

Determination of ultra-trace amounts of cadmium, cobalt and nickel in sea-water by electrothermal atomic absorption spectrometry with on-line preconcentration

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A miniature column packed with Muromac A-1 chelating resin and a laboratory-built automatic on-line preconcentration system for electrothermal atomic absorption spectrometry were used to determine Cd, Co and Ni in sea-water. The preconcentration system was modified from a Perkin-Elmer AS-40 autosampler by mounting a Muromac A-1 microcolumn near the tip of the autosampler capillary, and we replaced the pull-and-push pump of the autosampler with a peristaltic pump. Retention of the metal ions as a complex on the microcolumn was achieved by using Muromac A-1 as the chelating resin; 20% HNO₃ was then used for elution. The procedures of preconcentration were performed by using a four-way distribution valve and a programmable controller. Detection limits (and sample volumes) were $1.2 \times 10^{-4} \mu\text{g l}^{-1}$ for Cd (400 μl), $0.007 \mu\text{g l}^{-1}$ for Co (1800 μl) and $0.033 \mu\text{g l}^{-1}$ for Ni (800 μl). Relative standard deviations for the determination of Cd, Co and Ni in sea-water (CASS-3) were 2.9, 5.6 and 4.1%, respectively. The accuracy of the method was confirmed by the analysis of certified reference saline waters (NASS-4, CASS-3 and SLEW-1).

The direct determination of trace metals in sea-water by electrothermal atomic absorption spectrometry (ETAAS) is difficult even with sophisticated background correction and chemical modification; not only because of the presence of many trace metals at concentrations near or below the detection limit, but also because the sea-water matrix may cause serious interference. Preconcentration procedures can solve the above two problems and allow easy determination. There are many preconcentration methods, including co-precipitation, liquid-liquid extraction, column extraction and electrolysis.¹ Among these, the column extracting method is simpler and it has a higher concentration factor and the ability to treat a larger sample volume in a closed system free from contamination.

The solid phase materials used in column extraction contain reverse phase sorbents, ion-exchange resins and chelating resins.²⁻¹⁸ Among these, the chelating resins method is simpler and less time-consuming than the others. Chelating resins such as Chelex-100,²⁻⁶ Muromac A-1,⁷⁻¹² quinolin-8-ol immobilized on porous glass^{4,13-15} or silica,^{16,17} and poly(dithiocarbamate)¹⁸ have been used for the enrichment of natural water and biological materials.

A number of on-line chelating resin preconcentration systems for trace metal determinations have been reported.²⁻¹⁸ The on-line preconcentration systems are easily automated and more efficient, reproducible, have lower consumption of sample and reagent and lower risk of contamination than the off-line preconcentration system.¹⁹ On-line flow injection column preconcentration in atomic spectrometry was reviewed by Fang *et al.*²⁰ Azeredo *et al.*²¹ successfully integrated column preconcentration with ETAAS by using a column packed with silica-immobilized 8-hydroxyquinoline. Sperling and co-workers²²⁻²⁶ modified the on-line flow injection system of a flame atomic absorption spectrometer to achieve feasible determinations with ETAAS, based on sodium diethyldithiocarbamate (NaDDC) and C₁₈ silica gel. We reported that trace metals in sea-water could be determined using C₁₈ silica gel and ammonium pyrrolidine-dithiocarbamate (APDC) with an automated on-line preconcentration system coupled with ETAAS.^{27,28} Porta *et al.*¹³ used different materials in the

preconcentration column. Hirata and co-workers,⁹⁻¹¹ Taylor *et al.*¹² and Sung *et al.*^{29,30} used Muromac A-1 chelating resin for on-line column preconcentration coupled with ICP-AES,⁹ FAAS,^{10,11} ICP-MS¹² and ETAAS.^{29,30} Muromac A-1 and Chelex-100 both contain iminodiacetic acid [$-\text{CH}_2-\text{N}(\text{CH}_2\text{COOH})_2$] functional groups, but they differ in their chelating properties. The chelating ability of Muromac A-1 is comparable to that of Chelex-100,^{9,10,12} but Muromac A-1 resin is more highly purified and does not swell or shrink at a pH below 4.5.^{9,29,30} The backpressure in the microcolumn increases substantially when the resin swells, causing the aqueous solution to pass through the microcolumn with difficulty.^{29,30}

We have recently reported that trace amounts of Cu ($\approx 0.2 \mu\text{g l}^{-1}$) and Mo ($\approx 9 \mu\text{g l}^{-1}$) in sea-water can be determined using Muromac A-1 resin and the on-line preconcentration systems^{29,30} coupled to ETAAS. It is of interest to know whether this technique can also be used to determine other ultra-trace metals in sea-water at much lower concentration [*e.g.* Cd ($\approx 0.02 \mu\text{g l}^{-1}$) and Co ($\approx 0.009 \mu\text{g l}^{-1}$)]. In this work, we find that Cd, Co and Ni in sea-water can be determined with high accuracy and precision using Muromac A-1 resin and the on-line preconcentration system. The accuracy of the method was confirmed by the analysis of certified reference saline waters (NASS-4, CASS-3 and SLEW-1).

Experimental

Reagents and samples

High-purity water (18 M Ω) was prepared from a deionized water system (Milli Q, Millipore, Bedford, MA, USA). Nitric acid (Suprapur grade, Merck, Darmstadt, Germany) was purified by sub-boiling distillation. Diluted HNO₃ solution (20%, v/v; 0.2%, v/v) was prepared from the sub-boiled HNO₃. Commercial Cd, Co and Ni standards (1000 mg l⁻¹, Merck) were used. The standard solution (1000 mg l⁻¹) of Cd, Co and Ni was diluted to the desired concentration with purified HNO₃.

Table 1 Graphite furnace temperature program used for the determination of the elements

Procedure	Cd			Co			Ni		
	Temperature/°C	Ramp/s	Hold/s	Temperature/°C	Ramp/s	Hold/s	Temperature/°C	Ramp/s	Hold/s
Drying	150	1	60	110	1	70	110	1	70
	250	5	40	250	5	80	250	8	80
Ashing	600	9	20	1200	5	20	1200	9	20
Cooling	20	1	10	20	1	15	20	1	10
Atomization	1700	0	5	2300	0	5	2500	0	5
Clean-out	2600	1	5	2650	1	5	2650	1	5
							20	1	20
							2650	1	5

Table 2 Flow injection sorbent extraction preconcentration steps

Step	Fig. ^a	Volume delivered/ μ l	Pump running times/s	Sampler capillary position	Purpose
1	(i)	(100, 200) ^b	35–65	(20%) HNO ₃ solution cup	Clean column
2	(i)	70	20	Ammonium acetate buffer cup	Condition column
3	(i)	^c	35	Sample cup	Load sample
4	(i)	100	30	Ammonium acetate buffer cup	Wash sample matrix from column
5	(i)	^d	35	Empty cup	Dry tubing and column
6	(ii)	50	27–30	Graphite tube	Elute analyte

^a See Fig. 1. ^b Cd washing 100 μ l; Ni and Co washing 200 μ l. ^c Dependent on sample. ^d Pump running time: 35 s.

solution (0.2%, v/v). The buffer solution was 1 mol l⁻¹ ammonium acetate (Merck) solution which was purified by passing it through the Muromac A-1 column. The purified buffer solution (pH = 4.0) was used as the column conditioning and washing solutions in the preconcentration steps. The HNO₃ solution (20%, v/v) was used as the eluent and column-cleaning solution. A sea-water sample collected from coastal surface water near Hsinchu, Taiwan, was used to find the optimum conditions. The sea-water was filtered through a membrane (Millipore, 0.45 μ m), acidified with nitric acid and stored at 4 °C. Sea-water reference materials such as SLEW-1 (estuarine water), CASS-3 (nearshore sea-water), and NASS-4 (open ocean sea-water) were obtained from the Marine Analytical Chemistry Standards Program of the National Research Council of Canada (Ottawa, Ontario, Canada).

Microcolumn preparation

The Muromac A-1 microcolumn²⁹ was prepared using a PTFE capillary tube of an AS-40 autosampler (2.5 cm \times 0.94 mm id; Perkin-Elmer, Norwalk, CT, USA), packed with Muromac A-1 resin (Muromachi Chemicals, Tokyo, Japan; ca. 7 μ l, 100–200 mesh). Poly(ethylene) frits (porosity 0.5 μ m) were fixed in both ends of the microcolumn.

Blank sea-water preparation

Blank sea-water was prepared by passing the certified reference sea-water (CASS-3 or NASS-4) through a column packed with the Muromac A-1 resin. The residual Cd, Co and Ni concentrations in blank sea-water were less than 1.2 \times 10⁻⁴ μ g l⁻¹, 0.007 μ g l⁻¹ and 0.033 μ g l⁻¹, respectively.

Instrument and preconcentration system

An atomic absorption spectrometer (Perkin-Elmer model Zeeman 5100 PC) equipped with a graphite furnace (HGA-600), Zeeman background correction, and a laboratory-built automatic on-line preconcentration system were used.²⁹ The automatic on-line preconcentration system was modified from

the AS-40 autosampler. We replaced the pull-and-push pump of the autosampler with a peristaltic pump. The AS-40 autosampler was mounted to the 5100 spectrometer. Preconcentration was performed automatically and controlled digitally by a programmable controller (SYSMAC C210, Omron, Japan). The controller was also used to control the time to start the thermal program of the absorption measurement. The pyrolytically coated graphite tube with integrated platform was used. The electrothermal temperature program shown in Table 1 was used throughout this work and integrated absorbance (peak area) was used.

Preconcentration procedure

The HNO₃ solution (20%, v/v), ammonium acetate buffer solution (pH = 4.0; 1.0 mol l⁻¹), sample aliquot (or standard solution) and ammonium acetate buffer solution (pH = 4.0; 1.0 mol l⁻¹) were injected into sample cups arranged in the sample tray with cup numbers 0, 1, 2–16, and 18, respectively. The sample aliquots (or standards) were transferred accurately with a micropipette into the sample cups (Nos. 2–16). After the operating parameters were set on the controller, the system executed the preconcentration steps and the absorption measurements for all samples sequentially and automatically. The preconcentration procedures outlined in Fig. 1 and Table 2 were

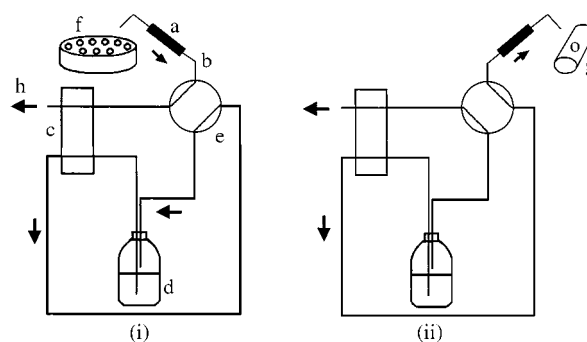


Fig. 1 Automatic on-line preconcentration system: (a) Muromac A-1 microcolumn; (b) sampler capillary; (c) peristaltic pump and pump tubes of channel-1 and channel-2; (d) 20% HNO₃ solution in bottle; (e) four-way distribution valve; (f) sample tray; (g) graphite tube; (h) to waste.

similar to those we used for the determination of Cu and Mo,²⁹ and are described as follows.

In the sample loading step (i), the sampler capillary (b) was connected to the channel-1 pump tube (c) and the sampler capillary was inserted into cup No. 0 in the sample tray (f) to draw HNO₃ solution (20%, v/v) to clean the Muromac A-1 microcolumn, then the sample tray rotated and the sampler capillary was inserted into cup No. 1 to draw ammonium acetate buffer solution (pH = 4.0; 1.0 mol l⁻¹) to alter the mobile phase of the Muromac A-1 microcolumn. The sampler capillary then drew one sample (loading flow rate at 3.5 µl s⁻¹) or standard aliquot from the sample cups (Nos. 2–16) (these aliquots had to be taken up completely). After the washing solution (ammonium acetate buffer solution) in cup No. 18 had been drawn to wash the microcolumn, the sampler capillary was inserted into cup No. 19 to draw air in order to dry the Muromac A-1 microcolumn. The above actions are shown in Fig. 1 (i) and Table 2 (step 1 to 5). After a series of samples, *etc.*, had been drawn from the sample tray, the four-way valve was turned counterclockwise and connected to the sampler capillary with the channel-2 pump tube. Then the pump began to draw HNO₃ solution (20%, v/v) from the bottle [Fig. 1(d)] in order to elute the metal ions from the microcolumn into the graphite tube (g) [Fig. 1 (ii) and step 6 in Table 2, elution flow rate = 1.7 µl s⁻¹]. After the elution procedure was completed, the four-way valve turned back to the start position [Fig. 1 (ii)], and the thermal measuring cycle of the furnace was initiated by means of the controller. While running the furnace measuring cycle for the analysis of a sample, the on-line system simultaneously started the preconcentration procedure for the next sample. The tube used for the peristaltic pump and the on-line preconcentration was a PharMed™ tube (0.51 mm id). Typical reagent and sample flow rates through the system were 3–4 µl s⁻¹. The period required to preconcentrate the sample depended on the sample volume, and to a lesser extent, on the sample matrix. The time required to preconcentrate a sea-water sample (400 µl) or aqueous standard was about 280 s or less, which conveniently fitted into the time interval between successive electrothermal firings.

Results and discussion

Effect of the sample pH on extraction efficiency

The effect of the sample pH on extraction efficiency (shown in Fig. 2) was evaluated by extracting the heavy metal ions from the aqueous standard and from the sea-water samples at sample pH values varying between 2.0 and 4.4. When the sample pH was adjusted to a value greater than 4.5, the backpressure increased significantly owing to the swelling of the resin, causing the aqueous solution to pass through the microcolumn with difficulty. Therefore, the effect of sample pH was evaluated at pH values below 4.5. No significant variation in recovery was observed over pH ranges of 3.7–4.3 (for Cd), 3.5–4.0 (for Co) and 3.5–4.5 (for Ni) with the aqueous standard and the sea-water samples. Therefore, the pH of the sample was adjusted to approximately 4.0 by adding ammonium acetate buffer before its determination by on-line preconcentration.

Effect of eluent volume

The analyte was eluted from the column using repeated injections after loading 20 µl of samples (Cd standard, 0.6 µg l⁻¹; Co standard, 10 µg l⁻¹; or Ni standard, 20 µg l⁻¹) onto the chelating column and each eluate was analyzed separately. The procedure of repeated injection can be performed by the programmable controller in the manual mode. As shown in Table 3, 50 µl (for Cd) to 100 µl (for Co and Ni) of 20% HNO₃

was required to elute the analyte from the column completely. However the volume of solution which can be introduced into the graphite tube with platform is limited to 50 µl or less. In order to keep the overall procedure simple and automatic, the determination of the heavy metal was made by passing only an aliquot of eluent (20% HNO₃; 50 µl) through the column and injecting it into the graphite furnace. The residue analyte was washed out effectively during the first step of the next

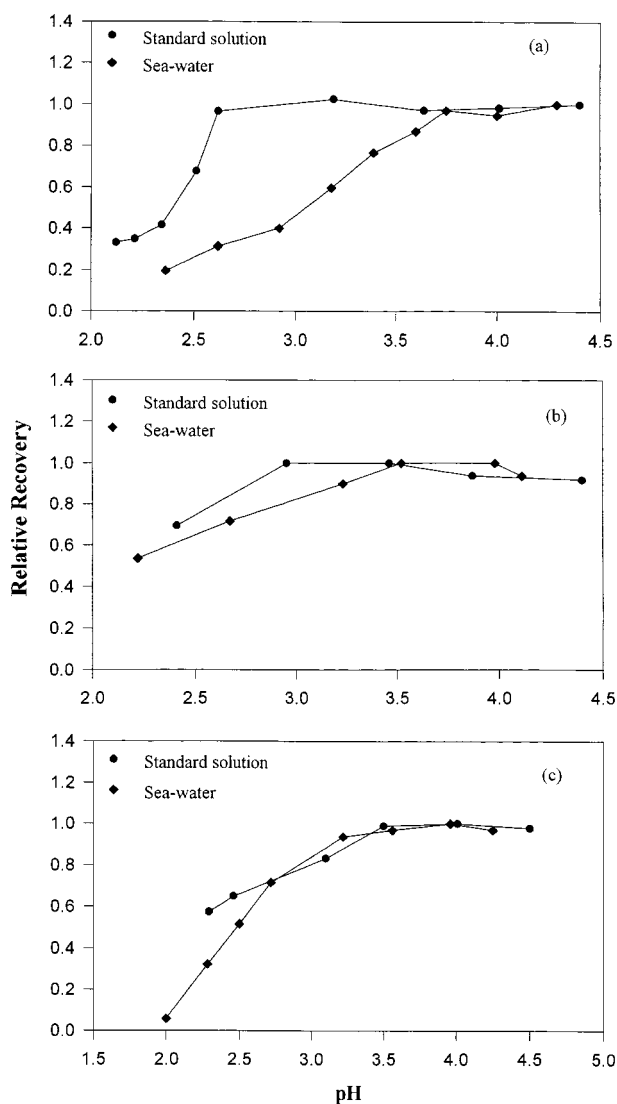


Fig. 2 Relative recovery of trace metal from aqueous standard or sea-water solution in relation to the sample pH, 20% HNO₃ solution (50 µl) as eluent; (a) (●) Cd standard (20 µl, 0.5 µg l⁻¹); (◆) sea-water (200 µl) spiked with Cd (0.1 µg l⁻¹); (b) (●) Co standard (20 µl, 20 µg l⁻¹); (◆) sea-water (200 µl) spiked with Co (1 µg l⁻¹); (c) (●) Ni standard (20 µl, 20 µg l⁻¹); (◆) sea-water (400 µl) spiked with Ni (1 µg l⁻¹).

Table 3 Integrated absorbance of several successively eluted samples after aqueous standard loading on microcolumn

No. of eluate portion ^a	Cd ^b	Co ^b	Ni ^b
1	0.148 ± 0.001	0.054 ± 0.001	0.078 ± 0.001
2	0.001 ± 0.001	0.013 ± 0.001	0.004 ± 0.001
3	-0.001 ± 0.001	0.000 ± 0.001	-0.000 ± 0.001
4	0.000 ± 0.000	-0.000 ± 0.001	-0.000 ± 0.001

^a Multi-injection, each injection (50 µl, 20% HNO₃) is measured sequentially. ^b Integrated absorbance (triplicate runs); sample 20 µl (Cd: 0.6 µg l⁻¹, Co: 10 µg l⁻¹, Ni: 20 µg l⁻¹).

preconcentration cycle. The same procedures were used to construct the standard addition curves or calibration curves.

Effect of volume of washing solution

The effects of the volume of washing solution on the atomic absorption and background absorption signals were studied. The atomic absorption signal (peak area) of Cd increased from 0.2 to 0.3 as the volume of washing solution increased from 0 to 100 μl . The sea-water matrix retained on the microcolumn caused interference to the Cd determination, and it should be removed by washing the column with washing solution after loading the column with the sea-water sample. The atomic absorption signals of Co and Ni did not vary too much with variation of the volume of washing solution. The background absorption signals decreased substantially with increasing volume of washing solution. At least 100 μl (for Cd determination) to 250 μl (for Co and Ni determinations) of washing solution were required to reduce the background absorption to the lowest levels. In order to reduce the preconcentration time and the reagent blank level (caused by the possible impurity in the washing solution), 100 μl of washing solution was used for further study.

Sea-water analysis

The slopes of standard addition curves of the sea-water samples are compared with the slopes of the calibration curves which were constructed from preconcentration of standards in 0.2% HNO_3 (20 μl). As shown in Table 4, the slopes of the standard addition curves of Co and Ni are very similar to the slopes of the calibration curves; hence Co and Ni in sea-water can be determined using the method of calibration curves. However the method of standard addition should be used to determine Cd in sea-water. The accuracy of the methods was examined by the analysis of several certified reference saline waters (SLEW-1, CASS-3 and NASS-4). Table 5 shows that this method provides

analytical results within the ranges of the certified values (Cd was determined using the method of standard addition).

Detection limits and precision

The detection limits and the relative standard deviation (% RSD) of the methods are reported in Table 6. These detection limits are based on three times the standard deviation of eight replicate measurements of sea-water blank. The detection limits were $1.2 \times 10^{-4} \mu\text{g l}^{-1}$ for Cd (400 μl), $0.007 \mu\text{g l}^{-1}$ for Co (1800 μl) and $0.033 \mu\text{g l}^{-1}$ for Ni (800 μl). The total chelation capacity of the column used is greater than 7 μmol of Cd equivalent. The detection limits of the method could be further decreased by increasing the sample volume. The absolute blank values were 0.02 pg for Cd (400 μl), 8 pg for Ni (800 μl) and 4 pg for Co (1800 μl). The precisions of the methods were examined by eight sequential replicate measurements of CASS-3 (400 μl for Cd; 1600 μl for Co; 800 μl for Ni). Relative standard deviations for the determination of Cd, Co and Ni in CASS-3 were 2.9, 5.6 and 4.1%, respectively. The actual recoveries of analyte in a given single elution volume of acid were 90% for Cd, 68% for Ni and 66% for Co. The preconcentration factors were 20, 40 and 90 for Cd, Ni and Co, respectively. The sample throughput was 6–15 samples h^{-1} which was dependent on the sample volume.

Conclusion

Our laboratory-built preconcentration system coupled with a Muromac A-1 microcolumn performed well and is fully automated. In addition to Cu, Mo and Ni, ultra-trace amounts of Cd and Co in sea-water (at 9–16 ng l^{-1} levels) can be determined accurately using this on-line preconcentration system.

Table 4 Comparison of methods of calibration curves (CC) and standard addition (SA) for the determination of Cd, Co and Ni in various certified reference sea-waters

Analyte	Method	Linear regression ^a	Correlation coefficient	Matrix of sample
Cd	CC	$Y = 0.2072X + 0.0003$	0.9998	0.2% HNO_3
	SA	$Y = 0.1689X + 0.0684$	0.9996	SLEW-1
	SA	$Y = 0.1554X + 0.1021$	0.9999	CASS-3
	SA	$Y = 0.1534X + 0.0596$	0.9994	NASS-4
Co	CC	$Y = 5.3 \times 10^{-3}X + 0.000$	0.9998	0.2% HNO_3
	SA	$Y = 5.3 \times 10^{-3}X + 0.022$	0.9995	SLEW-1
	SA	$Y = 5.25 \times 10^{-3}X + 0.023$	0.9996	CASS-3
	SA	$Y = 5.1 \times 10^{-3}X + 0.024$	0.9987	NASS-4
Ni	CC	$Y = 3.73 \times 10^{-3}X + 0.000$	1.0000	0.2% HNO_3
	SA	$Y = 3.38 \times 10^{-3}X + 0.0579$	0.9998	CASS-3
	SA	$Y = 3.74 \times 10^{-3}X + 0.0432$	0.9993	NASS-4

^a Y and X are integrated absorbance and metal concentration ($\mu\text{g l}^{-1}$), respectively

Table 5 Results of determination of trace elements in reference sea-water using on-line preconcentration and ETAAS

Sample	$\text{Cd}/\mu\text{g l}^{-1}$		$\text{Co}/\mu\text{g l}^{-1}$		$\text{Ni}/\mu\text{g l}^{-1}$	
	Certified	Found ^{a,b}	Certified	Found ^{a,c}	Certified	Found ^{a,d}
SLEW-1	0.018 ± 0.003	0.020 ± 0.002	0.046 ± 0.007	0.052 ± 0.005	0.743 ± 0.078	0.798 ± 0.008
CASS-3	0.030 ± 0.005	0.031 ± 0.004	0.041 ± 0.009	0.045 ± 0.004	0.386 ± 0.062	0.385 ± 0.005
NASS-4	0.016 ± 0.003	0.018 ± 0.003	0.009 ± 0.001	0.008 ± 0.001	0.228 ± 0.009	0.228 ± 0.008

^a Mean and standard deviation of triplicate runs. ^b Sea-water sample volume: SLEW-1 (400 μl), CASS-3 (400 μl), NASS-4 (400 μl). ^c Sea-water sample volume: SLEW-1 (1600 μl), CASS-3 (1600 μl), NASS-4 (1800 μl). ^d Sea-water sample volume: SLEW-1 (400 μl), CASS-3 (800 μl), NASS-4 (1000 μl).

Table 6 Detection limits and relative standard deviations (RSD) obtained for the determination of trace metals in sea-water

Element	Detection limits/ $\mu\text{l l}^{-1a}$	RSD (%) ^b
Cd	1.2×10^{-4c}	2.9
Co	0.007 ^d	5.6
Ni	0.033 ^e	4.1

^a These detection limits refer to preconcentration of an aliquot of sea-water blank based on three times the standard deviation of eight replicate measurements. ^b The precisions of the determinations were obtained by the preconcentration procedure for eight sequential replicate measurements of CASS-3 sea-water (400 μl for Cd; 1600 μl for Co; 800 μl for Ni). ^c Sea-water blank (400 μl) prepared from CASS-3. ^d Sea-water blank (1800 μl) prepared from NASS-4. ^e Sea-water blank (800 μl) prepared from CASS-3.

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