

## ANALYSIS OF SEAWATER FOR DISSOLVED CADMIUM, COPPER AND LEAD: AN INTERCOMPARISON OF VOLTAMMETRIC AND ATOMIC ABSORPTION METHODS

KENNETH W. BRULAND and KENNETH H. COALE

*Institute of Marine Sciences, University of California, Santa Cruz, CA 95064 (U.S.A.)*

LÉON MART

*Institute of Applied Physical Chemistry, Nuclear Research Center (KFA), P.O.B. 1913, D-1570 Jülich (F.R.G.)*

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### ABSTRACT

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An intercomparison study of voltammetric and atomic absorption spectrometric methods for determining cadmium, lead and copper in seawater samples was conducted. The voltammetric approach utilizes differential pulse anodic stripping voltammetry using a rotating, glassy carbon, mercury film electrode under conditions developed to minimize contamination sources and to enhance sensitivity for seawater matrices. The atomic absorption approach involves a concentration step using either an organic solvent extraction of metal dithiocarbamate chelates or a Chelex-100 column with detection by graphite furnace atomic absorption spectrometry. Similar and consistent results were obtained using both methods for the three trace metals studied on a wide range of natural seawater samples. Both methods are comparable in sensitivity for cadmium and copper, however the voltammetric method is better suited for the analysis of lead in seawater because of its enhanced sensitivity and low blank. An advantage of the voltammetric approach is its amenability towards real-time shipboard analysis.

### INTRODUCTION

In a review of trace elements in seawater, Bruland (1983) concluded that a first-order understanding of the oceanic distributions of Cd, Cu and Pb has only recently emerged. This recent revolution in our knowledge of the distributions of these trace metals in seawater has resulted primarily from major advances in instrumental and analytical chemistry and the elimination, or control, of contamination during sampling, storage and analysis.

The oceanographically consistent data for these three elements are based primarily upon graphite furnace atomic absorption spectrometry (GFAAS), differential pulse anodic stripping voltammetry (DPASV) and isotope dilution mass spectrometry (IDMS) detection methods. All of these methods require a selective concentration step prior to analysis. Concentration methods for GFAAS and IDMS include liquid–liquid organic extractions of metal chelates, such as dithiocarbamates (Danielson et al., 1978; Bruland

et al., 1979) or dithizone (Smith and Windom, 1980; Schaule and Patterson, 1981), coprecipitation with cobalt dithiocarbamate (Boyle and Edmond, 1977), or the binding of metals to immobilized chelating resins, such as Chelex-100 (Kingston et al., 1978). With DPASV, preconcentration is performed electrochemically, typically for deposition periods of 5–30 min (Mart et al., 1980b, 1983, 1984). The voltammetric methods and their attributes have been reviewed by Nürnberg (1984).

In most cases, the analyses described above were conducted on filtered seawater samples, which were stored acidified and in some cases UV oxidized prior to analysis. This treatment provides a measure of the total dissolved-metal content in seawater.

Techniques for the collection and analysis of seawater samples for trace metals are often unconventional and tedious to conduct. Consequently, laboratories performing these analyses have typically been forced to specialize in only one analytical approach. Due to the lack (until recently) of a suitable seawater reference material, there exist few detailed comparisons of different analytical methods for determining trace metals in seawater, with even fewer comparisons using open-ocean seawater.

Comparison studies have been performed on a coastal seawater sample (Sturgeon et al., 1980), on a single deep Pacific sample (Mart et al., 1980a), on vertical profiles from the North Sea and the North East Atlantic (Brügmann et al., 1983), and on a North Atlantic profile (Mart et al., 1984). For example, the study by Brügmann et al. (1983) demonstrated that GFAAS and voltammetric methods can be used to measure very low levels of trace metals in oceanic waters. However, the data exhibited a large degree of scatter and there were a number of discrepancies that were not fully explained. Mart et al. (1980b) demonstrated excellent agreement between DPASV and GFAAS results for Cd and Cu, and between DPASV and IDMS methods for Pb, the latter at ultratrace levels ( $3 \text{ ng kg}^{-1}$ ). Most recently, Mart et al. (1984) obtained similar results on comparing DPASV and GFAAS methods for Cd in the North Sea.

An alternative approach to assessing the validity of an analysis is based upon the concept of oceanographic consistency (Boyle et al., 1977). Detailed trace metal profiles should show smooth variations and be related to other hydrographic and chemical water-column features. Regional variations should be compatible with biogeochemical processes known to control constituent distributions in seawater, superimposed on large-scale physical mixing and deep-water circulation patterns. Using these criteria, Bruland (1983) concluded that profiles for Cd in the North Atlantic and Arctic Ocean by Bruland and Franks (1983), Danielsson and Westerlund (1983), Olafsson (1983) and Moore (1983), all by organic extraction/GFAAS techniques, and a profile by Mart et al. (1983), determined by DPASV, were all oceanographically consistent. This consistency implies that each of these investigations produced accurate and valid results.

In contrast to the GFAAS and IDMS approaches, DPASV has been shown

to be amenable towards real-time shipboard voltammetric determinations under adverse conditions (Mart et al., 1983). Shipboard analyses can enable scientists to evaluate and refine their sampling strategy readily; with respect to contamination control and the study of spatially varying oceanographic features. Trace metal speciation studies often require freshly collected samples, untreated by typical chemical preservation techniques. For such studies real-time analysis is of fundamental importance and DPASV is well suited for this purpose.

In this paper we present the results of a detailed intercomparison of DPASV and GFAAS techniques and assess the accuracy, precision and sensitivity of these methods over a range of metal concentrations in open-ocean seawater samples. These tests were conducted using acidified seawater samples from the eastern North Pacific, the North Sea, and the Canadian seawater reference material NASS-1 (from the North Atlantic, see Berman et al., 1983). Analyses were conducted on the same seawater samples by DPASV directly on 50-ml aliquots and by GFAAS using concentrated solutions.

#### SAMPLING

Intercomparison samples used for this study were collected and analyzed on several occasions. Details are presented in Tables I—III. Sample collection and storage methodologies have been described previously (Bruland et al., 1979; Mart, 1979a, b; Bruland, 1980; Berman et al., 1983) and are described briefly below.

Surface-water samples were collected from the bow of a rubber raft moving into the wind and more than 200 m crosswind or upwind from the research vessel. The eastern Pacific vertical profile was obtained using modified Teflon-coated 30-l General Oceanic's Go-Flo bottles deployed on Kevlar hydroline, and tripped with Teflon messengers. Samples were filtered through 0.3- $\mu$ m Nuclepore filters and processed at sea within a portable clean laboratory equipped with a filtered air supply and a class-100 clean-air bench. Samples (1 l) were acidified to pH 1.6—2, by the addition of ultrapure HCl. Samples were stored, triple-bagged, in acid-cleaned conventional polyethylene bottles at room temperature prior to analysis. Sample storage times varied from a few days to 3 years. The NASS-1 seawater reference material was collected, filtered and acidified to pH 1.6 with HNO<sub>3</sub> as described by Berman et al. (1983).

#### ANALYTICAL METHODS

##### *Graphite furnace atomic absorption spectrometry (GFAAS)*

Two different methods of metal concentration were employed prior to GFAAS analysis: (1) organic solvent extraction (org. ext.), and (2) columns

TABLE I

North Sea intercomparison of surface sea water ( $\text{ng kg}^{-1}$ ). Collected at  $54^{\circ}30'N$ ,  $4^{\circ}30'E$  on 17 May 1982. Samples 1 and 2 were collected a few hundred meters apart. Multiple sub-samples were collected at each site denoted (a)–(d)

| Sample         | DPASV                         | Org. Ext./GFAAS<br>at NIOZ |
|----------------|-------------------------------|----------------------------|
| <i>Cadmium</i> |                               |                            |
| 1 (a)          | $34.6 \pm 1.4$<br>( $n = 6$ ) | 32.2                       |
| 1 (b)          | $33.6 \pm 1.3$<br>( $n = 6$ ) | 33.3                       |
| 2 (a)          | 36.5                          | —                          |
| 2 (b)          | 35.1                          | 36.9                       |
| 2 (c)          | —                             | 37.4                       |
| <i>Copper</i>  |                               |                            |
| 1 (a)          | $362 \pm 20$<br>( $n = 6$ )   | 330                        |
| 1 (b)          | $368 \pm 10$<br>( $n = 6$ )   | 333                        |
| 2 (c)          | 368                           | 350                        |
| 2 (d)          | —                             | 378                        |

TABLE II

California Current intercalibration seawater sample ( $\text{ng kg}^{-1}$ ). Collected at  $37^{\circ}6'N$ ,  $123^{\circ}14'W$  on 21 August 1979. These samples were stored acidified with hydrochloric acid to pH 1.5. The samples for DPASV were UV oxidized prior to analysis

| Element | DPASV<br>KFA <sup>a</sup>     | Org. Ext./GFAAS               |                   |
|---------|-------------------------------|-------------------------------|-------------------|
|         |                               | UCSC <sup>a</sup>             | MLML <sup>a</sup> |
| Cadmium | $12.1 \pm 1.3$<br>( $n = 7$ ) | $12.3 \pm 0.2$<br>( $n = 6$ ) | $12.7 \pm 1.0$    |
| Lead    | $8.6 \pm 0.7$                 | $\leq 10$                     | $\sim 6$          |
| Copper  | $72 \pm 2$<br>( $n = 7$ )     | $70 \pm 2$<br>( $n = 6$ )     | $66 \pm 3$        |

<sup>a</sup>The analyses were carried out respectively in the Nuclear Research Center Jülich (KFA), the Institute of Marine Sciences, University of California, Santa Cruz (UCSC) and the Moss Landing Marine Laboratory (MLML).

of Chelex-100 ion exchange resin (Chelex). Both the organic solvent extraction and Chelex-100 concentration steps, as well as cleaning procedures, contamination precautions, and GFAAS analysis, are discussed in detail elsewhere (Bruland et al., 1979; Bruland, 1980).

Briefly, the solvent extraction technique involves transferring 250–300 g of acidified seawater to a Teflon separatory funnel and adjusting the pH to

TABLE III

Canadian seawater reference material NASS-I ( $\text{ng kg}^{-1}$ ). For NASS-I collection and analytical details see Berman et al. (1983). These samples were stored acidified with nitric acid to pH 1.5. Sub-samples (50 ml) were UV oxidized just prior to analysis by DPASV

| Element | DPASV                      | UCSC<br>Org. ext/GFAAS | Current assigned<br>value for NASS-I |
|---------|----------------------------|------------------------|--------------------------------------|
| Cadmium | $32 \pm 2$<br>( $n = 7$ )  | $28 \pm 1$             | $28 \pm 4$                           |
| Lead    | $32 \pm 2$<br>( $n = 10$ ) | —                      | $38 \pm 6$                           |
| Copper  | $107 \pm 6$<br>( $n = 7$ ) | $94 \pm 3$             | $96 \pm 10$                          |

4.5 using ultrapure ammonium acetate ( $\text{NH}_4\text{Ac}$ ) buffer. A solution (1 ml) containing 1% each of ammonium 1-pyrrolidinedithiocarbamate (APDC) and diethylammonium diethyldithiocarbamate (DDDC) [stabilized in a 1% ammonium hydroxide solution and purified by extraction with ultrapure chloroform ( $\text{CHCl}_3$ )] is added and the solution extracted twice with 7–8 ml of ultrapure  $\text{CHCl}_3$ . The mixtures are shaken vigorously for 2–3 min and allowed to stand for 5–10 min for phase separation. The  $\text{CHCl}_3$  phases are combined in a small Teflon separatory funnel and “back-extracted” with 4 ml of 7 N ultrapure nitric acid ( $\text{HNO}_3$ ). The  $\text{CHCl}_3$  phase is discarded and the acid phase placed in a fused-quartz beaker. The separatory funnel is rinsed with an additional 2 ml of 7 N  $\text{HNO}_3$  which is added to the beaker. This is slowly evaporated to dryness and the residue oxidized with 3 sequential 100–250- $\mu\text{l}$  volumes of concentrated ultrapure  $\text{HNO}_3$ . The residue is then redissolved in 1.25 ml of 1 N ultrapure  $\text{HNO}_3$  and transferred to a small conventional polyethylene vial for GFAAS analysis. This procedure results in a 200:1 concentration factor.

The ion exchange column technique employs Chelex-100 (sodium form, 100–200 mesh), pre-cleaned with 4 N hydrochloric acid ( $\text{HCl}$ ) and 2.5 N  $\text{HNO}_3$ , rinsed with ultrapure water, and converted to the ammonia form prior to loading in columns. At sea, 2-l seawater samples, adjusted to pH 6 with  $\text{NH}_4\text{Ac}$ , are drawn through a column containing 7.5 ml of Chelex-100 resin (flow rate: 1–2  $\text{ml min}^{-1}$ ). The columns are then capped and frozen. On shore, the columns are thawed, rinsed with 20 ml ultrapure  $\text{NH}_4\text{Ac}$  (pH 5.8) and 20 ml ultrapure water to rinse off the bulk of the alkali and alkaline earth metals (Kingston et al., 1978). The trace metals are then eluted with 20 ml of 2.5 N ultrapure  $\text{HNO}_3$ , providing a concentration factor of 100:1. For Pb analysis, 10 ml of the eluent is evaporated to dryness in a fused-quartz beaker and redissolved in 1 ml of 1 N  $\text{HNO}_3$  yielding a concentration factor of 1000:1.

Seawater concentrates are analyzed with a Perkin-Elmer 5000 atomic absorption spectrometer equipped with an HGA-500 heated graphite atomizer and deuterium-arc background corrector. Ashing and atomization conditions are similar to those recommended by the manufacturer. The analytical technique of standard additions is used to compensate for matrix effects.

### *Differential pulse anodic stripping voltammetry (DPASV)*

Detailed descriptions of the basic DPASV apparatus, electrodes, and instrumental modifications have been reported by Mart et al. (1980b, 1983). Recent modifications (Mart et al., 1984) and a brief description of the system are summarized below.

The voltammetric analyzers, PAR 174 A (EG&G, Princeton Applied Research), are used in the differential pulse mode. Modifications were made to increase sensitivity for analyzing seawater samples (Copeland et al., 1973; Valenta et al., 1977). The PAR 174 A voltammetric analyzer is designed to work with a wide variety of solvents. However, in highly conductive solutions such as seawater, the capacitive current decays rapidly with respect to the faradaic current. Thus, it was possible to shorten the decay period from 40 to 13 ms. This results in a larger faradaic current being sampled and an increase in sensitivity. The pulse repetition period was also shortened to 240 ms to accommodate a scan rate of  $10 \text{ mV s}^{-1}$  and reduce the time required to record a voltammogram. In addition, a 70 ohm resistor was placed in series with the working electrode to dampen the potentiostatic oscillations appearing at the beginning of the differential pulse.

The electrode system is depicted in Fig. 1. The working electrode is a rotating, glassy carbon type with a mercury film formed in situ. The  $28 \text{ mm}^2$  glassy carbon disc is imbedded in the end of a plexiglass shaft and polished to a high gloss using lapidary techniques. This electrode is secured to a stainless-steel axle which is connected to a driving motor completely encapsulated in a plexiglass housing. Although the axle is electrically isolated from the motor, electrical contact between the glassy carbon and the axle is made by immersion of the axle tip in elemental mercury (Hg) within the electrode. Contact of the axle to the cable leading to the voltammographic analyzer is made by Hg co-immersion of the mid axle segment and a platinum (Pt) cable lead. A coiled Pt wire serves as the counter electrode. This Pt wire is immersed in a saturated ultrapure potassium chloride (KCl) solution and sealed in a Teflon tube fitted with a porous Vycor tip. This arrangement provides a low ohmic junction to the sample solution. A coiled silver (Ag) wire onto which AgCl has been deposited (Ag/AgCl) serves as the reference electrode. This electrode is isolated in a manner similar to the counter electrode to reduce potential contamination. A slightly modified version of this electrode system, Rotel-2, has recently been developed by EG&G, Princeton Applied Research, Munich, F.R.G.

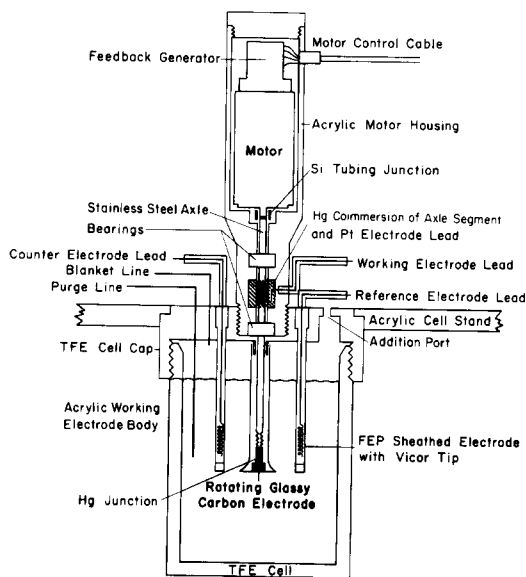


Fig. 1. Schematic diagram depicting DPASV electrode configuration, driver assembly and cell construction. Typically, two such assemblies and three purge cell positions are incorporated into one acrylic cell stand.

Samples are prepared and processed as follows. The sample (50–60 ml), previously acidified to pH 2 with ultrapure HCl or HNO<sub>3</sub>, is transferred to Teflon cells, weighed, and in some cases photooxidized for 3 h. It was necessary to UV oxidize coastal seawater samples to obtain a measure of the total dissolved metal in solution, particularly for the determination of Cu. However, oceanic deep-water samples did not appear to require this treatment. The samples are spiked with 30–50  $\mu\text{l}$  of a 5000  $\text{mg l}^{-1}$  solution of Hg<sup>2+</sup> and, if UV oxidized, are cooled and diluted back to 50 ml with ultrapure water before being deaerated for 15 min. Purge and blanket gas is 99.999% nitrogen scrubbed through a 30-cm column of acidified water.

A typical analysis proceeds as follows: the glassy carbon electrode is lightly polished at low rotation speed (200 rpm) with 0.05  $\mu\text{m}$  alumina using a wetted filter paper. The electrode is then rinsed with ultrapure water, weak acid, and again with ultrapure water. A Teflon cell containing a deaerated blank solution of 50 ml ultrapure water acidified to pH 2 with ultrapure HCl, and containing 30–50  $\mu\text{l}$  of the Hg<sup>2+</sup> solution and 200  $\mu\text{l}$  of a saturated ultrapure KCl solution, is moved from the degassing position on the acrylic cell stand into the analysis position (typically there are three degassing positions and two analysis positions on one stand). This blank solution undergoes electrodeposition at  $-1.0$  V for 6 min at an electrode rotation speed of 2000 rpm, while the sample is purged with N<sub>2</sub>. During

this step the Hg film is formed and metals in the blank solution are simultaneously deposited. At 6 min the electrode rotation and gas purge is stopped, the sample is blanketed with  $N_2$ , and the potential is adjusted to  $-0.85$  V. After a 30-s quiescent interval, a voltage scan from  $-0.85$  to  $-0.1$  V is conducted in the differential pulse mode at  $10$  mV s $^{-1}$  and the voltammogram is recorded. The Hg film is then held at  $-0.1$  V for 2 min while the electrode rotates and the solution is purged. Assuming the blanks are sufficiently low (typically  $\leq 5$  ng kg $^{-1}$ ), the electrode rotation is stopped and the applied potential is momentarily switched off as the blank cell is replaced by an identical Teflon cell containing a deaerated sample to be analyzed.

A three-point standard addition procedure is used to determine the metal concentration of the sample. Samples are analyzed identically to the blanks as an initial electrode-conditioning step. Based on this first voltammogram, a deposition time from 5 to 30 min is chosen for the zero addition sample run. Following a scan, while the electrode is being held at  $-0.1$  V, the sample is spiked with known amounts of Cd, Pb, and Cu, at levels estimated to approximate the amount of these metals in the solution. The sample analysis is then repeated, but with half the zero addition deposition period. For the final standard addition the sample is spiked a second time and analyzed again for one-third the zero addition deposition time. This procedure ensures that close to the same amount of metal is plated and stripped during each deposition cycle. Peak heights are then normalized to one deposition time and a standard addition plot obtained. The rationale for this procedure and its advantages have been outlined in detail elsewhere (Valenta et al., 1977; Mart et al., 1980b).

## RESULTS

The most direct way to compare DPASV and GFAAS methods is by analyzing aliquots of the same acidified seawater sample. Several inter-comparison studies using seawater samples from various locations were undertaken and the results are presented below.

### *North Sea intercomparison*

Unfiltered surface samples were collected in the central North Sea. Sample analysis was conducted at the Kernforschungsanlage, Jülich, GmbH, F.R.G., (KFA) by DPASV and at the Nederlands Instituut voor Onderzoek der Zee, Texel, NL (NIOZ) by the aforementioned extraction/GFAAS techniques, with the exception that methylisobutylketone (MIBK) was used as the solvent for the NIOZ determinations. The results, obtained using the DPASV method for both Cd and Cu are compared to the APDC/DDDC extraction/GFAAS method in Table I. Both analysis methods agree remarkably well. Due to limited sample, replicate analyses were not possible in every case. Single values in Table I represent the results of an individual analysis. Lead



results are not shown, since the reagent blanks using APDC/DDDC at NIOZ were too high to obtain meaningful results.

#### *California Current intercalibration seawater sample*

K. Bruland (UCSC), along with M. Gordon and J. Martin of Moss Landing Marine Laboratory (MLML) have conducted a trace metal intercalibration sponsored by the U.S. Environmental Protection Agency using California Current surface water samples with GFAAS analysis methods. For comparison, this sample was analyzed by DPASV as an example of typical oceanic surface-water with substantially lower metal concentrations than normally observed in the North Sea. It is important to note that this sample was stored  $\sim 3$  years prior to analysis by DPASV. The results of this comparison are presented in Table II. Again, excellent agreement was obtained between the methods. A two-sample Student's *t*-test showed no significant difference between DPASV and organic extraction GFAAS (UCSC) methods for Cd and Cu ( $P > 0.05$ ). Excellent agreement was also obtained between the DPASV and MLML GFAAS results. The MLML methods were similar to those used at UCSC.

#### *Canadian seawater reference material, NASS-1*

To further evaluate the DPASV method, a sample of the Canadian reference seawater standard (Berman et al., 1983) was analyzed by DPASV. These results are presented in Table III. In each case our DPASV mean values are not significantly different from the reported NASS-1 value (one-sample Student's *t*-test,  $P > 0.15$ ). At these concentration levels the relative precision of an individual analysis by DPASV ranges from 3 to 10%. Org. ext./GFAAS results are also in good agreement with the assigned NASS-1 values for Cd and Cu.

#### *VERTEX-I vertical profile*

As a final comparison of the two methods, samples from a vertical profile at the VERTEX-I site, located approximately 100 km off central California in the eastern North Pacific, were analyzed by each method. The results are presented in Tables IV–VI and illustrated in Figs. 2–4. For GFAAS analysis, these samples were concentrated both by dithiocarbamate/organic extraction and Chelex-100 ion exchange. The Chelex-100 concentration step was performed at sea immediately after sample collection. The organic extraction concentration and GFAAS analyses were conducted within 6 months of collection. For Pb, only the Chelex/GFAAS results (with a 1000-fold concentration factor) are reported, as the organic extraction/GFAAS results were near the instrumental detection limit. The Chelex concentration step is quantitative for Cd and Pb, however, Cu recovery appears consistently low,

TABLE IV  
 VERTEX-I intercomparison for cadmium

| Sample     | DPASV                  | Org. Ext./GFAAS | Chelex/GFAAS |
|------------|------------------------|-----------------|--------------|
| 25 m (a)   | 9.5                    | 11              | 8.1          |
| (b)        | 3.7; 4.7; 4.9          | 5.4; 5.6        | —            |
| 50 m (a)   | 19; 17                 | 17              | 19           |
| 75 m (b)   | 36; 34; 33; 37; 32; 32 | 36              | 33           |
| 100 m (a)  | 56; 54                 | 57              | 50           |
| 150 m (b)  | 79                     | 78              | 71           |
| 250 m (a)  | 91                     | 98              | 91           |
| (b)        | 90                     | —               | —            |
| 500 m (a)  | 108                    | 116             | 110          |
| (b)        | 117                    | —               | 108          |
| 750 m (b)  | 115                    | —               | 114          |
| 1000 m (d) | 121; 121; 114; 118     | 118; 111        | 116; 117     |
| 1500 m (b) | 124; 124; 103          | 116             | 120; 115     |
| 2000 m (b) | 109; 109               | 111             | 110; 93      |
| 2290 m (a) | 112                    | —               | 96           |
| (b)        | 107                    | 109; 107        | 93           |

TABLE V  
 VERTEX-I intercomparison for lead

| Sample     | DPASV            | Chelex/GFAAS  |
|------------|------------------|---------------|
| 25 m (a)   | 12.6             | 12.9          |
| (b)        | 6.8; 7.8; 8.3    | 7.0; 7.2      |
| 50 m (a)   | 12.7; 12.7       | 10.9          |
| 75 m (b)   | 10.4; 14.8; 14.1 | 8.3; 7.5      |
|            | 10.0; 9.6; 9.7   |               |
| 100 m (a)  | 12.9; 14.8       | 10.7; 11.1    |
| 150 m (b)  | 12.5             | 12.0; 15.2    |
| 250 m (a)  | 13.2             | 15.6; 15.8    |
| (b)        | 14.8             | —             |
| 500 m (a)  | 7.6              | 8.8; 9.4      |
| (b)        | 9.8              | —             |
| 750 m (b)  | 6.4              | 6.6           |
| 1000 m (d) | 3.9; 4.2; 5.1    | 4.9; 4.4; 3.9 |
| 1500 m (b) | 5.1; 6.6; 4.8    | 4.6           |
| 2290 m (a) | 4.1              | 4.3           |

possibly due to complexation with organic ligands. Therefore, Chelex Cu values are not reported. The samples were analyzed by DPASV approximately 2 years after collection.

Figures 2—4 demonstrate excellent agreement between the methods. However, a simple and straightforward statistical comparison is not possible because the vertical profile data are unbalanced (there are an uneven number

TABLE VI  
 VERTEX-I intercomparison for copper

| Sample     | DPASV      | Org. Ext./GFAAS |
|------------|------------|-----------------|
| 25 m (a)   | 68         | 69              |
| (b)        | 68; 68     | 68; 60          |
| 50 m (a)   | 75; 102    | 76              |
| 75 m (b)   | 90; 80; 85 | 79              |
| 100 m (a)  | 85; 72     | 89              |
| 150 m (b)  | 83         | —               |
| 250 m (a)  | 104        | 98              |
| 500 m (a)  | 136        | 137             |
| 1000 m (d) | 102; 146   | 118; 111        |
| 1500 m (b) | 157        | 156             |
| 2000 m (b) | 175        | 196             |
| 2290 m (b) | 195        | 190; 205        |

of replicates for each depth and in some cases, data are missing). To test for significant differences between analytical methods, the General Linear Models (GLM) package in the Statistical Applications Software (SAS version 82.3) was used. For cadmium, analysis of variance yields a significant difference between methods ( $F = 4.59, P < 0.03$ ). A Student–Newman–Keuls test indicates that org. ext./GFAAS is not significantly different from DPASV results ( $P > 0.05$ ), while Chelex/GFAAS results differ significantly ( $P < 0.05$ ) from the other two methods. The average magnitude of this difference is small ( $< 5\%$ ), but suggests that the Chelex method may give slightly and systematically lower results. However, by deletion of a single low Chelex value (for the 2290-m sample) no significant difference between methods for Cd is obtained ( $F = 2.96, P > 0.05$ ). If the Chelex value at 2290 m is treated as anomalous then the three methods yield indistinguishable results. The excellent agreement between methods in the upper portion of the profile supports this treatment (see Fig. 2). Finally, analysis of variance showed no significant difference between Pb values (Table V) obtained by DPASV and Chelex/GFAAS ( $F = 0.49, P > 0.49$ ), or Cu values (Table VI) obtained by DPASV and org. ext./GFAAS ( $F < 0.001, P > 0.94$ ).

## DISCUSSION

These intercomparison studies clearly demonstrate excellent agreement between DPASV and GFAAS methods of analysis over a wide range of metal concentrations in seawater. Unfortunately, there is no “absolute” seawater reference standard with which to rigorously determine the accuracy of the methods. Even the values assigned to the Canadian seawater reference material, NASS-1, can only be treated as approximate, for they are based upon multilaboratory blind analyses of individual aliquots drawn from a

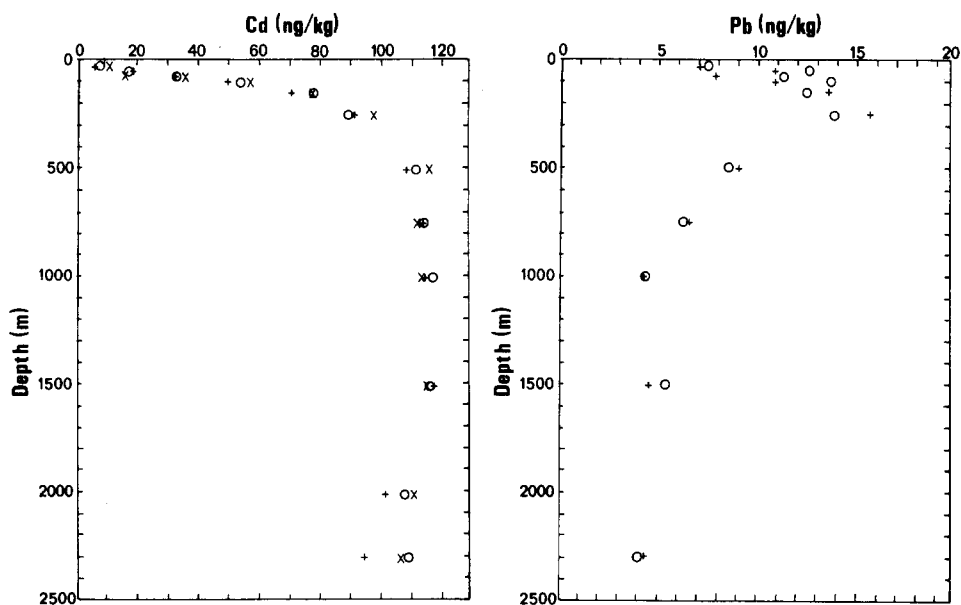


Fig. 2. Cd depth profile from the VERTEX-I station (24 August to 9 September 1980,  $36^{\circ}36'N$ ,  $123^{\circ}48'W$ ). (○) Analysis by DPASV; (×) analysis by org. ext./GFAAS; (+) analysis by Chelex/GFAAS.

Fig. 3. Lead depth profile from the VERTEX-I station (see coordinates, Fig. 2). (○) Analysis by DPASV; (+) analysis by Chelex/GFAAS.

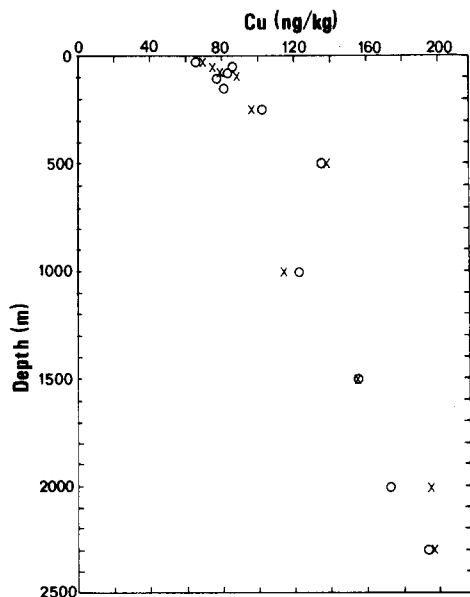


Fig. 4. Copper depth profile from the VERTEX-I station (see coordinates, Fig. 2). (○) Analysis by DPASV; (×) analysis by org. ext./GFAAS.

TABLE VII

Detection limits ( $\text{ng kg}^{-1}$ )

| Element | Org. Ext./<br>GFAAS <sup>a</sup> | Chelex/<br>GFAAS <sup>a</sup> | DPASV <sup>a</sup> | Range in<br>seawater <sup>b</sup> | Average seawater<br>concentration <sup>b</sup> |
|---------|----------------------------------|-------------------------------|--------------------|-----------------------------------|--|
| Cadmium | 0.02                             | 0.02                          | 0.1                | 0.1–120                           | 78   |
| Lead    | 5                                | 1.2                           | 1                  | 1–40                              | 2  |
| Copper  | 6                                | —                             | 10                 | 30–400                            | 250  |

<sup>a</sup>This study, GFAAS detection limits based upon 2S of blank determinations, DPASV detection limits based upon  $S/N = 2$  for 15 min deposition. DPASV detection limits can be further lowered by increasing plating times.

<sup>b</sup>Bruland (1983).

single sample. The errors established for the “accepted” values of NASS-1 range between 10 and 16%. The DPASV and GFAAS results are within these limits and agree to  $\pm 15\%$ .

An alternative approach to address the accuracy of the DPASV method is to compare DPASV results with those obtained using GFAAS methods from the VERTEX-I profiles (Figs. 2–4). The VERTEX-I station is an excellent region to make such a comparison because the metal profiles are typical of the eastern North Pacific and display vertical distributions which are “oceanographically consistent” with other hydrographic parameters and those processes known to control the distributions of these elements. Moreover, other investigations conducted in this oceanographic regime provide additional concentration and distribution information for Cu (Boyle et al., 1977; Bruland et al., 1979; Bruland, 1980; Boyle and Husted, 1983), Cd (Boyle et al., 1976; Martin et al., 1976; Bruland et al., 1978; Bruland, 1980; Boyle and Husted, 1983), and Pb (Schaule and Patterson, 1981, 1983) with which to compare our findings for this region. Because DPASV and GFAAS results did not differ significantly and were consistent with previous studies by other investigators in the same oceanographic regime, this lends strong support to the accuracy of both methods.

These data also suggest that seawater samples, stored acidified in acid-cleaned conventional polyethylene bottles (triple bagged) at room temperature, maintain their integrity (for dissolved Cd, Pb and Cu) for at least 2 years. Samples processed immediately at sea using Chelex 100/GFAAS procedures yield values which are indistinguishable from those processed 6 months to 1 year later by solvent extraction/GFAAS and with those analyzed 1 to 3 years later by DPASV. The stored and acidified samples gave similar results for Cd and Pb, whether they were UV oxidized or not. However, the precision for the determination of Cu by DPASV was improved by UV oxidation prior to analysis, especially in the case of the North Sea samples.

Presented in Table VII are detection limits for the org. ext./GFAAS,

Chelex/GFAAS and DPASV methods. Also presented are the ranges and average concentrations for these metals in seawater. Both the GFAAS and DPASV techniques show adequate sensitivity for Cd and Cu. However, deep Pacific Pb values are at or near the detection limits of these techniques.

## CONCLUSIONS

Results from this study enable us to make the following general conclusions.

(1) When DPASV and GFAAS methods are employed in accordance with the procedures described in this study, both approaches yield indistinguishable results for the analysis of total dissolved Cd, Cu and Pb in seawater.

(2) DPASV and GFAAS results show excellent agreement with accepted values on available reference materials (NASS-1) and are oceanographically consistent with results from other studies in the same water masses.

(3) Detection limits for the methods are comparable, however, DPASV exhibits a greater sensitivity for Pb.

(4) Seawater samples, stored acidified in the manner described, maintain their integrity for total dissolved Cd, Cu and Pb for at least two years.

(5) Due to the high sensitivity, low blanks, and the relative rapidity with which an analysis can be performed, DPASV is well suited to real-time, shipboard analysis.

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