, limiting interferences of Cd determination. Picomolar or subpicomolar trace metal blank concentrations and detection limits were obtained suitable for open ocean sample measurements. Regular analysis of reference seawater samples (SAFe, GEOTRACES and an in-house seawater) showed excellent short-term and medium-term precision (1-8% RSD) and accuracy of the method. Twenty four samples, 3 blanks, 6 standard addition calibration samples, 3 replicates of an in-house seawater and 2 reference seawater samples were extracted daily. The method has been successfully applied to the analysis of seawater samples from the Southern and Pacific Oceans.

1 Introduction

Earths terrestrial and marine environments contribute equally to global autotrophic primary production[1]. For the last 20 years, iron (Fe) has been shown to be an essential trace metal controlling phytoplankton growth and primary production in ∼50% of the worlds ocean[2]. Other trace metals such as manganese (Mn), cobalt (Co), nickel (Ni), copper (Cu) and cadmium (Cd) have not been studied as extensively, although they also play a key a role in many essential cellular cycles and may be (co)-limiting factors of oceanic primary production[3]. Elements such as Mn[4,5], Cu and Ni[6,7] are indeed used as co-factors in the formation of superoxide dismutase (SOD)[8], which are important enzymes for the defence of cells against harmful reactive oxygen species. Manganese is also needed in photosystem II for the oxidation of water during photosynthesis[9]. Cobalt has important biological implication, as it is the centre of the vitamin B_{12} synthesised by bacteria and assimilated by eukaryotic phytoplankton[10,11]. Nickel is contained in urease, an enzyme that hydrolyses urea to provide nitrogen (N) to the algal cell[12,13]. Cu limitation may be linked to Fe limitation, because of the replacement in the photosynthetic apparatus of Fe-rich cytochrome *c6* by Cu-containing plastocyanin[14], and of the use of a multi-copper oxidase in some phytoplankton Fe transport system[15,16]. Under low zinc (Zn) conditions, Cd-containing carbonic anhydrase (CA)[17–20], an enzyme catalysing the conversion of bicarbonate to carbon dioxide, can be substituted for Zn-containing CA for some biological functions[21]. Some phytoplankton species might be growth limited by the availability of these micronutrients in natural seawater as Mn, Co, Ni and Cu can be (co)-limiting factors for phytoplankton growth[4,7,12,14,15,22–24]. In addition, some trace metals, such as lead (Pb) and Mn, can be used as oceanographic tracers to identify the sources of trace metals[25–29]. The understanding of the biogeochemical cycle of trace elements is a major objective of international programs such as GEOTRACES[30]. There is a pressing need to develop

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fast and sensitive routine methods for the simultaneous analysis of multiple trace elements in seawater to have a better understanding of the relationships between the biogeochemical cycling of these inter-relating elements and the biota.

In order to help determine the distribution of trace elements as well as their sources and sinks in the ocean, many single element techniques such as flow injection analysis using chemiluminescence[31–34], voltammetry[35,36], high-pressure liquid chromatography extraction with fluorescence detection[37], graphite furnace atomic absorption spectrometry after liquid-liquid extraction[38] or ICP-MS[39] have been used with adequate detection limits and sensitivities[40]. Despite the importance of (co)-limiting metals on phytoplankton growth, simultaneous determination of multiple dissolved trace element concentrations has not been as common. Inductively Coupled Plasma Mass Spectrometry (ICP-MS) which features low detection limits combined with a large linear dynamic range is well suited to this application. Unfortunately, when analysing seawater, ICP-MS is very sensitive to matrix effects arising from the high level of dissolved salts[41], typically precluding direct sample introduction. Therefore, the dominant seawater matrix is typically separated from the elements of interest using a chelating column before ICP-MS analysis. In the past, different resins with multiple functional groups such as 8-hydroxyquinoline (8-HQ)[42], nitrilotriacetic acid (NTA)[43], or iminodiacetate (IDA)[44] have been tested for their retention of trace metals. A combination of ethylendiaminetriacetate (EDTriA) and IDA functional group, as in the Nobias-chelate PA1 resin has recently proved successful[45,46].

ICP-MS also suffers from spectral interferences resulting from isobaric or polyatomic interferences (e.g., Ar oxides on Fe or Mo oxides on Cd[47,48]). Sector Field ICP-MS allows many spectral interferences to be overcome, albeit at reduced sensitivity[41].

This study presents a novel adaptation of the offline matrix separation and preconcentration system presented by Milne et al. (2010) using the Nobias resin column[46] coupled with SF-ICP-MS detection to measure simultaneously dissolved trace metals (dTM) such as dMn, dCo, dNi, dCu, dCd and dPb in seawater samples. Method accuracy and precision were assessed through the regular analysis of SAFe[49] and GEOTRACES[50,51] reference materials. The method has been successfully applied to the analysis of seawater samples from the Southern and Pacific Oceans.

2 Experimental design

2.1 Shipboard procedures

2.1.1 Sampling

Seawater samples were collected during two oceanographic research cruises, GEOTRACES GP13 in the southwest Pacific Ocean (*R.V. Southern Surveyor*, 8/05/2011 - 9/06/2011, from 30°S to 32°30'S and from 153°E to 174°W) and KEOPS2 in the Southern Ocean (*R.V. Marion Dufresne*, 7/10/2011 - 30/11/2011, from 48°2'S to 50°4'S and from 66°4'E to 74°5'E). Samples were collected using a trace metal clean rosette (TMR, model 1018, General Oceanics) equipped with twelve 10 L externally closing Teflon-lined Niskin-1010X bottles mounted on a polyurethane-powder-coated aluminium frame specially adapted for trace metal work[52]. During GP13, the TMR was attached to 6 km of non-metallic Dynex rope through a stainless steel (SS316) D-Shackle. During deployment the rope passed through a trace metal clean block, which had a plastic sheave. During KEOPS2, the TMR was attached to 1500 m of Kevlar rope. The open sampling bottles were lowered into the water and closed automatically at preset depths on the return to the surface using a pressure sensor. Depth programming was carried out prior to the deployment of the TMR[52].

2.1.2 Sample preparation

After TMR recovery, Niskin-1010X bottles were transported to and stored within a containerised clean laboratory. During GP13 we used a Teflon tap connected to an acid cleaned 0.2 μm Pall Acropak filter to subsample seawater. During KEOPS2 we used a combination of 0.2 μm Pall Acropak filter and 0.2 μm Sartorius SARTOBRAN 300 filters. Acid cleaned sample bottles (see section 2.2.1) were copiously rinsed 3 times by seawater before final sampling. Seawater samples were acidified to pH 1.8 using concentrated ultrapure hydrochloric acid (HCl, BASELINE grade provided by SEASTAR (certified impurities below 10 parts per trillion (ppt) for all the elements considered) as recommended by the GEOTRACES program[53]. Finally, seawater sample bottles were double bagged and stored at ambient temperature in the dark until analysis.

2.2 Laboratory procedure

2.2.1 Cleaning procedures and preparation of reagents

The handling of samples and reagents was conducted under high-efficiency particulate air (HEPA) conditions, with samples processed in class 100 laminar flow hoods (AirClean 600 PCR workstation, AirClean System). All sample bottles and pipette tips were acid washed prior to use following recommendations from the GEOTRACES approved methods handbook[53]. Reagents and samples were prepared or stored in low density polyethylene (LDPE) bottles (Nalgene), teflon fluorinated ethylene propylene (FEP) bottles (Nalgene) or polypropylene (PP) tubes (Technoplas). All reagents used were BASELINE grade provided by SEASTAR (certified impurities below 10 parts per trillion (ppt) for all the elements considered). Ultra high purity (UHP $>$ 18MΩ cm) water was supplied from a Barnstead International, NANOpure DIa-

mond polisher, fed by a DIamond RO, reverse osmosis system coupled with an additional 3 stage pre-filter.

Nitric acid 1 M was prepared by adding 62.5 mL of concentrated (16 M) HNO_3 to UHP water to a final volume of 1 L in LDPE bottles. 0.28 M nitric acid was prepared by adding 17.5 mL of concentrated HNO_3 to UHP water to a final volume of 1 L in LDPE bottles. The 1 M HNO_3 eluent was spiked with Rhodium (Rh) (High-Purity Standards, 1000 g.mL^{-1}, USA) at a final concentration of 10 μg.L^{-1}.

Hydrochloric acid 1.5 M was prepared by adding 136.5 mL of concentrated (11 M) HCl to UHP water to a final volume of 1 L in LDPE bottles.

Ammonium acetate buffer (CH_3COO^- 3.5 M and NH_4^+ 4.5 M) was prepared by adding 48 mL of concentrated (18 M) CH_3COOH and 103 mL of concentrated (11 M) NH_3 to UHP water to a final volume of 250 mL in LDPE bottles. The pH of the solution was then adjusted to 9.0 $\pm$ 0.2 with either CH_3COOH or NH_3. Diluted ammonium acetate buffer (0.05 M) at pH = 6.2 $\pm$ 0.2 was used for column conditioning purposes.

Multi-element solution. Working solutions of Mn, Fe, Co, Ni, Cu, Cd and Pb were prepared via serial dilutions of a 100 mg.L^{-1} multi-element solution (QCD Analysts, MISA suite of solutions, Spring Lake, USA) using UHP in a final HNO_3 concentration of 0.28 M.

Cadmium free Mo solution was prepared via serial dilutions of a 1000 mg.L^{-1} Mo solution (QCD Analysts, Environmental Science Solutions, Spring Lake, USA) using UHP water with a final Mo concentration of 10 μg.L^{-1}.

2.2.2 Sample pre-treatment

Samples were pre-conditioned before loading onto the resin-packed column. The first stage involved the breakdown of organic matter in the sample to reduce competition with the resin binding sites. To do so, a portable custom-made UV digester in a polyvinylchloride (PVC) housing was built for shipboard and laboratory use. To avoid operator exposure to UV irradiation, manual and automatic safety switches were installed. Inside the box, three 85 cm long by 1.7 cm diameter lamps were mounted on removable racks. This orientation provided flexibility to fit a range of sampling bottles from 30 mL to 1 L and allowed for shipment and safe shipboard operation. Each lamp had an output of 30 mW.s.cm^{-2}. To UV irradiate samples under trace metal clean conditions, samples were stored in capped UV transmitting FEP bottles. FEP bottles filled with the sample were then placed between 2 lamps (1 cm away) for 1 h (this irradiation timing has been chosen following several tests that are detailed in section 3.1). Thirty mL of the UV digested samples were then subsampled in LDPE bottles. Finally, samples were buffered to pH=6.2 $\pm$ 0.2 by adding ammonium acetate solution (500 μL in 30 mL of sample). The concentration of added buffer in the sample varied with the sample pH and the time after buffer preparation as evaporation might change the concentration of the buffer if not freshly prepared before each extraction.

2.2.3 Offline extraction system

The extraction system (Figure 1) was made of three, solenoid operated, 3-way valves supplied by Bio-Chem Fluidics, two 14 lines selector valves (C25Z-31814EMH, VICI Valco instrument), one 10 port, 2 positions valve (C22Z-3180EH, VICI Valco instrument), a peristaltic pump with 2 or more channels (Gilson Minipuls 3) and finally a column filled with the Nobias-chelate PA1 resin (section 2.2.4). The inner part of these valves was made of polytetrafluoroethylene (PTFE). The 3 way valves (#1, #2, #3) consisted of a common outlet and two selectable inlets. The use of a selector valve at each end of the manifold allowed the automatic extraction of 14 samples in a single automated sequence. All the reagents, samples and valve lines consisted of PTFE 1/16" tubing (Cole Parmer) while the peristaltic pump tubing was made of 2 stop flow rated PVC (Cole Parmer). During operation the flow rate was set at 2 mL.min^{-1}. All valves and pumps were controlled using LabView 6 (National Instruments Corp.) with either a 5 V TTL signal or 5 V TTL to 12 V converter (DC relay switch, Jaycar Electronics).

2.2.4 Column

The column body was made of 2-stop flow rated PVC peristaltic pump tubing. Six cm of a 2.06 mm inner diameter (id) and 3.78 mm outer diameter (od) PVC tube (purple-purple) was used to obtain a column volume of approximately 200 μL. At both ends of the column, polyethylene frits (20 μm pore size) and quartz fiber were used to retain the resin. The Nobias-Chelate PA1 chelating resin (Hitachi High-Technologies) was used for the extraction of trace metals[46,54,55]. To reduce excessive back-pressures, the smallest resin beads were first excluded by gravimetric size fractionation before loading into the column. To do so, the resin was suspended in UHP water and shaken vigorously, with large particles settling while smaller particles remained suspended in solution. The suspended solution was then discarded and the process was repeated 10 times. The resin was loaded onto the column using a peristaltic pump (see section 2.2.3).

2.2.5 Extraction procedure

Before each extraction session, the manifold was cleaned in four steps. First, each line was flushed with 6 mL of 1.5 M HCl at 2 mL.min^{-1}. Next the manifold was thoroughly rinsed with UHP water for at least 15 min. Then all the lines were filled with the reagents described above. To finish and prepare for the seawater sample all 14 outlet lines were then filled with 1 M HNO_3 so that all dead spaces in the manifold matched the eluent matrix. Once prepared, the timing parameters for extraction were selected (Table 1). At the start of an extraction run, UHP water was extracted as a sample to load the first

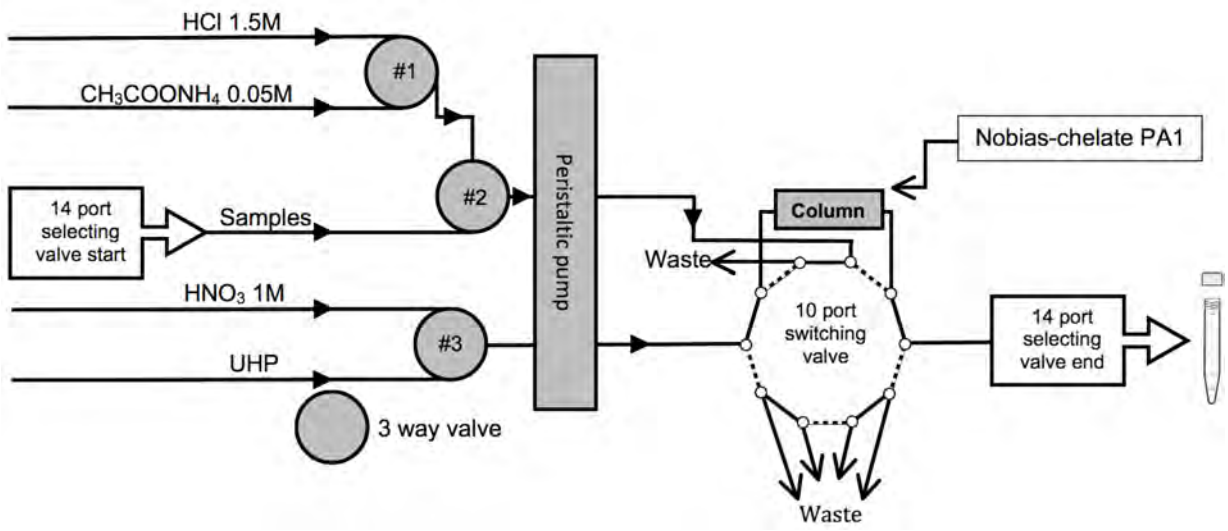


Fig. 1 Extraction manifold schematic for the determination of dissolved trace element concentrations in seawater. The 14 port selecting valves were actuated like autosamplers. The valve at the beginning of the manifold was always set 1 position ahead the ending one. Both selecting valves were advanced forward to the next sample at the beginning of the eluting phase. 27 mL of seawater were pre-concentrated through 200 μL of Nobias-chelate PA1 resin at 2 mL per min. Trace elements were eluted in 1.5 mL of 1 M nitric acid. Only one column was used in the manifold. The column was rinsed and reconditioned prior to loading of a new sample. The 10 port switching valve setup in position B is presented with a dashed line and for position A in black. An 8 port switching valve could be used with the same setup. See section 2.2.5 for further details.

Table 1 Extraction timing parameters

Process	Cleaning	Conditioning	Loading	Matrix removal	Eluting
Timing	60 seconds	30 seconds	810 seconds	90 seconds	45 seconds
3 way #1	HCl	CH_3COONH_4	CH_3COONH_4	CH_3COONH_4	CH_3COONH_4
3 way #2	HCl	CH_3COONH_4	samples	CH_3COONH_4	samples
3 way #3	UHP	UHP	UHP	Nitric 1M	Nitric 1M
10 port switching valve	B	B	B	B	A

sample. During sample extraction a flow-rate of 2 mL.min^{-1} was selected and verified by weighing the outflow of the sample waste line over 2 min. The extraction factor (ratio between the volume of seawater passing through the column (27 mL) and the volume of eluent (1.5 mL)) was also carefully monitored by weighing sample bottle and collected eluent before and after loading. First the column was cleaned for 60 seconds by 1.5 M HCl followed by the column conditioning step. Valve #1 (Figure 1) selected the diluted ammonium acetate buffer (0.05 M) at pH = 6.2 $\pm$ 0.2 in order to prepare the resin for sample extraction. Then, valve #2 selected the sample line during 13.5 min for the sample loading step. This was followed by the saline matrix removal by the diluted buffer solution. Then valve #2 was moved back to its previous position. At the beginning of this step, valve #3 selected the 1M nitric acid to fill the line with eluent and avoid UHP water loading during the elution step. Then both selecting valves were advanced forward to the next sample. Finally, the 10-port valve switched to position A to allow nitric acid through the column and into the correct sample vial. During this final step, valve #2 selected the sample line to load the next sample and avoid cross contamination and memory effect before the start of the next sequence.

2.3 ICP-MS analysis

Analysis was undertaken using a Thermo Fisher Scientific ELEMENT 2 Sector Field Inductively Coupled Plasma Mass Spectrometer (SF-ICP-MS). The instrument was operated with the capacitive guard electrode activated[56,57] providing enhanced sensitivity ($\sim$10-20x over standard conditions). Measured isotopes and spectral resolutions employed, along with typical operating conditions, are reported in Table 2 while further details are provided elsewhere[58,59]. Standard Ni sampler and skimmer cones were employed throughout. Rhodium added to the 1 M HNO_3 eluent was used to monitor

and normalise any variations in instrument sensitivity during the course of the analytical sequence in both resolutions[46]. Each day of analysis the instrument was warmed, conditioned and tuned to maximise sensitivity and stability (low resolution mode) with spectral resolution optimised (medium resolution mode). During the course of each sample sequence HNO_3 blanks and in-house seawater samples were measured regularly as quality control (QC) samples. The sample introduction line was rinsed with 1 M HNO_3 between samples for 2 min. A Cd free Mo solution was analysed during each batch of samples and used to determine the contribution of unresolvable $^{95}Mo^{16}O^+$ (m/z=111) interference on measured ^{111}Cd signal[47,60,61].

Table 2 Instrument conditions and measurement parameters

Instrument	ELEMENT 2 Sector Field ICP-MS (Thermo Fisher, Germany)
Torch	Fassel type (Thermo Fisher, Germany)
Spray chamber	20 mL Cyclonic (Glass Expansion, Australia)
Nebuliser	0.2 mL.min^{-1} Micromist (Glass Expansion, Australia)
RF power (W)	1350
Cool gas flow (L.min^{-1})	$\sim$ 15
Auxilary gas flow (L.min^{-1})	$\sim$ 0.7
Sample gas flow (L.min^{-1})	$\sim$ 0.95
Guard Electrode	activated
Sample uptake	100s, with pumping
Sample rinse	120s, 1M nitric
Scan type	E-Scan
Isotopes monitored in Low resolution (m/Δm$\sim$400)	^{95}Mo,^{103}Rh ^{111}Cd ^{207}Pb
Isotopes monitored in Medium resolution (m/Δm$\sim$4000)	^{55}Mn,^{56}Fe ^{59}Co,^{60}Ni ^{63}Cu,^{103}Rh

2.4 Elemental determination

For the determination of the dissolved element (Mn, Fe, Co, Ni, Cu, Cd, Pb) concentrations, a 6 point standard addition calibration was acquired per element. The 6 point calibration solutions were made volumetrically by adding 0, 100, 200, 300, 400 and 500 μL of a 10 μg.L^{-1} multi-element standard to 30 mL to the in-house seawater (of low-trace-metal concentrations see Table 3). The in-house seawater was collected in austral summer 2005 close to the Kerguelen Islands during the KEOPS-1 cruise in the Southern Ocean. This seawater was sampled with acid-cleaned Go-Flo bottles following trace metal clean protocols (Blain et al., 2008). Seawater was filtered using Sartobran cartridges (0.2 μm with 0.4 μm prefilter, Sartorius) and preserved in the dark and unacidified in an acid cleaned 50 L LDPE carboy. A chelating resin column was used to remove trace metals from this seawater for blank determination purposes only. Concentrations of this purified, in-house seawater was also measured (Table 3).Using the natural abundance of the element in the multi-element standard and the final volume of the sample before the extraction, added concentrations ranged from 4 ng.L^{-1} of Cd to 163 ng.L^{-1} of Mn. The elemental concentrations in each seawater sample were calculated after extraction factor (section 2.2.5) and ICP-MS drift correction (section 2.3).

3 Results and discussion

3.1 UV-irradiation

Iron, Cu and Co form chelates with dissolved organic ligands in seawater[62–66]. In previous studies, microwave and UV irradiation have been used to dissociate trace metals from organic ligands in seawater[44]. Microwave treatment did not show a significant release of trace metals, whereas UV irradiation resulted in a significant release of trace metals (detailed further in this section), in particular for Co and Cu[44,46,67]. No significant release of Fe was previously observed[44,46,67]. In this study, two powerful UV bulbs (30 mW.s.cm^{-2}) were used to irradiate 125 mL of sample in FEP bottles. As expected Cu and Co signals were affected by UV-irradiation but Fe signal was also affected. After 1 h of UV irradiation, the maximum Cu recovery was obtained and remained stable over a further 2 h of continued UV exposure (Figure 2). After 1 h, the Co signal increased by 287% to extremely high dCo concentrations. It was expected that a longer irradiation time would provide a stabilisation of the dCo (similar to dCu)[44,46] but in our studies dCo concentrations varied by 50% without obvious explanation. The Fe signal increased by 40% after 1 h and remained relatively stable up to 2 h of UV irradiation while after 3h, the Fe signal increased by 91%. Nonetheless 1 h of UV irradiation provided accurate and precise dCu and dCo concentrations over time for reference seawater samples with the exception of SAFe S dCu (Table 4). For the same reference seawater, dFe results were not accurate and not precise (discussed in section 3.5). The SAFe[49] and GEOTRACES[50,51] reference seawater samples were acidified in 2004 and 2008 respectively, whereas the KEOPS 2 reference station seawater was acidified for 1 year. A shorter acidification combined with UV irradiation might not be able to dissociate metal-ligand complexes as efficiently as long-term acidification, leaving unbound organic ligands in solution that may reform after UV irradiation. When analysing a surface to depth profile with or without UV irradiation (Figure 3), UV irradiation resulted in an increase from 17 to 26% of dCo concentrations at the sur-

Table 3 In-house seawater concentrations (± 1 Standard Deviation (SD)) and precisions (Relative Standard Deviation (RSD)) obtained during one analytical sequence and the mean of three replicate assays over 8 individual sequences. In addition, purified in-house seawater concentrations used for blank determination are described.

Average concentration		[dMn] nmol.L^{-1}	[dFe] nmol.L^{-1}	[dCo] pmol.L^{-1}	[dNi] nmol.L^{-1}	[dCu] nmol.L^{-1}	[dCd] pmol.L^{-1}	[dPb] pmol.L^{-1}
In-house seawater	from 1 sequence (± 1SD, $n = 3$)	0.359 ± 0.003	1.27 ± 0.09	7.2 ± 0.4	5.2 ± 0.1	0.85 ± 0.02	517 ± 4	77.5 ± 0.5
	Precision (RSD)	1%	7%	8%	1%	2%	2%	1%
	from 8 sequences (± 1SD, $n = 24$)	0.38 ± 0.02	1.3 ± 0.4	6.5 ± 1.1	5.2 ± 0.2	0.82 ± 0.06	508 ± 11	78 ± 2
	Precision (RSD)	2%	32%	8%	1%	4%	2%	3%
Purified in-house seawater	from 7 sequences (n=7)	0.004 ± 0.001	0.14 ± 0.03	2.6 ± 0.4	0.22 ± 0.02	0.12 ± 0.03	1.5 ± 0.5	2.4 ± 0.4

face (0 - 200 m) compared to an increase of 38 to 51% at depth (500 - 1300 m), suggesting that more ligands are found below the euphotic layer as mentioned by Bown et al. (2012)[68] and Ellwood et al. (2005)[69]. Dissolved Cu concentrations increased after UV irradiation, however this increase was constant (17%±4%) from 0 to 1300 m (Figure 3). Differences in the concentrations currently reported from oceanographic voyages might depend on the intensity and duration of the UV exposure used, therefore standardised UV treatments should be developed to provide operationally comparable total dCu or dCo data if a short acidification time is used.

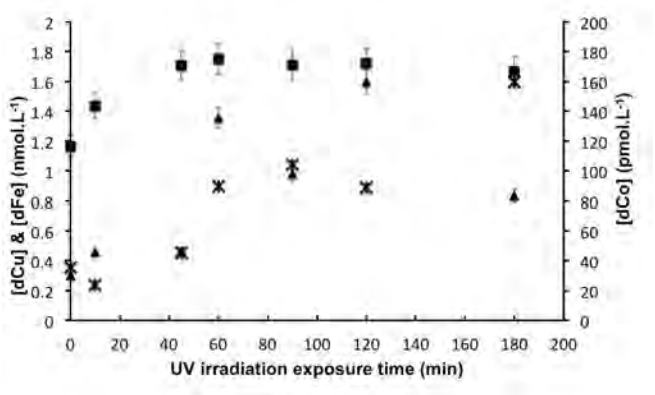


Fig. 2 dCu (filled square), dCo (filled triangle) and dFe (black star) concentrations measured in a sample mixture KEOPS 2 reference station East of the Kerguelen Plateau (50°21.53S, 66°42.44E) versus UV irradiation time

3.2 ICP-MS interference and drift

Molybdenum oxide isobaric interference with ^{111}Cd is known as a bias for dCd measurement in seawater by ICP-MS[47]. A single element Cd free Mo solution was used to correct for any contribution of MoO^+ interference on the measured Cd signal.

Table 4 Reference seawater samples results used for UV irradiation method validation. Samples were UV irradiated for 1 h. Measured values in pmol or nmol.L^{-1}. Consensus values were updated in May 2013 (pmol or nmol.kg^{-1}) and were adjusted using a density of seawater value of 1.025 kg.L^{-1}

	SAFe S (n=8)		GEOTRACES GD (n=7)	
	Measured	**Consensus**	**Measured**	**Consensus**
[**dFe**] nmol.L^{-1}	0.2±0.2	0.093±0.008	1.8±0.4	1.00±0.10
[**dCo**] pmol.L^{-1}	4±1	5±1	68±5	68±1
[**dCu**] nmol.L^{-1}	0.36±0.02	0.53±0.05	1.55±0.08	1.70±0.07

Mo was monitored for every seawater sample and a correction factor applied. Results suggested that the column retained Mo more efficiently at low pH ($1.8 < pH < 6$) as shown previously[70] (Figure 4a).

In order to minimize MoO^+ interferences associated with ^{111}Cd, a pH near 6 was employed during sample extraction. Careful instrument tuning enabled ^{56}Fe to be clearly and reliably separated from $^{40}Ar^{16}O$ interference. The inclusion and analysis of Rh (added to the eluent) revealed that the SF-ICP-MS typically provided excellent stability over the course of a 10 h analysis sequence, with a maximum and an average loss of signal intensity of 10% and 6%, respectively. After correction for any SF-ICP-MS drift, the measured in-house seawater concentrations were consistent across SF-ICP-MS assays for samples measured from two cruises (Table 3).

3.3 pH and recovery

Elemental recoveries were evaluated with regards to the maximal in-house seawater concentration measured and were found to vary depending on the extraction pH used (Figure 4b). For Mn, Co, Ni, Cd and Pb, recoveries were very stable

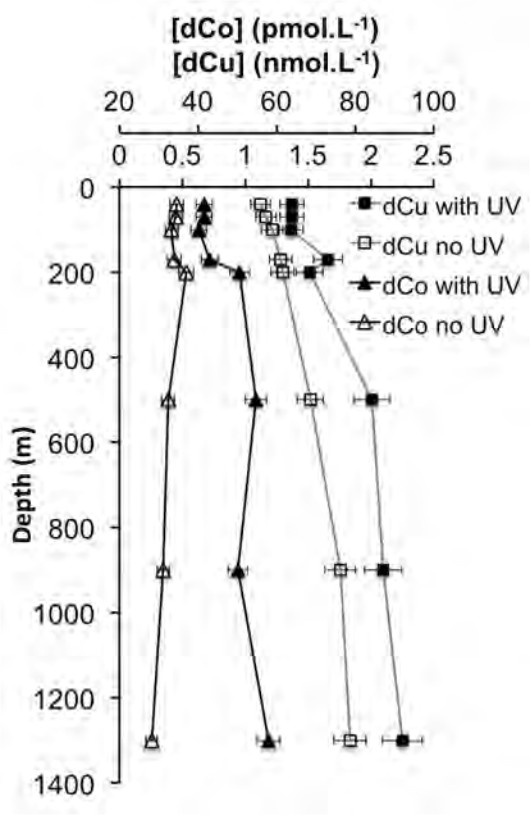


Fig. 3 dCo (triangle symbols) and dCu (square symbols) profiles at the KEOPS 2 reference station East of the Kerguelen Plateau (50°21.53S, 66°42.44E). Symbols are in black for UV irradiated samples and empty for non UV irradiated samples.

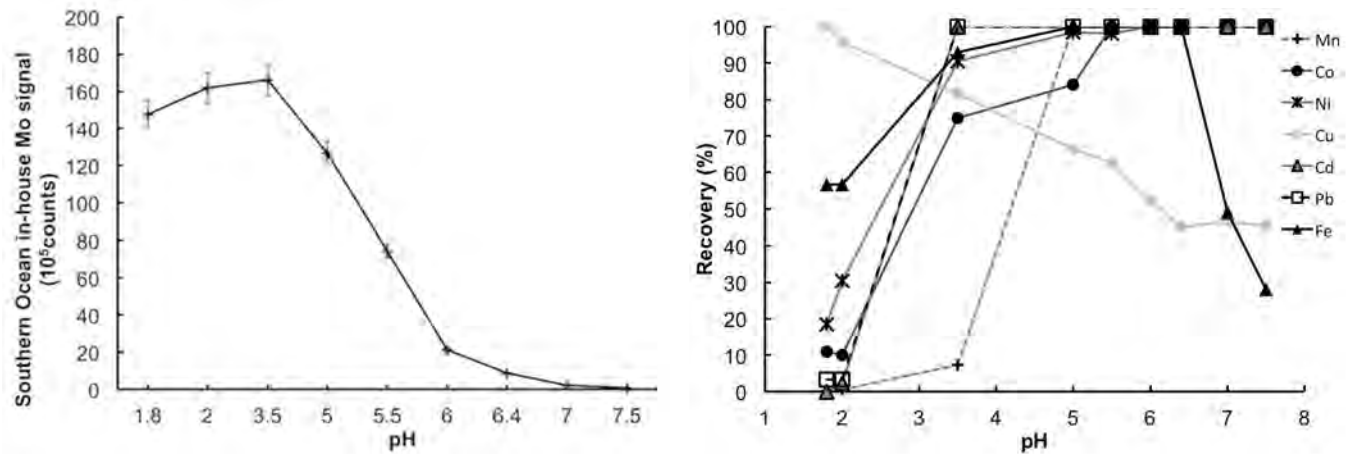
and maximum (>95%) for pH greater than 5.5 as observed by Sohrin et al. (2008), Biller and Bruland (2012) and Lagerström et al. (2013). For Fe, a recovery decrease was observed at pH greater than 6.4 probably due to Fe complex formation with organic ligand competing with the chelating resin binding sites. At high pH, aggregation, coagulation and Fe oxy(hydroxy) formation could also occur. For Cu, a maximum recovery was obtained at pH of 1.8 and generally decreased with increasing pH. Copper recovery reached a plateau at pH = 6.2. Organic ligands competing with the resin for the complex formation could explain the decrease in Cu recovery at pH >2. To allow the quantitative recovery of most elements of interest and minimum Mo retention, the optimum sample extraction pH selected was 6.2 ± 0.2. Our tests suggest that a rigorous control of the extraction pH was important to achieve reproducible recoveries for multi-element analyses.

3.4 Blanks and detection limits

The fundamental aim of our blank determination was to obtain a blank concentration of the reagents, the manifold and the SF-ICP-MS in a single analysis without a significant contribution from the seawater loaded to the column. To reduce the blank contribution of trace metals in the seawater matrix, the in-house seawater was run through a Nobias column offline to remove as much of the trace metals as possible before extraction (Table 3). Furthermore we increased the concentration of the reagents in the purified in-house seawater by a known factor (ammonium acetate buffer from 0.058 M CH_3COO^- to 0.783 M CH_3COO^- and from 0.075 M NH_4^+ to 1.01 M NH_4^+ and HCl from 0.024 M to 0.32 M) and then loaded across the column for less time by the same factor (13.5). This gives the blank contribution of the reagents with an insignificant contribution from the seawater matrix. The extraction with a shorter loading step remained representative of the usual extraction as the change of matrix (diluted ammonium acetate buffer/seawater) was still observed before and after the loading step. The average signal of triplicate blanks was then subtracted from the sample signal after interference and drift correction for the trace metal concentration determination. Dissolved Mn, Co, Cd and Pb blanks were at picomolar or sub picomolar levels whereas dNi and dCu blanks were at tens of picomolar levels. The blanks and detection limits (defined as 3 times the standard deviation of the blank) were comparable or lower than selected recent literature values[44–46] except for Cu which is higher than other studies by a factor 2 to 5 (Table 5). The dFe blank was comparable to the blank measured by Milne et al. (2010) but the detection limit was 4 times higher. Except for Fe, blanks and detection limits were suitable for open ocean sample measurements.

3.5 Precision and Accuracy

Instrumental (SF-ICP-MS) precision (RSD of the measured intensity per isotope and per sample) was below 2 % for most of the measured isotopes (including ^{56}Fe) from the in-house seawater extraction with the exception of Co (15 %) which displayed concentrations close to the detection limit. The precision of the method was assessed comparing results from the analysis of the in-house sample during short-term (up to 12 h) and medium-term (8 occurrences over 15 days) SF-ICP-MS analytical experiments (Table 3). The short-term precision was lower than 2% for all the studied metals except for dFe (7%) and dCo (8%). Dissolved Co was higher as the concentration was very close to the detection limit. The medium-term precision was also excellent (2-4%) with similar dCo medium-term and short-term precision (8%). For dFe the medium-term precision was very high (32%). The analytical precisions were better than in Lagerström et al. (2013) (2 to 4%) except for the medium and short-term dCo (8%), dFe (7% and 32%) and the



(a) **(b)**

Fig. 4 (a) In-house seawater Mo counts as a function of pH. **(b)** Elemental recovery as a function of pH

Table 5 Average blanks and extraction detection limits determined as 3 times the blank standard deviation during GP13 sample extractions (8 extraction and analysis replicates over 15 days)

	Blanks				Detection limits			
Elements	This Study	Lagerström et al. (2013)	Biller and Bruland. (2012)	Milne et al. (2010)	This Study	Lagerström et al. (2013)	Biller and Bruland. (2012)	Milne et al. (2010)
[dMn] (nmol.L^{-1})	0.004	0.008	0.005	0.04	0.002	0.002	0.002	0.007
[dFe] (nmol.L^{-1})	0.25	0.065	0.030	0.23	0.090	0.014	0.014	0.022
[dCo] (pmol.L^{-1})	1.7	0.74	0.42	6.2	0.70	0.29	0.13	2.0
[dNi] (nmol.L^{-1})	0.013	0.026	0.20	0.038	0.003	0.013	0.087	0.026
[dCu] (nmol.L^{-1})	0.053	0.013	0.033	0.015	0.030	0.003	0.053	0.007
[dCd] (pmol.L^{-1})	0.19	NA	0.79	3.84	0.12	NA	0.88	0.60
[dPb] (pmol.L^{-1})	0.72	NA	1.01	1.4	0.20	NA	0.57	0.20

medium-term dCu (4%) (Table 3). The dCo and dCu precisions in our study were higher due to the lower concentrations (by 5 and 2 times) in our in-house seawater. The precision for each element was comparable to or better than the uncertainties reported for SAFe and GEOTRACES reference seawater samples and comparable to or better than the precision reported in the literature[44–46]. Exceptions were dNi and dCu which were slightly higher. The analysis of samples from the GEOTRACES GP13 voyage over 15 days of extraction using seawater reference material, along with the in-house seawater, revealed very good medium-term precision of the method (Table 3 and 6) for all the studied metals except for dFe. Reference seawater samples were also used to assess method accuracy (North Pacific SAFe Surface and Deep2 samples[49] as well as North Atlantic GEOTRACES Surface samples[50,51]). The measured values for each studied element were in excellent agreement with the consensus values further validating our method except for dFe (Table 6). Only measured dCu was 50% lower than the SAFe S consensus value without obvious explanation whereas dCu measured concentrations were close to the SAFE D2, GEOTRACES S & D consensus values. Due to the poor accuracy and precision of dFe measurements, high blanks and detection limit, Fe was not considered further for open ocean seawater assays.

3.6 Application of the method to open ocean seawater analysis

The method was applied to ∼500 samples from 38 stations collected during the GP13 cruise and to ∼180 samples from 17 stations from the KEOPS 2 cruise. In addition, 140 standard addition points, 120 blanks, 70 in-house seawater aliquots, 60 reference seawater samples and 23 Mo oxide correction samples were analysed over 2 months requiring 16 and 8 days of ICP-MS analysis for GP13 and KEOPS 2, respectively. The entire datasets will be published and discussed

Table 6 Reference seawater sample results used for the method validation during the analysis of GP13 samples. Samples were not UV irradiated. Measured values in (pmol or nmol.L^{-1}) compared to the consensus values in (pmol or nmol.L^{-1}). Consensus values were updated in May 2013 (pmol or nmol.kg^{-1}) and were adjusted using a density of seawater value of 1.025 kg.L^{-1}. No UV irradiated SAFe S and D2 dCo and dCu consensus values were published in August 2009.

	SAFe S (n=15)		SAFe D2 (n=15)		GEOTRACES S (n=9)	
	Measured	**Consensus**	**Measured**	**Consensus**	**Measured**	**Consensus**
dMn(nmol.L^{-1})	0.89±0.02	0.81±0.06	0.43±0.02	0.36±0.05	1.54±0.04	1.5±0.1
dFe(nmol.L^{-1})	0.4±0.2	0.093±0.008	1.00±0.4	0.933±0.023	1.2±0.3	0.546±0.046
dCo(pmol.L^{-1})	3.8±0.1	2.8±0.7	31±2	26±2	28±1	36±7 (UV)
dNi(nmol.L^{-1})	2.2±0.1	2.34±0.09	8.1±0.5	8.8±0.3	2.00±0.06	2.13±0.06
dCu(nmol.L^{-1})	0.26±0.05	0.50±0.04	2.2±0.2	2.17±0.08	0.74±0.06	0.85±0.08 (UV)
dCd(pmol.L^{-1})	1±1	1.1±0.3	1004±30	959±23	2.3±0.4	2.2±0.6
dPb(pmol.L^{-1})	49±1	49±2	27±2	28±1	28.5±0.7	29±1

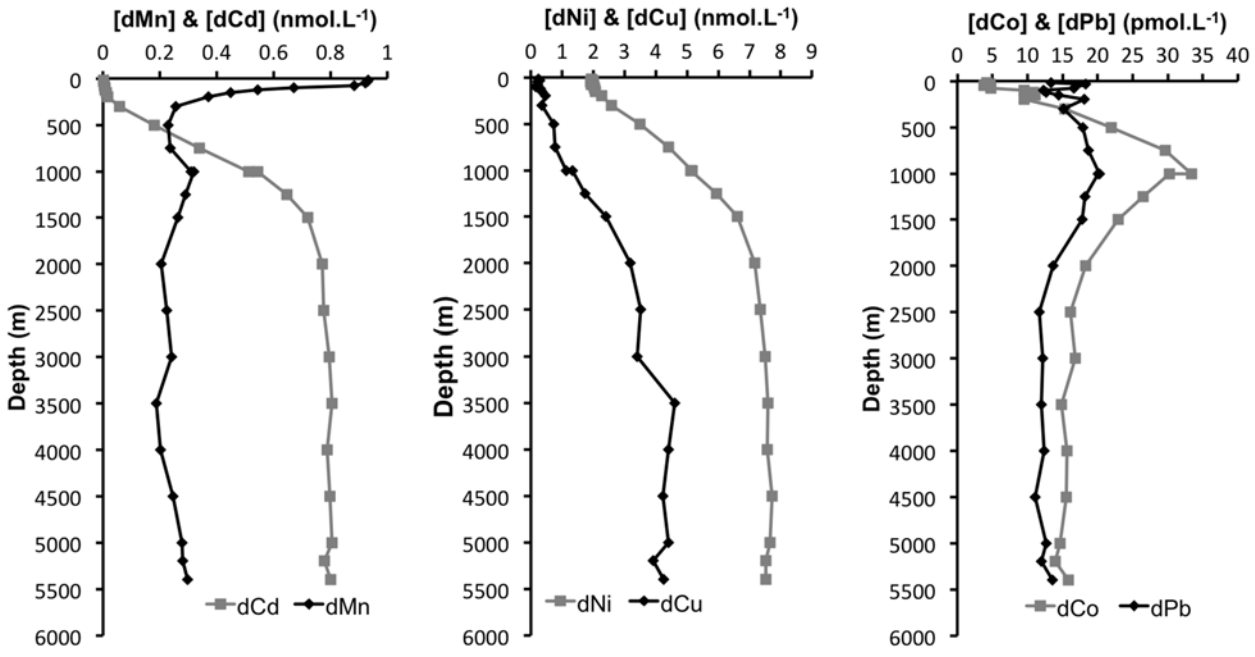
elsewhere. As an example, results are shown for station 23 (30°S, 175°E, 25/05/11) of GP13 cruise. Two consecutive TMR deployments of 12 bottles were achieved at this station (1 shallow and 1 deep) to get high vertical resolution profiles (=24 depths in total for this station). Dissolved Mn (Figure 5a) presented a typical scavenged-type vertical profile[29] with higher surface mixed layer values in the upper 96 m of 0.92 ± 0.02 nmol.L^{-1} (n=4) consistent with photo reduction maxima[9,71] or atmospheric input[72,73] followed by depletion at lower depths (>500 m, 0.25 ± 0.04 nmol.L^{-1}, n=16)[25,26] because of likely adsorption of dMn onto settling particles[71]. Elements such as Ni, Cu and Cd revealed nutrient-like profiles that are typical of these elements (Figure 5a and 5b). The surface depletion of these profiles is indicative of the biological uptake of these metals. Dissolved Cd displayed very low surface mixed layer concentrations (0.001 ± 0.001 nmol.L^{-1}). Dissolved Co displayed a hybrid profile with a mix of a nutrient- and a scavenged-like profile with a deep water depletion below 1000 m. Dissolved Pb concentrations were low 15.8 ± 5.0 pmol.L^{-1} (n=24) throughout the vertical profile suggesting no anthropogenic influence[27,74] (Figure 5c).

3.7 Comparison with other methods

The manifold presented in this study is a novel version of the manifold published by Milne et al. (2010) using the Nobias-chelate PA1 resin[46]. Our method did not use the isotope dilution quantitation approach[43–45,75,76] but rather a standard addition quantification method[44–46] for the determination of the dissolved trace elements of interest. This was a simplified method using only one sample of 27 mL to analyse dMn, dCo, dNi, dCu, dCd and dPb. Milne et al. (2010) analysed 4 aliquots of 12 mL per sample using a combined isotope dilution and standard addition approach. Moreover the manifold was improved to extract 12 samples (usually one TMR cast) in a single automated sequence with the use of two 14 lines selector valves as an auto-sampler (section 2.2.3). With the off-line extraction only 5 min of ICP-MS per sample were required to get precise and accurate measurements, which is very valuable considering that the most expensive component of the entire extraction and analysis is the ICP-MS running cost. Low blanks and detection limits revealed that a peristaltic pump can be used to carry the sample and eluent to the column, thus simplifying the manifold compared to pressurised eluent manifold[46] that were introduced to reduce blanks and detection limits. Our method has an extraction factor of 18 which is higher than previously reported in Milne et al. (2010) and Biller and Bruland (2012) with extraction factors of 12 and between 10 and 13, respectively. Nonetheless our extraction factor was lower than in Lagerström et al. (2013) where the elements were eluted to a very small volume (0.045 mL compared to 1.5 mL in our study) to gain an extraction factor of 200. However, an extraction factor of 18 resulted in measured concentrations over the ICP-MS instrumental detection limits. Similar to the methods reported by Milne et al. (2010) and Biller and Bruland (2012), the manifold was custom made with parts and software commercially available. It required electronic and programming knowledge that can be learned and applied in a relatively short period of time to reproduce the manifold which is very valuable for rapid laboratory implementation. The compact footprint of the manifold permits possible use at sea (if required, not considered here) to extract samples quickly and efficiently after collection and acidification, with subsequent analysis in the shore-based laboratory.

4 Conclusions

This study presents a novel method which allows the simultaneous measurement of multiple trace elements such as dMn, dCo, dNi, dCu, dCd, dPb in seawater with low blanks, detection limits, good reproducibility and very good accuracy. Excellent results from reference seawater samples and in-house seawater showed that the method could be reliably and repro-



(a) dCd and dMn profiles **(b)** dCu and dNi profiles **(c)** dCo and dPb profiles

Fig. 5 dMn, dCo, dNi, dCu, dCd, dPb vertical profiles from samples collected during GP13 cruise at station 23 (30°S, 175°E, 25/05/11). The 'typical' RSD error was below 2% based on the triplicate analysis of the in-house seawater.

ducibly used to analyse samples from oceanographic cruises in a relatively short period of time. If necessary, it is proposed that extraction could be achieved at sea after sample collection with subsequent post-cruise measurement by SF-ICP-MS in the shore-based laboratory. Future work will be focusing on the automation of the buffer addition with on-line pH sensor with very low internal volume and improvement of Fe measurements. This method simplifies the analysis of trace elements in seawater providing an approach that is simpler and could be adapted as routine.

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