Low Blank Preconcentration Technique for the Determination of Lead, Copper, and Cadmium in Small-Volume Seawater Samples by Isotope Dilution ICPMS

Jingfeng Wu* and Edward A. Boyle

Department of Earth, Atmospheric, and Planetary Sciences, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

A simple low-blank method is described for the analysis of Pb, Cu, and Cd in seawater using $Mg(OH)_2$ coprecipitation and isotope dilution inductively coupled plasma mass spectrometry (ICPMS). Here, 20−40 μL of 9 M aqueous NH_3 is mixed into a 1.3 mL seawater sample spiked with enriched isotopes of Pb, Cu, and Cd. After centrifugation, the supernatant is discarded and the $Mg(OH)_2$ precipitate dissolved in 100 μL of 5% HNO_3 for ICPMS analysis. This method is simple, accurate, and precise, with detection limits of Pb = 1.3 pM, Cu = 39 pM, and Cd = 5.0 pM and blanks of Pb = 0.62 pM, Cu = 27 pM, and Cd = 6.0 pM. The method is demonstrated by oceanographically consistent profiles of these trace metals at an ocean station in the eastern North Atlantic.

Lead, copper, and cadmium exist at picomolar (1×10^{-12} mol/L) to nanomolar (1×10^{-9} mol/L) levels in oceanic waters.[1,2] Accurate and precise measurement of Pb, Cu, and Cd is desirable for studies of the penetration of anthropogenic Pb into the ocean,[3−6] seawater Cu speciation and its toxic effect for phytoplankton,[7,8] and the use of Cd/Ca as a paleooceanographic tracer.[9] The major difficulties in seawater Pb, Cu, and Cd analysis come from their extremely low concentrations and the high salt matrix (3.5%). The most common analytical methods for the determination of Pb, Cu, and Cd in seawater are anodic stripping or absorptive cathodic stripping voltammetry direct measurements[10,11] and graphite furnace atomic absorption spectrometry (AAS) and thermal or inductively coupled plasma mass spectrometry (MS) detection after some forms of preconcentration steps

Table 1. Pb, Cu, and Cd Blanks per Liter of Reagents

	Pb (pM/L)	Cu (nM/L)	Cd (pM/L)
Vycor-distilled H_2O	1.2	0.05	0.07
Vycor-distilled HNO_3	5.6	0.38	4.28
Q-NH_3	3.9	0.14	0.07

such as solvent extraction,[12,13] Co-APDC coprecipitation,[14] and Chelex-100 ion exchange[15] or on-line preconcentration.[16−19] All of these techniques are relatively time consuming and subject to contamination, especially for Pb and Cd at picomolar levels.

We present here a simple, rapid, and highly sensitive technique for Pb, Cu, and Cd in seawater using low-blank $Mg(OH)_2$ coprecipitation, with subsequent determination of these trace elements by inductively coupled plasma mass spectrometry (ICPMS). The total analytical blanks by this method are low because the preconcentration procedures are simple and because of the ease with which NH_4OH and HNO_3 can be purified. To ensure accuracy and precision regardless of recovery efficiency or analytical interferences, the isotope dilution (ID) method is employed prior to the separation step.

EXPERIMENTAL SECTION

Reagents. High-purity water was prepared by redistillation of "ultrapure" deionized water in a Corning "Mega-Pure" Vycor/borosilicate still. Nitric acid and hydrochloric acid were triply distilled in a Vycor still. Ammonium hydroxide was prepared by vapor phase transfer from concentrated aqueous NH_3 into Vycor-distilled H_2O. The reagent blanks (reported as per liter of reagents, Table 1) were individually determined by evaporation of a large volume down to a small volume followed by ID-ICPMS.

To examine isobaric ICPMS interferences, trace metal-free Mo and Mg standards were prepared by passing concentrated solution

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Table 2. ICPMS Data Collecting Conditions

Aquisition Method
peak jump mode
3 points/peak
5 DAC between points
30 s aquisition
512 channels

element	Element Menu mass (amu)	dwell/peak (ms)
Pb	202	4.4
	204	10.2
	208	10.2
	220	2.2
Cu	63	4.4
	65	4.4
	66	4.4
	68	4.4
	220	1.2
Cd	95	1.2
	106	10.2
	110	4.4
	114	10.2
	118	10.2
	220	4.4

Table 3. Target Spike Ratios

	Pb	Cu	Cd
isotope 1	204	65	110
isotope 2	208	63	114
"1"/"2" of sample (R_s)	0.02615	0.4472	0.4314
"1"/"2" of spike (R_t)	5.837	233.7	77.38
geometric mean of R_s, R_t	0.3949	10.2	5.778
"1"/"2" target ratio	1	15	8
error magnification factor at target ratio	1.2	1.1	1.2

through a Chelex-100 ion exchange column and then diluting with Vycor-distilled H_2O to make working standards.

Isotopically enriched ^{204}Pb (20 ppm), ^{65}Cu (1000 ppm), and ^{110}Cd (20 ppm) primary standards were prepared by dissolution of $^{204}Pb_2CO_3$, ^{65}CuO, and ^{110}CdO (purchased from Oak Ridge National Laboratories) in 1% Vycor-distilled HNO_3. Working standards were prepared from the primary standards as needed by further dilution in dilute Vycor-distilled HNO_3 (pH 1.5). The exact concentrations of the enriched isotope spike solutions were determined by isotope dilution calibration against known standards of natural abundance, after correcting for ICPMS mass fractionation using natural abundance standards. All reagent and sample preparations were carried out in a Class 100 clean flow bench.

Seawater Samples. Seawater samples for Cu and Cd vertical profile were collected using modified Niskin bottles (with rubber O-rings replaced by silicone and the internal rubber spring replaced by an epoxy-coated steel spring), suspended on hydro-wire. Samples for Pb vertical profile were collected by a specially designed weather-vaning sampler made of polypropylene and Teflon.[3] All samples were left unfiltered and acidified to pH 1.5 with vycor-distilled HCl soon after collection. In addition, a large-volume surface seawater sample ("SS") was collected by the "pole sampling" method.[20] This sample was used throughout the course of the method development work. A portion of this sample was acidified, UV irradiated, and passed through a Chelex-100 ion exchange column to make a trace metal-free seawater.

Instrumentation. The inductively coupled plasma mass spectrometer used for this work was the VG Plasma Quad II + (VG Element, Denver, MA), with a typical sensitivity of 200 000 (counts/s/ppb of uranium). A standard concentric glass nebulizer (for 10 mL sample size) or CETAC microconcentric nebulizer (for 1.3 mL sample size) was used in conjunction with a water-cooled spray chamber. A Gilson four-channel peristaltic pump (Gilson Minipulse 3) was used with the standard nebulizer. A free-draw method was used for the microconcentric nebulizer. Details of

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data collection parameters are given in Table 2. Typically, signals were acquired for 30 s in peak jump mode beginning 3−5 s after the signal reached the detector.

General Procedure. Acidified seawater samples (1.3 mL) in 1.5 mL polypropylene microcentrifuge vials were spiked with enriched isotope ^{204}Pb, ^{65}Cu, and ^{110}Cd spikes (50 μL) and allowed to equilibrate overnight. Aqueous NH_3 (20−40 μL, depending on its concentration and the sample acidity) was mixed into the sample to precipitate $Mg(OH)_2$. The amount of NH_4OH used for $Mg(OH)_2$ precipitation was determined empirically each day, which will be discussed in detail below. After the mixture was centrifuged, the supernatant was discarded and the $Mg(OH)_2$ precipitate washed three times with 200 μL of pH 10 dilute NH_4OH prepared with Vycor-distilled H_2O and concentrated purified NH_4OH. The precipitate was then dissolved in 100 μL of 5% triply Vycor-distilled HNO_3 and analyzed for Pb, Cu, and Cd by ICPMS with a CETAC microconcentric nebulizer. To estimate the procedural blank, a few replicates of 50 μL trace metal-free seawater samples were processed in the same way as samples (spiked with same amount of the reagents as for the samples). The metal content of these small samples is negligibly small, so the measured metal content of these samples was attributed to the procedural blank.

The washing step is necessary for Cu analysis but not for Pb and Cd (see explanation below). A standard concentric glass nebulizer (uptake rate of 0.6−1.0 mL/min) can be used to replace the microconcentric nebulizer (uptake rate of 20−40 μL/min) if sample and reagent sizes in the above procedure are scaled up by 10-fold.

The procedure separates Pb, Cu, and Cd from the 3.5% matrix salts present in the seawater sample and provides a 7−12-fold preconcentration ratio, depending on recoveries for each element (see below for recovery details). Higher concentration ratios can be achieved by repeating the precipitation procedure, although this additional step usually is not necessary for routine seawater analysis. A double precipitation method is needed to achieve a detection limit of less than 1 pM for Pb, which will be necessary for old, deep water, especially in the Pacific Ocean. After the $Mg(OH)_2$ from the first precipitation step was redissolved in dilute HNO_3, aqueous NH_3 was added into the solution to reprecipitate 5−10% of the Mg in the solution. The second precipitate was then dissolved in 5% HNO_3 having a volume 1.0% of the original sample, leading to a 40−90-fold concentration ratio depending on recoveries of each element (see below for details).

RESULTS AND DISCUSSION

An isotope dilution (ID) quantitative method (equilibrating a known amount of spike of known isotopic composition with a known amount of sample and measuring the isotopic ratio of the mixture) was used to avoid corrections for the Mg matrix effect

Table 4. Isobaric Interferences in ICPMS

element	isotope	abundance (%)	interference	abundance (%)
Pb	204	1.4	^{204}Hg	Hg, 6.8
Cu	63	69.1	^{40}Ar^{23}Na	Na, 0.0001
	65	30.9	^{40}Ar^{25}Mg	Mg, 0.00001
Cd	110	12.4	^{110}Pd	Pd, 11.8
			^{94}Mo^{16}O	Mo, 0.007
	114	28.8	^{114}Sn	Sn, 0.65
			^{98}Mo^{16}O	Mo, 0.04

and other interferences, ICPMS sensitivity fluctuations, and recovery variations in the $Mg(OH)_2$ coprecipitation and washing steps. To achieve accurate results by ID, background variations and ICPMS mass biases must be considered, contamination must be eliminated in sample handling and analysis, and isotope equilibration and isobaric interferences must be taken into account. In addition, the precision of the analysis is affected by factors such as sample and spike pipetting precision, ICPMS stability, spike ratio, isotopic abundances of spike and sample, counting statistics, reproducibility of procedural blanks, and error propagation in isobaric interference corrections.

Spike Ratio. Table 3 lists spike ratios used for Pb, Cu, and Cd analysis. The target spike ratios are chosen by compromise among several factors. To minimize the uncertainty introduced by error propagation through isotope dilution equation, one would like a ratio close to the geometric mean of the "1"/"2" ratios of the spike and sample, where "1" and "2" refer to the two isotopes of the element and the spike is enriched in isotope "1". On the other hand, when there are isobaric interferences occurring at

isotope "1", such as ^{204}Hg for Pb, ^{110}Pd and ^{94}Mo^{16}O for Cd, and ^{40}Ar^{25}Mg for Cu, increasing "1"/"2" spike ratios decrease the relative standard error during the correction for these isobaric interferences (see below for details). Thus, we chose target spike: sample ratios higher than geometric means of "1"/"2" (see Table 3). To obtain the target ratio, however, one would have to know the exact Cu, Cd, and Pb concentrations in the sample before adding the enriched isotope spike. It is more practical to limit the spike ratio in a range ("1"/"2" = 1−2 for Pb, 8−30 for Cd, and 15−80 for Cu) within which the error magnification factor estimated from the isotope dilution equation (defined as the ratio of relative error in calculated concentration to the relative error in measured ratio) is below 1.6.

Isotope Equilibration Time. Equilibration times from 2 min to 2 days were tested with a surface seawater sample collected near Bermuda and acidified to pH 1.5. It was found that there was no detectable difference in analytical outcome during this period, suggesting rapid equilibration between added enriched isotope spikes and their natural isotopes present in the sample at pH 1.5. Although Pb, Cu, and Cd have been found to be complexed by strong natural organic ligands at seawater pH (8.1),[11,21,22] these complexes would not be as stable at pH 1.5. As a result, the metal ions can be quickly equilibrated by spike isotopes.

$Mg(OH)_2$ Precipitation. When a complete isotope equilibration has been achieved, a loss of Pb, Cu, and Cd during coprecipitation with $Mg(OH)_2$ will not affect the analytical result. However, analyte loss may affect the detection limit, and excess residue seasalt and Mg matrix could suppress the ICPMS signal,

Table 5. Mo Interference in Cd Analysis by ICPMS

sample	95 amu	106 amu	110 amu	114 amu	118 amu	^{95}Mo/^{94}Mo^{16}O	^{95}Mo/^{98}Mo^{16}O
	count rate (counts/s)					
1% HNO$_3$	85	41	42	32	200		
5 nM Mo	52572	44	86	200	239	324	1714
	51373	39	87	231	240	266	1644
	49993	33	93	209	195	289	1443
	53123	39	94	203	189	318	1508
	53563	44	91	193	198	342	1598
10 nM Mo	93751	46	158	357	357	296	1310
	95809	45	150	376	397	287	1430
	98170	48	161	355	357	312	1340
	97762	45	152	345	345	321	1434
12 nM Mo	121096	48	172	450	184	293	1523
	121140	48	166	466	187	282	1592
	124480	39	182	448	197	302	1461
40 nM Mo	363447	42	452	1285	202	291	1524
	349961	52	467	1242	174	290	1417
	355142	45	477	1304	193	280	1406
average						300	1490
SD (%)						7	6

Table 6. Mg Interference in Cu Analysis by ICPMS

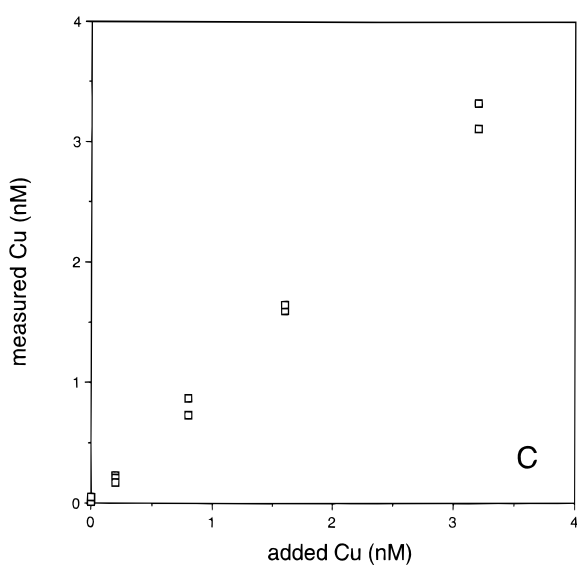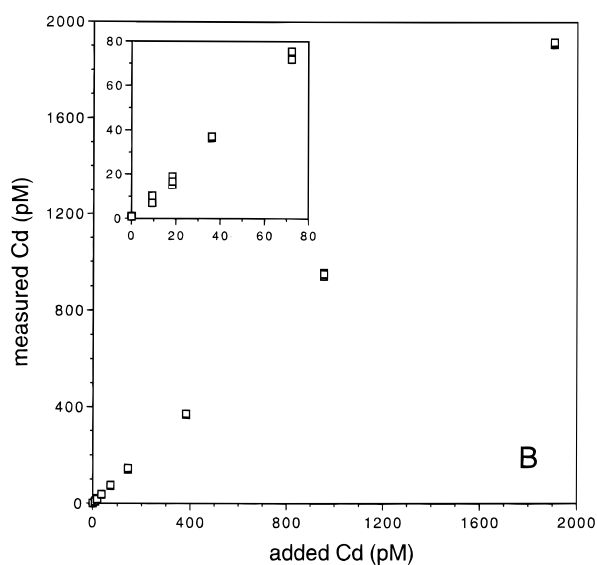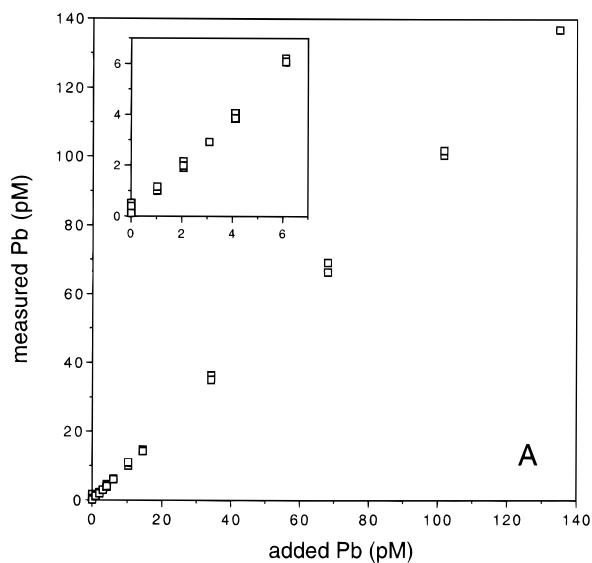| sample	63 amu	65 amu	66 amu	68 amu	220 amu	^{40}Ar^{26}Mg/^{40}Ar^{25}Mg
	count rate (counts/s)		
1% HNO$_3$	475	349	167	285	31	
4 mM Mg	432	6052	8263	1387	39	1.07
18 mM Mg	432	23818	29150	1770	24	1.12
35 mM Mg	451	32099	36906	1488	38	1.09
80 mM Mg	385	41605	47405	1125	34	1.11
160 mM Mg	385	48209	53912	988	29	1.09

Figure 1. ID-ICPMS recoveries of Pb, Cu, and Cd added to a trace metal-free seawater. The linear regressions of the data are $Pb_{measured}$ (pM) = 0.004 + (0.9997 ± 0.004)Pb_{added} (pM), r^2 = 0.9989 (n = 39); $Cu_{measured}$ (nM) = 0.017 + (0.9962 ± 0.017)Cu_{added} (nM), r^2 = 0.9948 (n = 11); and $Cd_{measured}$ (pM) = 0.022 + (0.9974 ± 0.002)Cd_{added} (pM), r^2 = 0.9998 (n = 22).
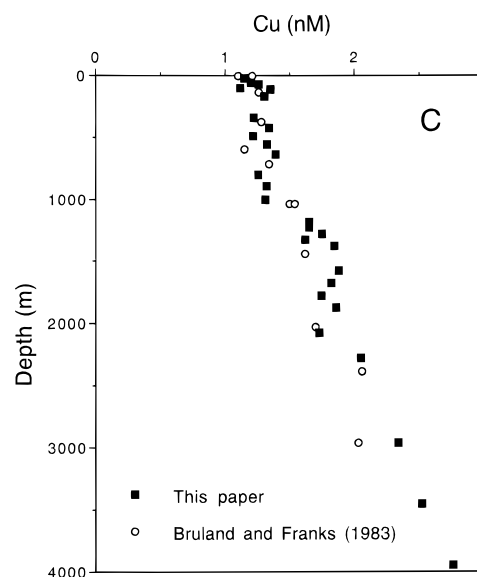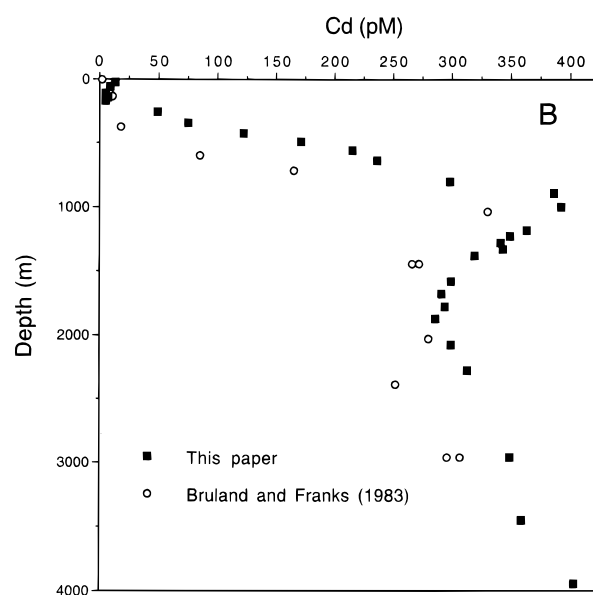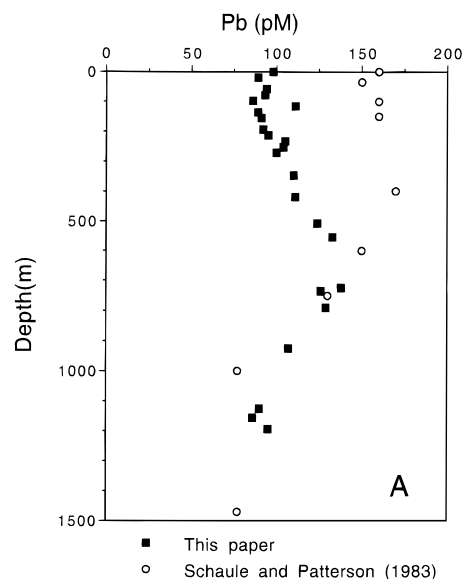
Figure 2. Profiles of Pb, Cu, and Cd in the northeastern Atlantic (AII 123, Station 3, 26°25′ N, 33°40′ W and station 8, 31°00′ N, 31°00′ W) analyzed by ID-ICPMS after coprecipitation with $Mg(OH)_2$ (■) as compared with the profiles from the northwestern Atlantic[1,2] measured by TIMS and AA methods (○).

Table 7. Data from AII 123 Cruise in October 1989

(A) Cu and Cd Data at Station 3 (26°25′ N, 33°40′ W)

depth (m)	Cu (nM)	Cd (pM)	P (μM)	depth (m)	Cu (nM)	Cd (pM)	P (μM)
24	1.15	13	<0.01	1000	1.31	363	1.62
61	1.20	9	<0.01	1182	1.65	349	1.47
72	1.26	5	<0.01	1227	1.65	341	1.49
102	1.12	8	<0.01	1280	1.75	343	1.38
113	1.35	7	<0.01	1326	1.62	319	1.46
145	1.70*	5	0.02	1378	1.85	299	1.33
170	1.31	49	0.12	1577	1.88	291	1.27
257	1.56*	75	0.39	1676	1.82	294	1.44
342	1.22	122	0.41	1778	1.75	286	1.23
425	1.34	171	0.57	1873	1.86	299	1.26
489	1.22	215	0.86	2077	1.73	313	1.33
558	1.33	236	0.93	2278	2.05	349	1.33
637	1.39	298	1.03	2960	2.34	359	1.40
802	1.26	386	1.45	3454	2.52	403	1.46
892	1.32	392	1.59	3948	2.76	395	1.50

(B) Pb Data at Station 8 (31°00′ N, 31°00′ W)

depth (m)	Pb (pM)	depth (m)	Pb (pM)
0	98	271	100
17	89	347	110
55	94	419	111
75	93	508	124
95	86	554	133
117	111	724	138
133	89	750	126
154	91	790	129
189	92	925	107
208	95	1125	90
231	105	1155	86
251	104	1194	95

clog the nebulizer, or deposit at the sampling cone and skimmer openings. Thus, conditions in the $Mg(OH)_2$ precipitation and washing steps were optimized for maximum recovery and minimum matrix carryover.

Seawater contains a high Mg concentration (1.29 g of Mg/kg of seawater at a salt content of 3.5%). This Mg concentration is close to the 0.1% upper limit for total dissolved solids in solutions introduced into ICPMS. Thus, with a 13-fold volume ratio for Pb, Cu, and Cd, the Mg precipitate should not exceed 7% of total Mg in the seawater sample. The amount of aqueous NH_3 needed to precipitate 7% of total Mg in seawater was determined empirically (because of variation in acidity of the sample and in the concentration of ammonium hydroxide prepared by vapor phase equilibration). An incremental amount of aqueous NH_3 is introduced into two replicate 1.3 mL samples. The $Mg(OH)_2$ precipitate is visually compared with that resulting from two replicate 0.1 mL samples which have had 60 μL concentrated aqueous NH_3 added (reagent volume should, of course, be scaled up proportionally for larger sample sizes). For Cu analysis, the precipitate must be washed to remove residual Na, which causes isobaric interferences at mass 63 ($ArNa^+$). Hence, for Cu, it is necessary to precipitate about 10−20% of total Mg in the seawater sample to compensate for the analyte loss during the washing step. At pH 10, dilute aqueous NH_3 is used to wash the precipitate, but $Mg(OH)_2$ loss may occur by resuspension of fine particles into solution phase as stable colloids which cannot be effectively centrifuged.

The amount of $Mg(OH)_2$ precipitated at the bottom of the centrifuge vial was found to increase with increasing reaction time

between the addition of aqueous NH_3 and centrifugation. In other words, a small precipitate can be obtained by a large addition of aqueous NH_3 when the mixture is immediately centrifuged after the addition of aqueous NH_3, whereas a large amount of $Mg(OH)_2$ can precipitate when solution spiked with a small amount of aqueous NH_3 is allowed to react for a longer time before centrifugation. Thus, both aqueous NH_3 quantity and reaction time were controlled experimentally when changes in sample acidity and aqueous NH_3 concentration were suspected. Because the ratio of $Mg(OH)_2$ to coprecipitated Cd and Cu was not found to change significantly with increasing reaction time, we used a reaction time of 2 min to take advantage of faster and easier separation of the precipitate from the solution phase compared to that at longer reaction times. The precipitate formed at long reaction times appeared to be larger in its particle size, less sticky, and more easily lost during centrifugation and decantation. The separation method involves two centrifugation steps. The first centrifugation was performed at 9000 rpm for 1.5 min, starting 2 min after the addition of aqueous NH_3. The upper solution was gently decanted and shaken away, while the precipitate was left in the vial. A second centrifugation and shaking step was necessary to ensure that no visible solution droplets (<2 μL) remained in the vial.

Recovery. Although yield determination is not necessary in isotope dilution measurements, recovery estimates are useful in calculating preconcentration ratios. By mixing enriched isotopic spike into the sample after the $Mg(OH)_2$ precipitation and washing steps and by comparing the result with the known concentrations in the sample, we can determine the preconcentration efficiency through the above procedures. It was found that the recoveries

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were $90 \pm 0.05\%$ ($n = 10$), $32 \pm 6\%$ ($n = 3$), and $57 \pm 2\%$ ($n = 2$) for Pb, Cd, and Cu, respectively. The recovery of Cu was affected by the loss of precipitate during the washing step. For Pb, the recovery does not change with the amount of $Mg(OH)_2$ precipitated or the reaction time between the addition of NH_3 and centrifugation. For Cd, the recovery increased with increasing amount of $Mg(OH)_2$ precipitate.

Isobaric Interferences. Table 4 lists isobaric interferences for Pb, Cu, and Cd occurring with this method. These interferences can be calculated and eliminated precisely by monitoring other ions or molecular ions of the interfering elements at the same time as the analyte isotopes and then correcting the interfered mass by applying the isotope abundance ratio of the measured isotope and interfering isotope.

Mercury interferes with Pb analysis at mass 204 by ^{204}Hg (6.8% Hg). Although seawater Hg concentration ($0.2-1.0$ pM) is normally much smaller than Pb concentration ($2-100$ pM), Hg contamination from the reagents, sample handling, and instrumental background can be a problem. Therefore, it is necessary to correct precisely for the Hg interferences. This was done by substracting ^{204}Hg counts calculated from ^{202}Hg (29.7% Hg) using the natural ratio of $^{202}Hg/^{204}Hg$ from the total counts at mass 204 before calculating the $^{204}Pb/^{208}Pb$ ratio. Depending on Hg contamination levels from sample handling and analysis, we observed that the correction for ^{204}Hg ranges from 5 to 15% of the ^{204}Pb signal, given a 40 pM Pb sample with a $^{204}Pb/^{208}Pb$ spike ratio of 1.0.

Interferences for Cd are possible both at mass 110 from $^{110}Pd^+$ (11.8% of Pd) and $^{94}Mo^{16}O^+$ (about 0.007% of Mo) and at mass 114 from $^{114}Sn^+$ (0.65% of Sn) and $^{98}Mo^{16}O^+$ (about 0.04% Mo). Pd, Sn, and Mo exist in oceanic waters at $0.2-0.7$ pM, $1-20$ pM, and 100 nM, respectively. Pd and Sn interferences were corrected by monitoring ^{106}Pd (27.3% of Pd) and ^{118}Sn (24.1% of Sn) and then calculating ^{110}Pd and ^{114}Sn from $^{110}Pd/^{106}Pd$ and $^{114}Sn/^{118}Sn$ natural ratios. The MoO^+ interference was corrected by counting ^{95}Mo and applying ratios of $^{95}Mo/^{110}Cd$ and $^{95}Mo/^{114}Cd$ measured with a set of Cd-free Mo standards in Mg matrix (Table 5). Since oxide interferences may change with the lens settings, gas flows, and other ICP setup aspects, the $^{95}Mo/^{110}Cd$ and $^{95}Mo/^{114}Cd$ ratios must be measured using Cd-free Mo standards when any change in ICPMS conditions is suspected (usually at the beginning and the end of a continuous daily run has proven sufficient). At a seawater sample Cd concentration of 50 pM and a $^{110}Cd/^{114}Cd$ spike ratio of 8, Pd and MoO^+ corrections are about 3% of total counts at mass 110, as compared to $4-8\%$ for Sn and 10% for MoO^+ at mass 114.

$^{40}Ar^{23}Na^+$ and $^{40}Ar^{25}Mg^+$ interfere with Cu analysis at mass 63 and 65. Sodium, with a concentration of 3.5% in seawater, forms $^{40}Ar^{23}Na^+$ (0.0001% of Na) at mass 63. This interference was eliminated by washing the $Mg(OH)_2$ precipitate three times with 200 μL of pH 10 dilute aqueous NH_3 (for 1.3 mL sample size) before dissolution in 5% HNO_3. It is found that, after three washes of the precipitate, the concentration of the remaining Na was often below 1 μM, at which point the $ArNa^+$ interference was negligible (<1 pM), and the $ArNa^+$ correction is unnecessary. However, the Na peak should be monitored during the ICPMS measurement to ensure the data quality, and the correction should be made whenever it is necessary. By using the dual mode (a combination of both pulse counting and analog mode in a single nebulization),
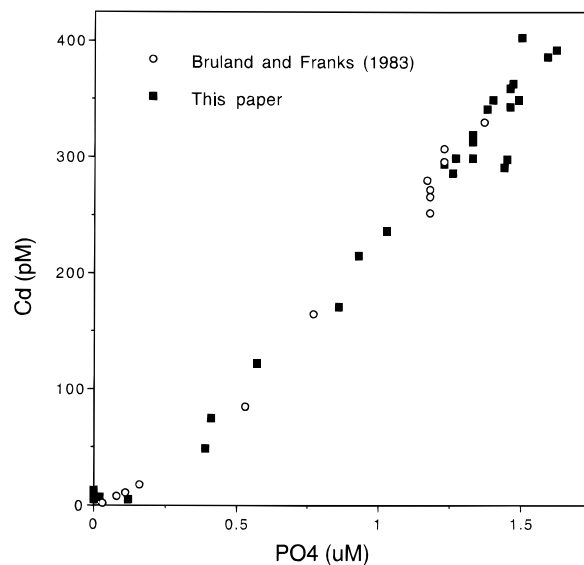

Figure 3. Cadmium vs phosphate in the northeastern Atlantic (AII 123, station 3, 26°N, 33°W) (■) compared with that from the northwestern Atlantic.[1]

it is possible to monitor high concentrations of Na together with low levels of Cu in a single run. The $^{40}Ar^{23}Na^+$ interference can then be corrected through a set of Cu-free Na standards prepared from dilutions of a seawater sample with Vycor-distilled H_2O. An Mg concentration of $20-50$ mM in the analyte solution can generate a significant interfering peak at mass 65 (equivalent to $10-30\%$ of total counts at mass 65 for Cu concentrations of about 1 nM and a $^{65}Cu/^{63}Cu$ spike ratio of $10-20$) by forming $^{40}Ar^{25}Mg^+$ (0.00001% of Mg). These interferences can be corrected precisely by applying a constant $^{40}Ar^{26}Mg/^{40}Ar^{25}Mg$ ratio. Table 6 shows that, for Mg concentrations of $4-80$ mM, the $^{40}Ar^{26}Mg/^{40}Ar^{25}Mg$ ratio was constant at 1.10 ± 0.06, which is identical to the $^{26}Mg/^{25}Mg$ natural ratio. Before applying the above correction, the ^{66}Zn counts which can be calculated from ^{68}Zn counts at mass 68 using the natural ratio of $^{66}Zn/^{68}Zn$ were subtracted from the total counts at mass 66.

Accuracy, Precision, and Detection Limit. Recoveries compared to standards of Pb, Cu, and Cd spiked into trace metal-free seawater were measured with this ID-ICPMS method to assess accuracy. Figure 1 shows the excellent consistency between concentrations of these trace metals added into the trace metal-free seawater and those measured by the isotope dilution method. The validity of the method is further demonstrated by Pb, Cu, and Cd profiles measured with this method (Figure 2, Table 7). These profiles in the eastern North Atlantic are very similar to previous trace metal data from the western North Atlantic Ocean,[1,2] except for some slight differences in deep water Cu and in surface water Pb. The difference for Cu is due to the older Antarctic bottom water (which contains higher Cu) penetrating into the eastern North Atlantic below 3000 m depth, as compared to lower concentrations in the younger North Atlantic deep water in the western North Atlantic at the same depth. Lead concentrations in the upper 500 m depth of the eastern North Atlantic in 1989 are generally lower than those in the North Atlantic in 1979. This may be due to the ongoing phasing out of leaded gasoline in the United States and to differences in prevailing wind patterns and Pb source inputs between the two areas.[5] The higher Cd concentration in the eastern North Atlantic compared to that in the western North Atlantic[1] is correlated with higher

Table 8. Precision and Detection Limits

	Pb (pM)	Cu (nM)	Cd (pM)
procedural blank	1.27	0.005	4.89
	0.26	0.027	7.84
	0.48	0.041	6.16
	0.26	0.035	5.37
	0.47	0.041	2.79
	0.45	0.022	7.83
	0.41	0.013	6.34
	1.34	0.031	7.01
average	0.62 ± 0.43	0.027 ± 0.013	6.03 ± 1.68
detection limit	1.29	0.039	5.04
seawater sample	50.8	1.62	341
	50.6	1.69	347
	52.3	1.61	357
	48.9	1.57	349
	50.4	1.55	350
	50.6	1.71	348
	49.0	1.58	348
	50.8	1.59	346
	49.9	1.58	347
	50.3	1.59	350
average	50.3 ± 1.0	1.61 ± 0.05	348 ± 4
precision (%)	2.00	3.10	1.10

phosphorus in the eastern North Atlantic Ocean and shows a consistent Cd−P relationship in both regions (Figure 3).

The precisions of the methods are estimated from the analysis of 10 replicates of a spiked surface seawater sample collected near Bermuda (Table 8). The standard deviations of these replicates are 1.1%, 3.1%, and 2.0% for Cd, Cu, and Pb at 348 pM, 1.62 nM, and 50 pM levels, respectively, which are generally better than those previous preconcentration methods, which relied upon recovery estimates and standard curve calibrations.[12,14]

The detection limit is defined here as 3 times the standard deviation of the replicate procedural blanks, which was Pb = 1.3 pM, Cd = 5.0 pM, and Cu = 0.039 nM (Table 8). This detection limit can be decreased to below 1 pM for Pb by using a double-precipitation method. The procedural blank for Pb analysis was dominated by the ICPMS instrumental blank and not by Pb blanks in the reagents (see Tables 1 and 8). Therefore, the increase in preconcentration ratio reduces the effect of the machine's blank. The detection limits for Cd and Cu were primarily controlled by the uncertainties in the correction for isobaric interferences and by counting statistics (especially for Cd). The above detection limits are equal to or lower than those obtained by previous methods for seawater analysis[12−14] for a significantly smaller sample size.

CONCLUSION

This paper describes a technique for determination of Pb, Cu, and Cd concentrations in seawater using isotope dilution ICPMS after their coprecipitation with $Mg(OH)_2$. The method uses 1.3 mL samples with detection limits of Pb = 1.3 pM, Cd = 5.0 pM, and Cu = 40 pM, which are sufficiently low for open ocean seawater samples. The preconcentration procedure is simple, and the reagents used are easily purified. The use of the isotope dilution technique guarantees accuracy and precision. The eastern North Atlantic Pb, Cu, and Cd profiles measured with this method are in excellent agreement with known trace metal distributions in the open ocean.