

## SAMPLING AND ANALYTICAL METHODS FOR THE DETERMINATION OF COPPER, CADMIUM, ZINC, AND NICKEL AT THE NANOGRAM PER LITER LEVEL IN SEA WATER

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### SUMMARY

Sea-water samples collected by a variety of clean sampling techniques yielded consistent results for copper, cadmium, zinc, and nickel, which implies that representative, uncontaminated samples were obtained. A dithiocarbamate extraction method coupled with atomic absorption spectrometry and electrothermal atomization is described which is essentially 100% quantitative for each of the four metals studied, has lower blanks and detection limits, and yields better precision than previously published techniques. A more precise and accurate determination of these metals in sea water at their natural  $\text{ng l}^{-1}$  concentration levels is therefore possible. Samples analyzed by this procedure and by concentration on Chelex-100 showed similar results for cadmium and zinc. Both copper and nickel appeared to be inefficiently removed from sea water by Chelex-100. Comparison of the organic extraction results with other pertinent investigations showed excellent agreement.

One of the most recent comprehensive reviews dealing with trace metals in sea water is that by Brewer [1], but few definitive conclusions could be drawn concerning the distributions and marine geochemistry of individual trace metals. This was presumably the result of the severe problems encountered by investigators in both laboratory analysis and contamination-free sampling of sea water for trace metals at parts-per-trillion ( $\text{ng l}^{-1}$ ) concentrations.

In the past three years, however, more consistent results have been presented in several papers; for cadmium, nickel and copper [2], copper [3–7], cadmium [8–10] and nickel [11]. In addition, an oceanographically-consistent zinc profile has recently been reported [12]. This recent research leads to the conclusions that these trace metals are present in sea water at much lower concentration levels than previously believed, and that they appear to have well-defined distributions in the world's oceans.

The first step toward an understanding of the geochemistry of any trace element in sea water is the development of sample collection and analytical procedures that provide accurate, meaningful data. Presented in this paper are

the clean sampling and analytical techniques developed in this laboratory to allow the accurate determinations of cadmium, copper, nickel, and zinc.

In order to validate these procedures, it was necessary to demonstrate that agreement could be obtained by using completely different sampling and concentration techniques. In April 1977, a station in the California Current off Central California (37°05'N, 123°22'W) was occupied in order to perform such an intercomparison for these trace metals. Samples from a vertical profile of 18 depths were collected with two types of deep water samplers. Subsurface samples were collected from a small, inflatable raft. These samples were then analyzed for the four metals by two different extraction-concentration techniques.

## EXPERIMENTAL

### *Collection methods*

Surface samples were collected from a small raft rowed crosswind and more than 200 m away from the research vessel. Acid-cleaned polyethylene bottles (500 and 1000 ml) were submerged off the bow, rinsed and filled with sea water.

Deeper samples were collected by using two different sampling systems. Teflon-coated 30-l PVC ball-valve samplers (General Oceanics, Go-Flo) were modified by replacement of the standard stopcock with a teflon valve. The Go-Flo samplers are designed to enter the water in a closed, sealed position. At a depth of 10 m, a pressure release allows the ball valves to open and the sampler to fill with water. It then free flushes until tripped by a teflon messenger. The sampler was clamped on Dacron-sheathed, plastic Phillystran hydroline 10 m above a polypropylene-enclosed lead weight. The hydroline was led through a stainless steel snatch block-meter wheel to a portable winch with a stainless steel drum. The other sampling system used in this comparative study was the CIT deep-water, common-lead sampler designed and constructed by Schaule and Patterson [13].

Sample handling and processing were done on board ship inside a modular Porta-lab equipped with a positive pressure filtered air supply and specifically designed for trace metal analysis. After collection, the Go-Flo samplers were secured in a rack on the outside of the Porta-lab where the teflon valve was rinsed with ultra-clean water and connected to a length of teflon tubing. This tubing led through the wall of the Porta-lab to a polypropylene ball valve used to control the flow of sea water. In addition, trace metal samples from the CIT sampler were taken by Schaule while collecting samples for lead analysis.

The sea-water samples were preserved after collection by the addition of 4 ml of 6 M quartz-redistilled (Q-) hydrochloric acid per liter.

Because of the potential for contamination, most of the sea-water samples were not filtered. The primary purpose of this study was to compare sampling techniques; this comparison could be performed more easily without the extra processing step of filtration. However, two of the Go-Flo samples were filtered

to determine, (1) the feasibility of, and contamination potential from, the filtering procedure, and (2) the percentage of each metal associated with the particulate phase. The sea water was filtered through pre-cleaned, 142-mm, 0.4- $\mu\text{m}$  Nucleopore filters contained in teflon filter holders. The Go-Flo samplers were pressurized through a Swagelok fitting at the top of the sampler with filtered, high-purity nitrogen. Dissolved trace metal samples were collected from the filter effluent line.

### *Cleaning procedures*

Much of the development of cleaning techniques was prompted by the work of Patterson and Settle [14]. Plastic ware was initially rinsed in acetone, washed with Micro detergent, rinsed with glass-distilled deionized water (dd-water), soaked for at least one day in hot 3 M (GFS) hydrochloric acid (or for one week in 6 M hydrochloric acid at room temperature), rinsed with dd-water, soaked in 0.5–1 M (GFS) nitric acid for at least three days and rinsed with dd-water. In addition, plastic ware in which samples would be stored or processed was further rinsed with quartz-distilled water (Q-water), soaked in 0.5–1 M Q-nitric acid for at least a week, rinsed with Q-water, and dried in a laminar-flow clean air bench.

The Go-Flo samplers were thoroughly cleaned with Micro detergent, rinsed with deionized water, filled with 1 M (GFS) hydrochloric acid for several days and rinsed with dd-water.

### *Solvent extraction*

Two separate concentration techniques were utilized: a solvent extraction technique and a column ion-exchange technique with Chelex-100.

The organic extraction technique was developed as a modification of that presented by Kinrade and Van Loon [15]. The technique involves chelation with ammonium 1-pyrrolidinedithiocarbamate (APDC) and diethylammonium diethyldithiocarbamate (DDDC), a double extraction into chloroform, and back-extraction into nitric acid. Approximately 250 g of acidified sea water was transferred to a 250-ml teflon separatory funnel and buffered to about pH 4 with 2 ml of ammonium acetate (prepared by bubbling purified ammonia through 11 M Q-acetic acid); 1 ml of a solution containing 1% (w/v) each of APDC and DDDC (stabilized in a 1% ammonium hydroxide solution and purified by chloroform extraction) and 8 ml of Q-chloroform were then added, and the mixture was shaken vigorously for 2 min. After 5 min to allow phase separation, the chloroform fraction was drained into a 125-ml teflon separatory funnel, and 4 ml of 7.5 M Q-nitric acid was added to initiate degradation of the dithiocarbamates. An additional 6 ml of Q-chloroform was added to the original sea-water sample for a second extraction of the chelated species, as well as to rinse the solution and the separatory funnel. After phase separation, the chloroform was combined with the first fraction and shaken vigorously for 2 min. The phases were allowed 5 min to separate, after which the chloroform phase was discarded.

The 4-ml acid phase containing the back-extracted metals was then drained into a 10-ml fused quartz beaker, and 2 ml of 7.5 M Q-nitric acid was used to rinse the 125-ml separatory funnel and stem. This rinse was combined with the acid in the quartz beaker. The 6-ml back-extract was evaporated to dryness in a clean-air fume hood, and the residue was further oxidized by 250  $\mu$ l or 500  $\mu$ l of concentrated Q-nitric acid. The residue in the quartz beaker was redissolved in warm 1 M Q-nitric acid and quantitatively transferred with 250- $\mu$ l rinses (ca. 1.25 ml total) to a 1.8-ml polyvial. This solution was subsequently analyzed by flameless atomic absorption spectrometry (f.a.a.s.).

This procedure yields a 200:1 concentration, and at the same time removes the Group I and II elements that can interfere with the f.a.a.s. Because of the high sensitivity of f.a.a.s. for zinc and cadmium, the procedure can often produce samples with zinc and cadmium concentrations too high for direct analysis. When necessary, these samples were diluted (by weight) with 1 M Q-nitric acid to bring the metal concentration into the proper working range. This dilution was seldom necessary for copper or nickel.

The most important criterion in the development of the organic extraction technique was to achieve quantitative yields with a high degree of precision. The dithiocarbamates (APDC and DDDC) were chosen after a study by Kinrade and Van Loon [15] showed that the combination of these chelating reagents worked well for the extraction of a variety of metals over a fairly wide pH range. In addition, APDC and DDDC discriminate extremely well against the major cations in sea water. Chloroform was chosen as the organic solvent since it allowed a double forward extraction with two relatively small volumes of solvent. Ammonium acetate was used because it has a good buffering capacity at the optimum pH for extraction (about pH 4) and because it could be made quite cleanly. It should be noted that acetate ion can form complexes with some metals that may interfere with extractions, but there is no interference for cadmium, copper, zinc, and nickel. This extraction technique developed independently here is similar to that recently described by Danielsson et al. [16]. The major differences are the use of a citrate buffer and Freon TF as the organic solvent by the earlier investigators.

Detailed radiotracer studies for cadmium, copper, and zinc were employed in development of the method. The overall recoveries by the prescribed procedure for sea-water samples spiked with  $^{115m}\text{Cd}$ ,  $^{64}\text{Cu}$ , and  $^{65}\text{Zn}$  were  $98.9 \pm 0.7\%$  ( $n = 10$ ),  $97.9 \pm 1.2\%$  ( $n = 3$ ), and  $99.0 \pm 0.8\%$  ( $n = 5$ ), respectively. The first chloroform fraction extracted 90–92% of all three metals. Combined extraction into two batches of chloroform prior to back-extraction was  $99.4 \pm 0.4\%$  ( $n = 11$ ) for cadmium,  $98.0 \pm 1.2\%$  ( $n = 11$ ) for copper and  $99.2 \pm 0.7\%$  ( $n = 5$ ) for zinc. APDC alone extracted 99.2% of the cadmium, 98.5% of the copper, and 100.0% of the zinc, while DDDC alone produced yields of 96.0% for cadmium, 97.5% for copper, and 90.6% for zinc. These studies show that either the APDC/DDDC combination or APDC alone provide nearly 100% quantitative recoveries with relatively small standard deviations. The standard deviations observed were of the same order as would be expected from the tracer  $\gamma$ -counting error alone.

### *Chelex-100 technique*

The Chelex-100 ion-exchange concentration technique [17] was modified somewhat. The resin (sodium form, 100–200 mesh) was cleaned with 6 M (GFS) hydrochloric acid by daily suspension, decantation and addition of fresh acid for one week. It was then rinsed with Q-water and 2 M Q-nitric acid, followed by a final rinse with Q-water. The resin was then changed to the ammonia form and 7.5 ml of resin was loaded into polypropylene disposable columns. The excess of ammonia was rinsed from the columns with about 50 ml of Q-water until the pH dropped below 9. The columns were topped up with 1 cm of Q-water over the resin bed and stored upright in individual plastic bags.

The Chelex concentration step was performed at sea immediately after sample collection. Sea water (4 l) was drawn from the samplers into acid-cleaned polyethylene bottles, and water was pumped through teflon tubing directly into the columns. A multi-channel peristaltic pump, located downstream of the columns, was used to maintain the flow rate at 3.5–4.5 ml min<sup>-1</sup>. The effluent was collected and measured volumetrically. Upon completion of pumping, the columns were capped at both ends, placed in individual polyethylene bags, and frozen for storage. At no time during preparation, processing, or storage was the resin allowed to go dry. After return to the shore lab, the columns were thawed, washed with 50 ml of Q-water to remove excess of salts, and eluted with 30 ml of 2 M Q-nitric acid into small polyethylene bottles. The concentration factor resulting from this technique was approximately 120:1.

Radiotracer studies, with <sup>65</sup>Zn- and <sup>115m</sup>Cd-spiked sea-water samples, showed recoveries of 99 and 100%, respectively, for this concentration procedure. Stable tracer studies also indicated that quantitative yields are obtained for relatively high levels ( $\mu\text{g l}^{-1}$ ) of copper and nickel. Studies by other investigators support these results [17–19].

In addition to the trace metals of interest, large amounts of calcium and magnesium are also retained on the Chelex resin and eluted with the acid. This sample matrix can markedly suppress the absorbance signal during f.a.a.s. The amounts of these interfering salts were found to be constant from column to column, and a matching matrix of precleaned alkali metal and alkaline earth salts was used in the preparation of the f.a.a.s. standards (Ca, 1800 ppm; Mg, 1700 ppm; Na, 150 ppm; and K, 20 ppm). The instrumental sensitivity for standards prepared in this manner was identical to that for stable spikes concentrated from Chelex-treated, metal-free sea water.

### *Flameless atomic absorption analysis (f.a.a.s.)*

Cadmium, copper, nickel, and zinc in the extracted samples were determined by f.a.a.s. A Varian AA-6 spectrometer with a model 90 carbon rod atomizer (CRA-90) and a BC-6 hydrogen continuum automatic background corrector, and a Perkin-Elmer 603 spectrometer with a Model 2100 graphite furnace (HGA-2100) and deuterium-arc background corrector were used. Hollow-cathode lamps were used as light sources. In general, manufacturer-recommended

procedures were followed, except that relatively higher temperatures for shorter durations were utilized during atomization. In addition, with the Varian CRA-90, P-10 gas (90% argon, 10% methane) was mixed with the nitrogen flow (flow ratio 1:6) during the ashing and atomization steps. The use of P-10 gas prolonged the life of the pyrolytic coating of the carbon rods and increased precision.

#### *Blanks, detection limits and precision*

The blanks and detection limits for the two concentration techniques are presented in Table 1. Blanks were determined by extracting previously-processed sea water and/or Q-water. The solvent extraction blanks were below the instrumental detection limits for cadmium and nickel. The zinc blank was small compared to sea-water values other than for surface water, and the copper blank, while significant, was uniform with a standard deviation of only 4 ng l<sup>-1</sup>. The detection limits for copper and zinc are based on 2.5 times the standard deviation of the blanks, while those for cadmium and nickel are governed by the instrumental detection limits. The blanks for the Chelex concentration technique are set primarily by the instrumental detection limits for the concentrated sample.

The precision of the solvent extraction technique, expressed as a pooled relative standard deviation (RSD) for replicate samples, is 5.3%, 6.3%, and 3.8% for copper, nickel, and cadmium, respectively. Excluding samples containing less than 50 ng l<sup>-1</sup>, the pooled RSD for zinc is 4.5%. The lack of sufficient replicates for the Chelex technique precluded an estimate of its precision.

## RESULTS AND DISCUSSION

The results of the comparison study are presented in Table 2. Technically, the data presented for unfiltered samples should be called "acid-soluble" or "labile". The solvent extraction results are equivalent to the dissolved fraction plus the particulate and colloidal metal leached into solution during acidification of the samples for storage. This technique should closely approximate

TABLE 1

Blanks and detection limits  
(All values in ng l<sup>-1</sup>)

Element	Solvent extraction		Chelex-100	
	Blank	Detection limit	Blank	Detection limit
Cu	23 ± 4	10	4	6
Cd	<0.2	0.2	<0.6	0.6
Zn	2 ± 1	2	5	15
Ni	<8	10	40 ± 2	15

TABLE 2

Results of comparison study

(All values in ng l<sup>-1</sup>. Values in parentheses are suspected to be contaminated, see text.)

Depth (m)	Sampler	Copper		Cadmium		Zinc		Nickel	
		Ext.	Chelex	Ext.	Chelex	Ext.	Chelex	Ext.	Chelex
0	Raft	105,106	69	15.1,16.2	15	7,10	<15	304,339	217
25	Go-Flo	109,102	60	23.9,23.3	22	33,29	18	232,228	166
50	Go-Flo	106,97	50	38.3,36.5	35	(186,202)	(214)	261,295	190
100	Go-Flo	92,98	28	61.8,60.8	61	69,82	63	284,301	198
110	CIT	94,93	45	60.2,62.3	64	76,74	63	349,320	213
200	Go-Flo	96,94	26	73.3,77.5	70	180,175	149	323,314	248
300	Go-Flo	94,100	—	80.9,80.3	—	186,192	—	378,378	—
400	Go-Flo	93,99	26	85.3,89.6	92	229,226	180	364,440	371
410	CIT	95,94	—	86.7,87.9	—	248,244	—	434,442	—
600	Go-Flo	112,94	33	118,—	109	314,—	310	445,—	407
630	CIT	(125,129)	—	(102,104)	—	(322,352)	—	(527,557)	—
800a	Go-Flo	110,98	40	110,118	109	404,378	428	521,501	470
b		123,—	—	116,109	—	407,375	—	521,536	—
1020	CIT	116,124	—	110,108	—	419,445	—	576,589	—
1200	Go-Flo	151,132	26	110,98	109	519,510	456	693,605	576
1560	CIT	(220,223)	—	(93,93)	—	(547,567)	—	(2000,1900)	—
1800	Go-Flo	173,170	81	107,102	103	579,588	500	556,693	579
2030	CIT	209,204	—	96,95	—	641,576	—	569,645	—
2500	Go-Flo	224,222	98	99,95	94	628,617	654	626,568	599
2950	CIT	239,240	—	78,84	—	600,603	—	676,627	—

the total metal values in open ocean waters. The Chelex results are equivalent to the dissolved metals that chelate to the resin, plus that fraction of particulate metal leached with 2 M nitric acid from any particulates that accumulate on the resin bed.

#### Comparison between sampling methods

A primary objective of this study was the comparison of several different clean sampling methods. Consistency of results among samplers would imply that the samples collected are, in fact, uncontaminated and meaningful in terms of understanding the marine geochemistry of these elements. A direct statistical comparison of the samplers is not possible, because the samples were collected from different depths. However, the samples collected closest together (100, 110 m; 400, 410 m) can be compared to demonstrate the consistency between the Go-Flo and CIT samplers. The copper, cadmium, and zinc results obtained by solvent extraction for the different samplers appear identical. The nickel values are in fair agreement. The samplers can also be compared indirectly by means of the vertical profiles obtained. Figure 1 presents plots of replicate results obtained by solvent extraction for the four metals. Although marked

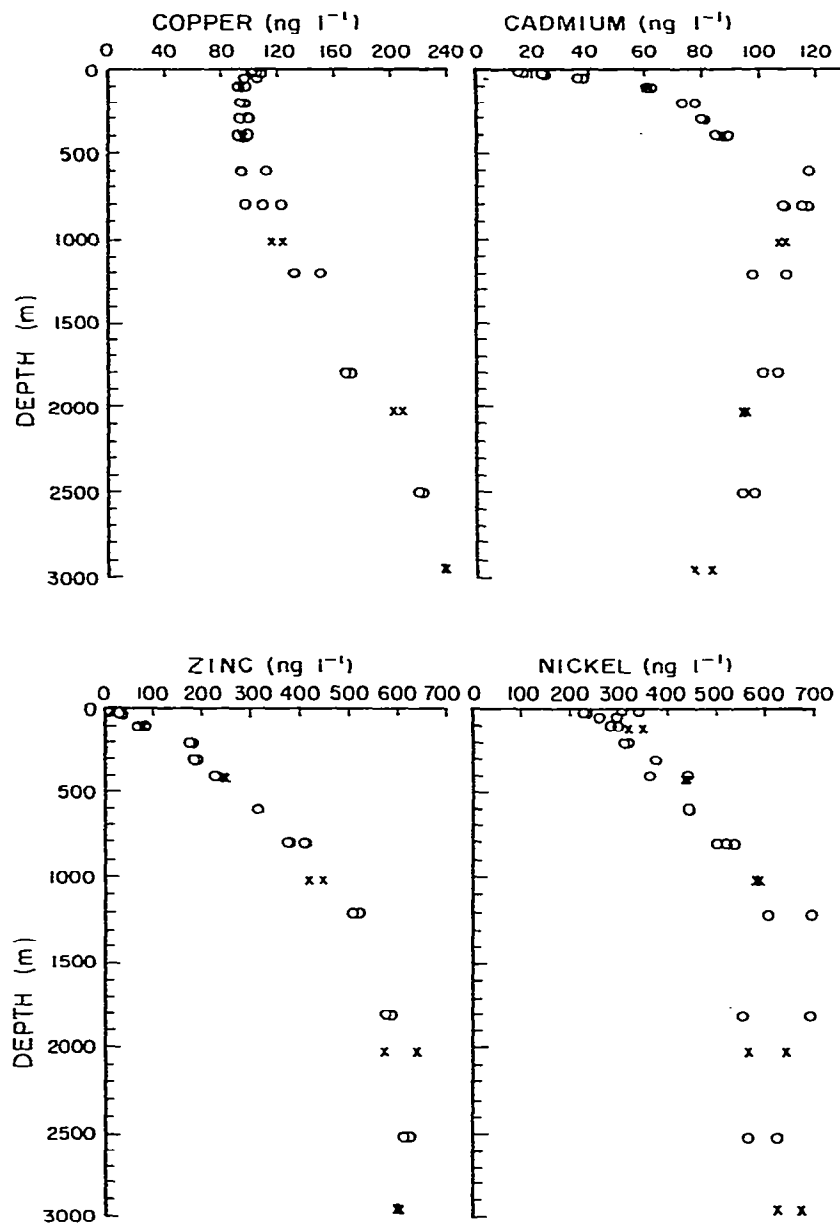


Fig. 1. Comparison of profiles obtained with Go-Flo (O) and CIT (X) samplers. Data points represent replicate extraction values.

vertical gradients exist, it is readily apparent that the samples collected by the various sampling techniques yielded consistent data which fit smoothly into the observed profiles.

Three of the samples from Table 2 have not been included in the plots of Fig. 1. The 630-m and 1560-m CIT samples were contaminated because of a



faulty seal. This allowed leakage of water that had been in contact with the inside of the stainless steel sampler into the polyethylene sample bags. Schaule and Patterson found these two samples to be contaminated for lead (personal communication). On the basis of the present results, the copper and nickel concentrations were increased by 20–60 ng l<sup>-1</sup> and 100–1500 ng l<sup>-1</sup>, respectively, but, the cadmium and zinc results show no evidence of such contamination. The problem with this seal was subsequently corrected by Schaule, and it appears that these two are the only questionable CIT samples. In addition, the first Go-Flo sample collected on the cruise (50 m) appeared to be contaminated for zinc by approximately 150 ng l<sup>-1</sup>; this was most likely a result of either inadequate flushing of the sampler before collection, or contamination during transfer from sampler to storage bottle. Whatever the cause, this was the only Go-Flo sample that showed a discrepancy from the other samples collected.

#### *Comparison of concentration techniques*

Another primary objective was to compare the results obtained by solvent extraction concentration with an independent technique (Chelex-100). Figure 2 presents vertical profiles for the mean extraction data along with the Chelex-100 results.

The copper results show a major discrepancy, with a mean difference between extraction and Chelex values of  $72 \pm 27$  ng l<sup>-1</sup>. The Chelex column effluent from the samples at 25 m and 2500 m was collected and analyzed by solvent extraction (Table 3). The mean amounts of copper found, 63 and 135 ng l<sup>-1</sup>, respectively, were approximately equal to the difference between the Chelex and extraction data for the two samples. Thus, it appears that about 60% of the copper in sea water is not removed by the Chelex technique. This result confirms a reassessment of Chelex-100 for trace metal concentration from sea water [20], which showed that quantitative removal of copper required prior acidification and heating, followed by readjustment of the pH to 5.4. Riley and co-workers [20] assumed that a fraction of the copper is associated with colloidal and fine particulate matter and is not affected by the chelating resin. The acidification and storage involved in the present solvent extraction technique should liberate this fraction so that quantitative results for total copper can be obtained.

The cadmium profiles show excellent agreement. The difference between techniques averaged 1.3 ng l<sup>-1</sup>, well within the precision expected, and cadmium could not be detected ( $< 0.5$  ng l<sup>-1</sup>) in the Chelex effluent. The zinc values appear reasonably consistent. The Chelex results are somewhat lower ( $19 \pm 38$  ng l<sup>-1</sup>); the large standard deviation is attributable to the lack of precision in analysis of the Chelex samples. The average difference is similar to the amount of zinc found in the Chelex effluent (ca. 8 ng l<sup>-1</sup>). While this comprises only a few percent of deep-water zinc values, it can be an appreciable fraction of the surface-water zinc. Nickel values are also lower when the Chelex method is used. The mean difference of  $65 \pm 35$  ng l<sup>-1</sup> between the two techniques agrees well with the average value of 57 ng l<sup>-1</sup> found in the Chelex

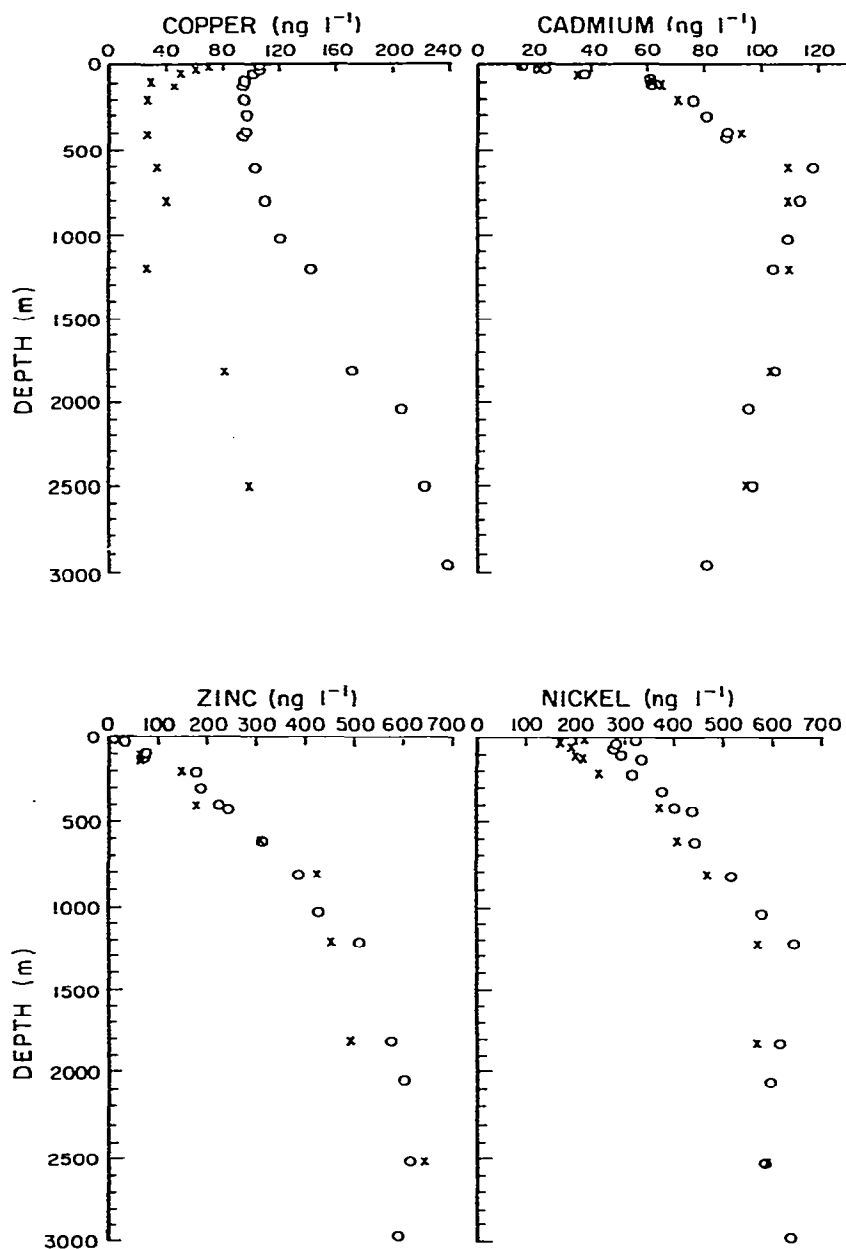


Fig. 2. Comparison of profiles from solvent extraction (O, values expressed as average of two or more replicates) and Chelex-100 (X) techniques.

effluent.

Thus, the Chelex technique yields substantially lower values for copper and nickel than the solvent extraction, and the differences are approximately equal to the amounts found in the effluent from the Chelex column.

TABLE 3

Chelex effluent measured by solvent extraction ( $\text{ng l}^{-1}$ )

Sample	Copper	Cadmium	Zinc	Nickel
25 m after 1 h	59	<0.5,<0.5	8	70
after 8 h	66,64	<0.5,<0.5	27,31	62,58
2500 m after 1 h	152,114	<0.5,<0.5	8,7	68
after 8 h	135,140	<0.5,<0.5	8,6	28

*Storage and filtering experiments*

Two additional experiments were also undertaken. The first involved taking additional samples from the Go-Flo bottles after they had stood for 2 h on the ship, to check for contamination and/or absorption of the trace metals; significant changes of concentration were not found (Table 4). This indicates that the composition of the samples is not altered during the transit time involved in bringing a deep sample to the surface. The second experiment entailed filtering the sea water through 0.4- $\mu\text{m}$  Nucleopore filters and collecting the dissolved phase; this was designed to test for possible contamination during filtration. The results are given in Table 5, which also shows upper and lower limits of the particulate metal concentrations in the California current determined in this laboratory. In general, the values for the filtered samples plus the particulate fraction fall within the estimated precision of the unfiltered or total metal concentration. In deep waters, the particulate trace metals are less than 1% of the total metal concentration so that filtration causes insignificant differences. In the 25-m sample, the ranges of particulate values are 1–9, 1.5–4, 3–27, and 0.3–2% of the total copper, cadmium, zinc, and nickel, respectively. Thus, it can be concluded that filtering the sea water did not contaminate the samples to any appreciable extent.

*Comparison of results with other investigations*

The lack of a suitable standard reference sea water precludes a rigorous determination of the accuracy of the solvent extraction technique, hence the

TABLE 4

Comparison of sea water drawn from Go-Flo samplers immediately and after 2 h by the solvent extraction method  
(All values in  $\text{ng l}^{-1}$ )

Sample	Copper	Cadmium	Zinc	Nickel
25 m: initial	110,109	30.9,31.5	24,28	332,320
after 2 h	107,107	30.5,30.9	26,33	323,348
2500 m: initial	224,222	99,95	628,617	625,568
after 2 h	222,236	95,99	646,625	661,678

TABLE 5

Comparison of filtered and unfiltered Go-Flo samples by the solvent extraction method  
(All values in  $\text{ng l}^{-1}$ )

Sample	Copper	Cadmium	Zinc	Nickel
25 m: unfiltered	110,109	30.9,31.5	24,28	332,320
filtered	104,111	28.8,25.0	22,31	325,321
particulate	1-9	0.4-1.0	1-7	1-6
1800 m: unfiltered	173,170	107,102	579,588	556,693
filtered	158,162	107,109	525,565	603,-
particulate	1.5-3	0.05	1.5-2	5-10

accuracy is estimated to be similar to the precision. An additional estimate of the reliability of the sampling and analytical techniques can be made by comparing the oceanic profiles determined here with other relevant investigations.

The copper profiles (determined by solvent extraction) presented here and by Bruland et al. [5] are in good agreement with the vertical profile of copper in the California current reported by Boyle et al. [4], and are similar to results reported for the Atlantic Ocean [2, 6, 7]. The cadmium profile shown here exhibits a marked correlation with the labile nutrients, phosphate and nitrate [10]; similar correlation and depth distribution have been reported earlier [2, 8, 9]. The nickel profiles described by Sclater et al. [11] are very similar to the profile determined by the extraction technique in the present study. Zinc data comparable to those presented here and by Bruland et al. [12] are not available, but the consistency obtained and the excellent correlation with silicate [12] provide a degree of confidence.

### Conclusion

The combination of sampling methods, solvent-extraction concentration, and analysis by f.a.a.s. provides a valuable procedure for obtaining precise and apparently accurate measurements of copper, cadmium, zinc and nickel in sea water. The large concentration factor (200:1), together with low reagent blanks, provides detection limits that are well below those of other published techniques, and are substantially below even the lowest reported natural levels of these trace metals. Studies of the dynamics and biogeochemical processes involved in establishing the oceanic distributions of these metals can therefore be made with greater confidence.

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