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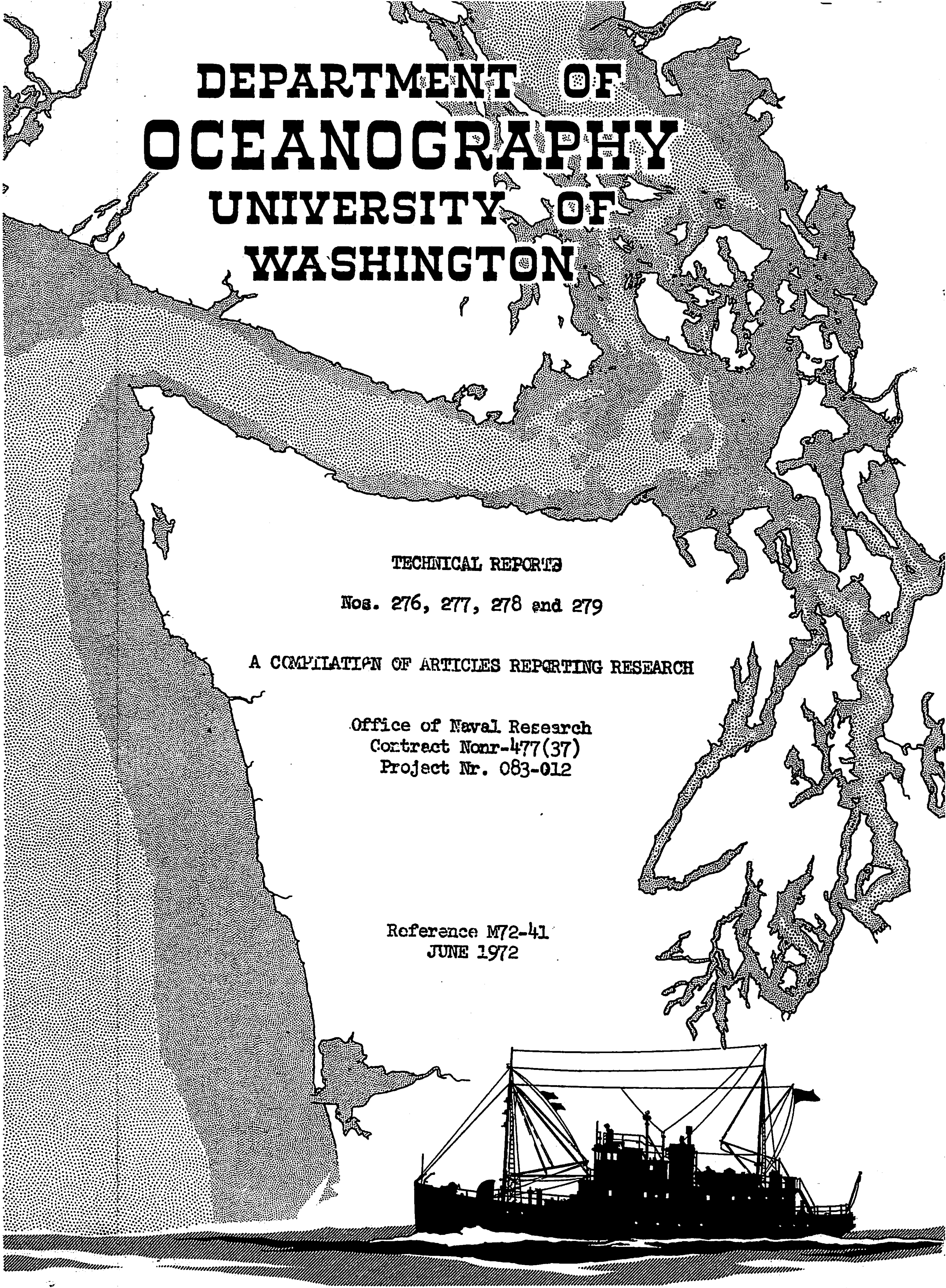

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Technical Reports

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FRANCIS A. RICHARDS
Principal Investigator

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Technical Report No. 276

LATE QUATERNARY TECTONICS, NORTHERN END OF JUAN DE FUCA RIDGE (NORTHEAST PACIFIC), by Dean A. McManus, Mark L. Holmes, Bobb Carson and Sandra M. Barr. Marine Geology, 12: 141-164. 1972

Technical Report No. 277

A GYROCOMPASS FOR MEASUREMENT OF CORE ORIENTATION AND CORE BEHAVIOR, by Douglas R. Morrison and Bobb Carson. Deep-Sea Research, 18: 935-939. 1971.

Technical Report No. 278

VOLTAMMETRIC MEASUREMENT OF ZINC IN THE NORTHEASTERN TROPICAL PACIFIC OCEAN, by Alberto Zirino and Michael L. Healy. Limnology and Oceanography, 16(5): 773-778. 1971.

Technical Report No. 279

PH-CONTROLLED DIFFERENTIAL VOLTAMMETRY OF CERTAIN TRACE TRANSITION ELEMENTS IN NATURAL WATERS, by Alberto Zirino and Michael L. Healy. Environmental Science & Technology, 6(3): 243-249. 1972.

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pH-Controlled Differential Voltammetry of Certain Trace Transition Elements in Natural Waters

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pH-Controlled Differential Voltammetry of Certain Trace Transition Elements in Natural Waters

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■ The technique of anodic stripping voltammetry has been made applicable to the direct analysis of Zn, Cd, Pb, and Cu in natural waters. The state and concentration of these ions were studied in the parts-per-billion range in fresh, saline, and artificial media. The sensitivity of conventional stripping analysis has been enhanced by opposing two hanging mercury drop electrodes; this differential approach eliminates the large background current and allows maximum signal amplification.

Advantage to the direct analysis of trace metals in natural waters include the elimination of reagents and preconcentration steps. Anodic stripping voltammetry (ASV) is well suited for analysis of metal ions such as Zn, Cd, Pb, and Cu, which form amalgams on mercury electrodes. The method is highly sensitive, requires few or no reagents, and major ions such as the alkaline earths do not interfere. The process has been described by Shain (1963) and Nickelly and Cooke (1957).

Several workers have applied ASV to the analysis of natural waters. Ariel and Eisner (1963) and Ariel et al. (1964) used ASV to analyze Dead Sea brine. They determined Zn, Cd, and Cu by using the hanging mercury drop electrode (HMDE) described by Ross et al. (1956). Macchi (1965) used a synchronized dropping mercury electrode with long dropping times to measure the ionic zinc content of a Mediterranean Sea water sample. Matson et al. (1965) developed a composite mercury graphite electrode (CMGE), and Matson determined the Pb content of various natural waters other than open ocean water (Matson, 1968). Recently, Whitnack and Sasselli (1969) determined Zn, Pb, Cd, and Cu in seawater samples by single electrode anodic stripping voltammetry and discussed some of the problems encountered in the determinations.

This paper describes a method which was developed primarily for open ocean water but has general applicability. Even with conventional strip chart recorders it is highly sensitive, incorporates a simple, noncontaminating technique for controlling the pH, and has been used successfully at sea for several months. Increased sensitivity has been achieved by opposing two hanging mercury drop electrodes in the same cell, thus eliminating the large residual current. The cancellation of both the residual currents and to some extent the hydrogen reduction current allows high amplification of the signal from the plated trace metals, making possible slow voltage scans and improved resolution. This approach is differential and varies from that of Martin and Shain (1958) because both electrodes are immersed in the same solution.

The determination of metals in natural waters can be highly dependent on pH (Fukai and Huynh-Ngoc, 1968; Duursma and Sevenhuysen, 1966). Treating samples for pH studies generally involves the purification of an acid and subsequent titration of the water sample, a procedure that risks contamination and is cumbersome in the field. In our work, the pH of the sample is controlled by replacing the usual inert purging gas with a mixture of CO_2 and N_2. By varying the ratios of the gases, the pH can be controlled over a range of three or four units.

The scope of this paper is to present a routine method for the determination of ionic and labile Zn, Cd, Pb, and Cu in natural waters under a given set of experimental conditions. In open ocean water, with a 5-min plating cycle, the sensitivity is $0.005 \mu M$ for Zn and $0.001 \mu M$ for Pb, Cd, and Cu. However, the Cu determination is qualitative in seawater. All four metals were determined quantitatively in distilled water with approximately the same detection limit as in seawater. For freshwater samples, the dissolved carbonic acid acts as the supporting electrolyte, thus the addition of foreign salts is eliminated. Nonroutine experiments become necessary to obtain information about chelation, ion pairing, and total metal content in organic rich or polluted waters. These experiments are described by Matson (1968) and are beyond the scope of this work.

Experimental

The basic console, designed by Enke and Baxter (1964), is constructed with chopper-stabilized operational amplifiers and is marketed by the Heath Co. as the Controlled Potential Polarography System. The differential display is achieved by connecting the second working electrode to the input of an additional variable gain inverting operational amplifier with a gain of −1. The output of the added amplifier is coupled in parallel with the conventional cell circuitry to the summing point of the cell-current amplifier in the analyzer (Figure 1).

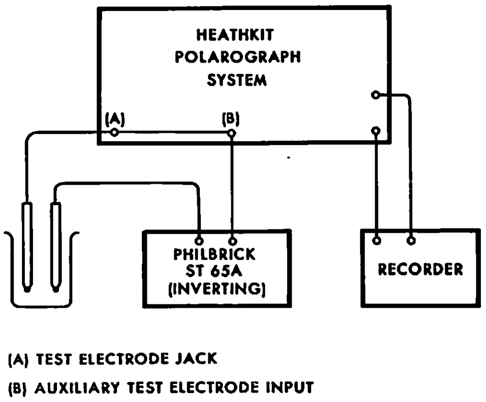

Figure 1. Schematic diagram of the assembly for differential anodic stripping voltammetry

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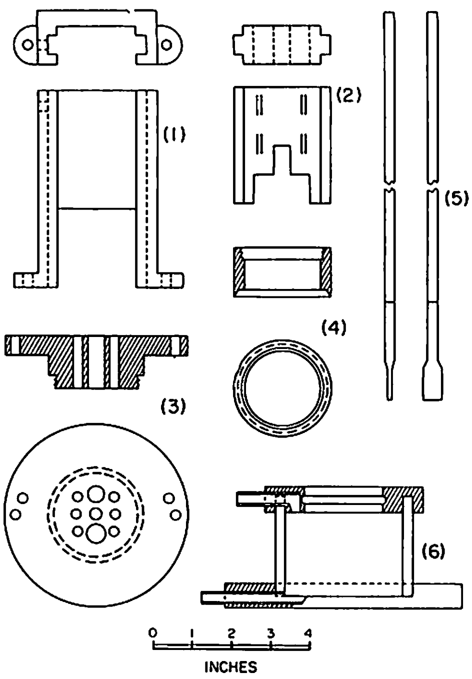

Figure 2. Diagram of the cell assembly parts

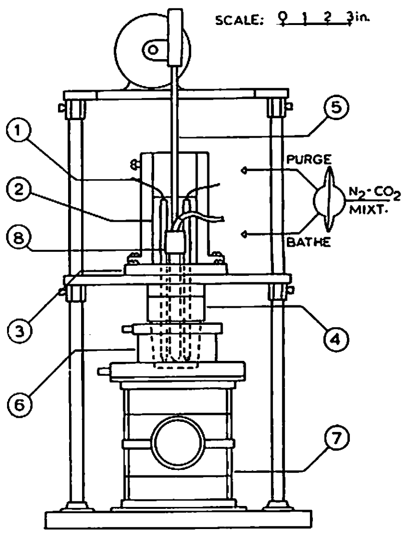

Figure 3. Installed cell assembly

The inverting amplifier is a Philbrick SP 65A chopper-stabilized solid-state unit. Circuit design and details have been given by Healy and Chapo (1969).

The first working electrode is active during the plating stage. The second working electrode is active only during the stripping cycle and its signal is opposite in polarity from the first. With matched electrodes, the summation of these two signals results in cancellation of nearly all residual currents, and only the current resulting from metal oxidation passes.

Apparatus

The electrolysis cell is installed in framework of four Flexaframe (*R*) rods. Its seven principal parts, described below, are shown in Figures 2 and 3.

Electrode Slide and Support Assembly (1, 2). The two pieces are machined from polyvinyl chloride (PVC). The electrodes are attached to the slide by means of electrical fuse clips and the entire assembly is fastened to the cell cover by 0.6-cm ($^1/_4$-in.) nylon bolts.

Cell Cover (3). Since the electrodes must be placed symmetrically, the machined PVC cell cover has nine openings placed to give two planes of symmetry across the center. The central opening is for the stirrer shaft. The two holes lateral of center permit the electrodes to be raised or lowered and also act as vents. The large hole forward of the shaft opening seats the reference electrode (SCE) without binding to permit its removal during standard additions. The anode chamber, a hollow PVC cylinder, fits into the opening behind the shaft. A thin plug of porous polyethylene (Bel-Art Products) is fitted in the lower end of the chamber to decrease the exchange of solution between the chamber and the rest of the cell.

The two openings on the sides of the reference seat accommodate short glass tubes. Since no stirring is required during the stripping cycle, gas flows through these tubes above the solution. The two holes on each side of the anode chamber seat two longer glass tubes that permit passage of gas during the purging stage. Construction of the ends limits the size of the bubbles.

Plexiglass (*R*) Cylinder (4). This piece is threaded at one end to screw into the cell cover while the other end is recessed to fit the 50-ml Teflon beaker (Cole-Palmer Instruments Co.)

Paddle Stirrer (5). The paddle section of machined PVC screws into a threaded stainless steel shaft. The paddle-shaft connection is well above the level of the solution. The paddle shaft is attached with Tygon tubing to the slow shaft of a variable-speed laboratory mixer (Gerald K. Heller Co.) and turned at about 200 rpm.

Water Jacket (6). The water jacket is machined from Plexiglas (*R*) and incorporates the Teflon beaker for maximum heat conduction. An "O" ring provides a water-tight seal between the beaker and the jacket. The water jacket rests on a laboratory jack (7).

Hanging Mercury Drop Electrode. The HMDE's are constructed by sealing 0.4-mm platinum wire in 4-mm flint glass tubing. The platinum-glass surface is sanded flat with 120 emery paper and polished with 240 emery paper. The platinum cross section is plated for about 15 min with mercury from a saturated $Hg(NO_3)_2$ solution using a 1.50-V dry cell as current source. The freshly plated surface readily takes up one or two mercury drops from a DME. Although the DME of a Polarotron Polarographic Analyzer (Leeds and Northrup Co.) was used, a conventional DME would be suitable. The electrodes need to be plated about once a day and are sanded with 240 emery paper just before electrolysis. The preparation of these electrodes is simpler than the procedure recommended by Ross et al. (1956) and can be done conveniently in the field. Although the HMDE's are not as sensitive as the CMGE, they can be consistently duplicated as matched pairs for the differential application.

To transfer the Hg drops, a small glass ladle was constructed from the conical end of a centrifuge tube. The ladle is filled with water, and the mercury drops are exposed to air as little as possible during the transfer from Polarotron to electrolysis cell.

Platinum Anode. Platinum wire (3.8 cm long) is imbedded in 4-mm flint glass tubing, leaving about 2.5 cm exposed. The wire is wound into a small coil, and the assembly is submerged in the anode chamber. Liquid from each sample automatically flows through the porous plug into the anode chamber to provide electrolyte.

Reagents and Solution. MERCURIC NITRATE. A concentrated solution of mercuric nitrate is prepared by placing an excess of triple-distilled mercury in concentrated nitric acid. Distilled deionized water is then added. This solution has a pH of approximately 1.

NITRIC ACID ($8N$). Concentrated reagent grade HNO_3 (Baker and Adamson, 70.0–71.0%) is diluted with an equal amount of deionized water.

DEIONIZED WATER. Distilled water is passed through a mixed-bed ion exchanger (Illinois Water Treatment Co.).

ARTIFICIAL SEAWATER. This is prepared according to the recipe of Sverdrup et al. (1942), with the omission of SrCl.

Nitrogen and Carbon Dioxide. The flow of gas from the respective cylinders was controlled by needle valves and rotometers. To prevent contamination of the sample, mixing was effected in a coil. Although the gases were not water-saturated, evaporation of the sample during an analysis was found to be negligible. Nitrogen purging for extended periods can strip CO_2 from seawater samples and cause pH changes. To reduce such changes a large seawater trap can be installed between the tank and flowmeter. However, care should be taken not to contaminate the sample with condensed water vapor from the trap.

Standard Stock Solutions. Standard solutions of $5 \times 10^{-3}M$ Zn, Cd, and Cu are prepared by dissolving the appropriate amount of the pure metal in 3 ml of concd HNO_3 and diluting to 1 liter with deionized water. A Pb stock solution of the same concentration was made from reagent grade $Pb(NO_3)_2$. Portions of these solutions were diluted as required to $5 \times 10^{-6}M$ for standard addition.

Cell Design

The cell (Figure 3) was designed with three objectives: geometrical stability, facility of sample handling, and reduction of contamination.

It has been shown by Macchi (1965) that fixed cell geometry is essential for reproducible measurements. Although all elements of the electrolysis cell are in fixed positions relative to one another, the electrodes can be moved in and out of solution (sometimes necessary to remove gas bubbles from the Hg drops) without changing the geometry of the cell. Electrodes can also be removed from the solution and drops can be changed without exposing the cell contents to the atmosphere.

Stirring is from above to eliminate the variations in magnetic stirring caused by irregularities in the bottom of the cell. This makes possible the use of commercial 50-ml Teflon beakers. In addition, the sample can be replaced in the beaker without handling a stirring bar. Warming of the sample by a magnetic stirring motor is avoided.

Plastics are used whenever possible to reduce metal contamination. Because purging causes samples of seawater to froth, the sample occupies only the lower half of the Teflon beaker, preventing the liquid from climbing above the beaker-Plexiglas ring joint and eliminating the scavenging of dust from the cell cover, a major source of contamination. When samples are changed or after replacement of the Hg drops, the surfaces in the cell are rinsed first with deionized distilled water and then with the sample. Contamination is minimized by limiting sample and equipment handling between runs.

Sampling

Seawater samples were collected in PVC oceanographic sampling bottles and, when possible, were transferred immediately to the 50-ml Teflon beaker for analysis. Samples that could not be run within a few hours were stored and frozen in 500-ml polyethylene screw-cap bottles. These bottles were previously rinsed once with $8N$ nitric acid and four times with the water sample.

Procedure

The following controls are set before an analysis is carried out: (1) Preelectrolysis potential and voltage scan rate are selected on the instrument. (As the parts-per-billion level, a scan of 0.5 V/min combined sufficient sensitivity with maximum peak resolution.) (2) Instrument selector switch is placed on "standby." (3) Both HMDE's are turned off. (4) The recorder pen is nulled in the middle of the chart paper.

A complete run is carried out as follows: New Hg drops are placed on the electrodes and the beaker is filled to the 25-ml calibration mark with the sample. The gas valve is turned to purge and the stirring motor is activated. The sample is purged for 5 min or longer, then both electrodes are turned on and the selector switch is placed on "cell." The voltage scan is initiated and allowed to progress to 0 V vs. SCE, at which point the selector switch is returned to "standby" and the scan is turned off. This procedure cleans the Hg drops of any sur-

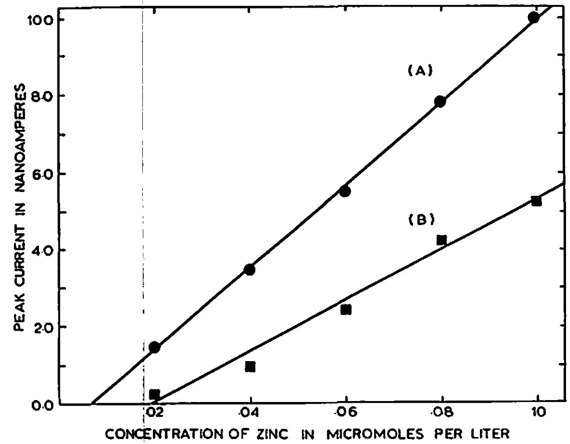

Figure 4. Calibration curve for zinc in seawater

Curve (A), pH = 5.8; curve (B), pH = 8.3; voltage scan rate, 0.5 V/min

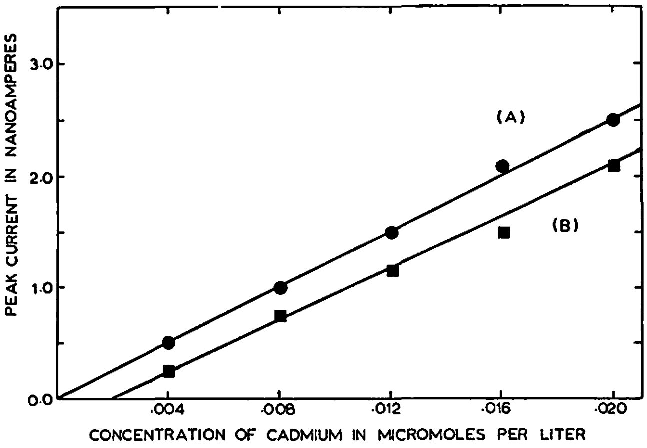

Figure 5. Calibration curve for cadmium in seawater

Curve (A), pH = 5.8; curve (B), pH = 8.3; voltage scan rate, 0.5 V/min

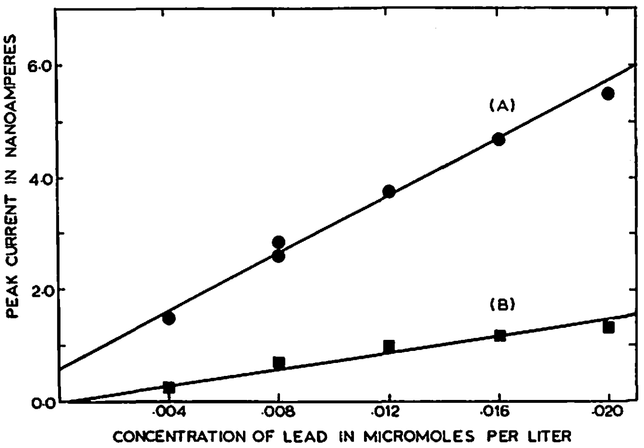

Figure 6. Calibration curve for lead in seawater

Curve (*A*), pH = 5.8; curve (*B*), pH = 8.3; voltage scan rate, 0.5 V/min

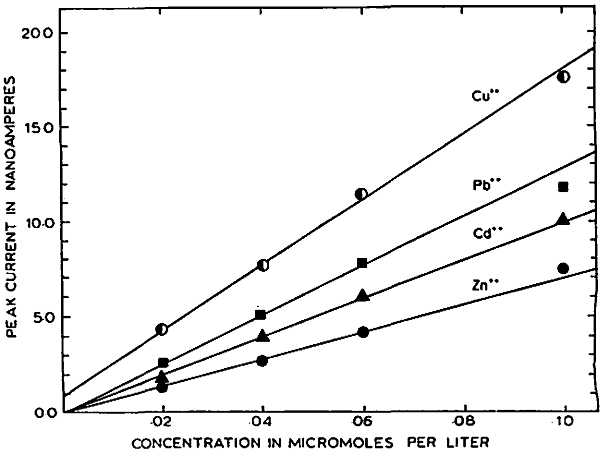

Figure 7. Standard curves in dilute carbonic acid–distilled water solution, pH = 4.4; voltage scan rate 0.5 V/min

face coatings that may have developed during purging. The differential electrode is now switched off. Purging and stirring are continued for an additional 2 min to homogenize the ion distribution in the sample.

Electrolysis is initiated by placing the selector on "cell," and a preset potential is applied to the first working electrode. Plating is continued for an accurately timed, desired period, usually 300 sec. On completion of the electrolysis, the gas valve is turned to bathe, the stirrer is turned off, the differential electrode is turned on, and the recorder selector switch is placed on "pen." While the solution comes to rest, the sensitivity control of the instrument is turned to the desired value, and the cell current is nulled by manipulating the feedback control on the differential amplifier. The procedure requires at least 60 sec, after which time the voltage scan and the recorder are turned on simultaneously and the cell current is recorded. The instrument is allowed to scan through 0 V vs. SCE and is then returned to "standby." The recorder and differential electrode are turned off, purging gas and stirrer are turned on, and the entire process can be repeated if desired. For standard addition, the calomel electrode is removed, standard solution is introduced into the sample with a microburet, and the calomel electrode is replaced. The standard is allowed to mix in the solution, and the procedure is repeated.

Peak currents are obtained by drawing an appropriate base line under the current-voltage curves and measuring the distance from the base line to the inflection point of the peak ($di/dv = 0$). From the peak height of the sample and sample plus standard, the concentration is calculated by direct proportion. For greater precision, or as a check on linearity and the presence of strong complexing agents, standard addition may be repeated.

Results

Standards. To establish linearity between peak current and concentration, standard curves for Zn, Cd, and Pb in seawater were run at pH 5.8 and 8.3 (Figures 4–6), the lower pH being produced by purging with the CO_2–N_2 gas mixture. Standard additions were made by adding to the 25-ml sample 0.100-ml volumes of a solution $5.00 \times 10^{-6}M$ in Zn and Cu and $1.00 \times 10^{-6}M$ in Cd and Pb. A standard curve was also developed for a dilute carbonic acid–distilled water solution of pH 4.4 (Figure 7). Each standard addition increased the concentration of the solution by 0.02 μM/l. in Zn, Cd, Pb, and Cu.

Precision. Unfiltered seawater samples were analyzed for Zn aboard the University of Washington research vessel *Thomas G. Thompson*. Replicate analyses (4 each) at Zn concentrations of 5.9, 4.7, and 2.7 μg/l. produced an almost constant standard deviation of 0.7 μg/l. At the 1 μg/l. level, the coefficient of variation (σ/μ) was estimated to be 50% (Zirino and Healy, 1971).

A bucket sample was collected off the Washington coast and analyzed for Pb and Cd. The Pb content was 0.9 μg/l. (σ = 0.3 μg/l.) and the Cd content was 0.4 μg/l. (σ = 0.1 μg/l.). These values should be taken as a measure of precision only.

Repeated plating and stripping analysis in a closed cell produced highly reproducible Zn peak currents. Standard additions also performed with a closed cell produced calibration curves of much greater precision than would be expected from the analytical error observed from the replicate analyses (Figures 4–6). Thus, the large analytical error may be introduced during the transfer of samples into the cell. It may be caused by incomplete flushing of the cell (Whitnack and Sasselli, 1969) between analyses.

Peak Height vs. Plating Time. Peak height was proportional to plating time for an indefinite period. Zn, Cd, and Pb were plated out of a 0.5*N* NaCl solution (0.044μM in Zn and 0.0088μM in Cd and Pb) for periods of up to 2 hr (Figures 8 and 9). The Pb curve in Figure 9 shows a small positive deviation from linearity owing to contamination from the SCE. The insert illustrates the increase in Pb peak current of a seawater sample with storage time in the cell. The amount of contamination, 2.9×10^{-9} g Pb/15 min, is consistent with impurity and leakage rate specifications supplied by the manufacturer of the SCE. By use of a mercury pool electrode, this source of contamination can be reduced by electroplating the Pb in the saturated KCl reference electrolyte.

Analyses of some natural water samples by standard addition are shown in Tables II and III. The freshwater samples were collected in clean 500-ml polyethylene containers held several inches below the water surface. Eastern Pacific seawater samples were collected and analyzed on Cruise 34 of RV *Thomas G. Thompson* during January 1968.

Discussion

Sorption. At the 0.01 and 0.001μM levels, sorption must be reckoned with during analysis. Robertson (1968) has shown that it is nearly impossible to find materials totally free of trace metals. However, the rates at which trace metals are transferred from material surfaces to the sample can be con-

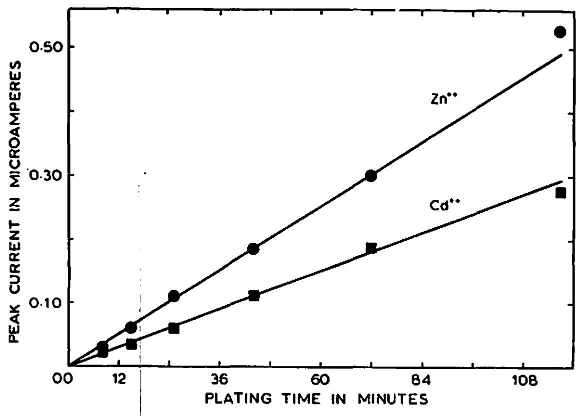

Figure 8. Increases in peak height vs. plating time for Zn^{2+} and Cd^{2+} in 0.5*N* NaCl solutions

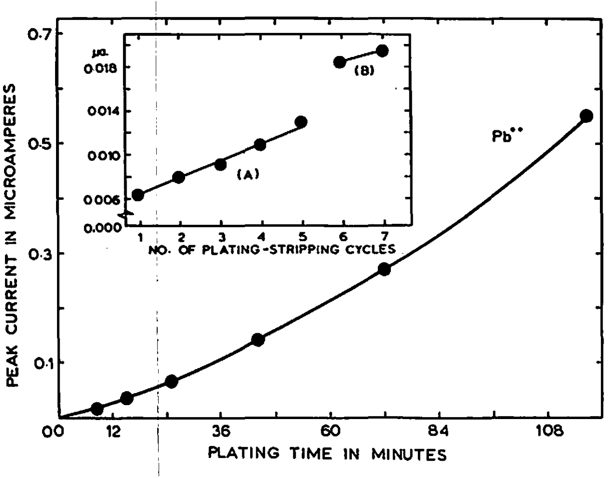

Figure 9. Increases in peak height vs. plating time for Pb^{2+} in 0.5*N* NaCl solutions

Insert: Increase in peak height with successive cycles of plating and stripping the same sample

trolled. We have tried to limit the amount of trace metals gained or lost by sorption by equilibrating the sample with all surfaces with which it comes in contact.

Before analysis, all containers (polyethylene storage bottles, Teflon beakers, cell parts, etc.) are rinsed with dilute nitric acid, followed by deionized water, to remove contaminants and to reduce the problem to one of adsorption. Therefore, all surfaces are equilibrated with subsamples of the sample for extended periods (hr); these subsamples are then discarded. Since exchange of the trace metal from the surface to the sample is pH-controlled, the container walls should be rinsed at approximately the pH used in the final analysis. Drastic changes of pH between samples will lead to a desorption error. Although these steps are time-consuming, it is generally necessary to perform them only once for a particular sample locality. If the concentration range of the samples to be analyzed covers less than a factor of 10, repeated acid cleaning is not necessary. Open ocean samples have a narrow concentration range, and it is not necessary to equilibrate each sample with the cell environment.

Generally, newly machined cell parts should be acid-cleaned and equilibrated with the medium for periods of days. After several days, contamination from the cell components becomes negligible, as can be verified by storing deionized water in the cell for an extended period. If the cell parts are well equilibrated with the medium, adsorption becomes negligible. In a 5-hr experiment, Alexander and Corcoran (1967) found that aged PVC bottles removed no copper from seawater.

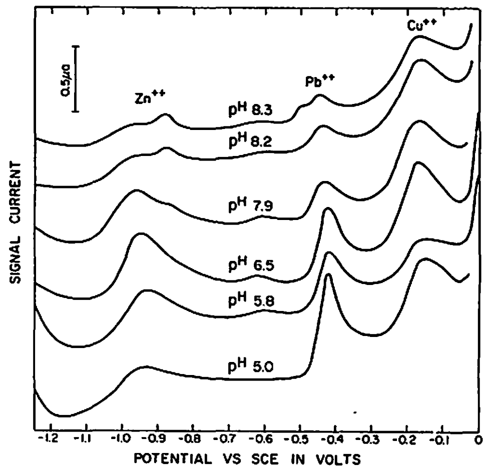

Figure 10. Current-voltage traces at various pH values of metal contaminants remaining in purified artificial seawater

Zinc adsorption peak at −0.87 V vs. SCE

Influence of pH. In seawater, Zn and Pb calibration curves produced at pH 5.8 have greater slopes than those produced at pH 8.3 (Figures 4 and 6), presumably because these metals combine with weak acid anions to form inert complexes. The increase in peak current at the lower pH is accompanied by an anodic shift in peak potential of approximately 30 mV. Cu also appears to be complexed by these agents, but the latter effect is more difficult to determine because, in seawater at the 1 μg/l. level, it is usually difficult to resolve the Cu peak from the Hg dissolution peak. Open ocean samples that were analyzed produced higher Zn peaks at the lower pH, providing additional evidence that pH-dependent complexes occur in seawater. Pb and Cu were generally undetectable unless the acidity of the sample was increased.

The pH dependence of metals in artificial seawater was studied in the laboratory (Figure 10). The artificial seawater showed no absorbance at 260 mμ on the Beckman DK spectrophotometer, indicating that little organic matter was present. Peaks are due to metals that have remained in solution after purification by precipitation (Joyner et al., 1967). The acidity was changed by using various ratios of CO_2 and N_2. The Cu and Zn stripping current reached a maximum value at a pH of about 6 and became small at pH 8. The Pb peak current appeared to be directly proportional to the acidity of the solution. The decrease of Zn and Cu peak currents at low pH values may indicate some interference from carbonic acid. In the more basic solutions, a small, symmetrical peak appeared at a potential approximately 100 mV less negative than the main Zn peak (Figure 10). This is attributed to the adsorption of $ZnCO_3^0$ or $Zn(OH)_2^0$ or a mixed Zn hydroxycarbonate on the electrode as the Zn(Hg) amalgam is oxidized. Adsorption on stationary electrodes has been studied by Wopshall and Shain (1967). The pH dependence of the stripping currents of Zn, Pb, and Cd in seawater has been studied by Zirino and Healy (1970) and Zirino and Yamamoto (1971). In seawater, the increased concentration of carbonic acid does not appear to affect the determination if the pH is not lowered below 5.6. The major effect of adding CO_2 is to decrease the concentration of CO_3^{2-}, thus any complexation with that species would be reduced. Complexing of the metals by the

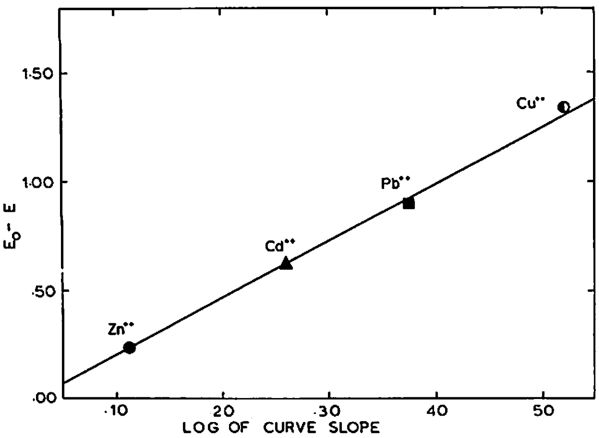

Figure 11. Difference in applied potential and standard potential vs. log of the slope of calibration curves in Figure 7

various species of carbonic acid in distilled water has not been studied but does not appear to interfere with the analysis.

Identification of Peaks. Peaks in the current-voltage trace can be identified tentatively by the potentials at which they appear. Both the peak potential E_p, and the potential at half-peak height, $E_{p/2}$, have been used (Macchi, 1965; Ariel and Eisner, 1963). In a seawater–carbonic acid medium with a pH of 5.8, the peak potentials agree closely with polarographic half-wave potentials ($E_{1/2}$) measured in dilute KCl, which can be used as a guide. Although two metals may have the same stripping potentials in natural media (Ariel and Eisner, 1963) this does not present a great problem for most seawater samples. Despite the great variety of trace metals present, few of those present in measurable amounts have peak potentials between 0 and 1.25 V vs. SCE (Table I).

Interferences. The electrodeposition of Zn from seawater appears to be free of interferences. Macchi (1965) has verified that at an initial plating potential of −1.3 V, small quantities (less than 20 times the concn of Zn) of Co, Ni, Mn, Cr, Fe, and Al do not interfere with its determination. At pH 5.6, $10^{-6}M$ Ni(II) and Fe(III) do not affect the peak current from 10^{-7} Zn. However, at pH 8.1, both metals suppress this current, presumably by adsorption of Zn on Ni and Fe hydroxides.

The reaction Sn(0) → Sn(II) may interfere with the determination of Pb in seawater. Spikes of $SnCl_2$ are not resolvable from Pb over the interval of pH 5.6 to pH 6. Above pH 6, the Sn peak is greatly suppressed, but the Pb determination is not very sensitive. The addition of a suspension of Sn(IV) to seawater at pH 5.6 produced no peaks but slightly broadened the peak current from $10^{-7}M$ Zn.

Table I. Characteristic Stripping Peak Potential

(E_p in volts vs. SCE)

Metal	$E_{1/2}$[a]	SW, pH 5.8	DW, pH 4.4
Zn	−0.995	−0.98	−0.93
Cd	−0.599	−0.63	−0.53
Pb	−0.396	−0.43	−0.35
Sn(II)	−0.47[b]	−0.43	not obsd
Cu	+0.02[b]	−0.15	+0.07

[a] Kolthoff and Lingane (1941).
[b] 0.1N HCl.
[c] 0.1N KNO_3.

Addition of $SnCl_2$ to distilled water at pH 4.4 does not produce a peak. Unlike seawater, complexation with chloride does not occur to retard hydrolysis and colloid formation.

The formation of intermetallic compounds of Zn and other metals present in seawater may reduce the Zn peak current (Shain, 1963). However, because Zn is considerably more concentrated in seawater than other metals which may interact, such interference is probably small and should not affect analysis by standard addition. Freshwater samples are less similar than seawater samples, and each body of water must be examined individually.

Interaction between Zn, Cd, Pb, and Cu at the 0.01μM concentration level is negligible as indicated by the results in Figure 11. A linear relationship exists between the mantissa of the logarithm of the slopes of the calibration curves in Figure 7 and the difference between the applied potential (E = −1.25 V) and the standard potential (E^0) of each metal as predicted by the Nernst equation. Therefore, barring kinetic effects, the system is most sensitive for Cu and least sensitive for Zn.

Measurements of Natural Waters. If thermodynamic equilibrium between the added standard and the sample is assumed, the method described herein should measure all of the metal present in solution as the hydrated ion or as a labile complex. For natural samples analyzed at low pH values, the measured concentration includes those metallic ions which might be desorbed from particulate surfaces by the increase in the hydrogen ion concentration. The assumption of equilibrium was tested for seawater by spiking a freshly collected surface sample from San Francisco Bay with enough Zn, Cd, and Pb to increase the concentration of the sample to 0.03μM in Zn and 0.006μM in Cd and Pb. The peak currents

Table II. Comparison of Zinc Data from Eastern North Pacific

Slowey (1966)			Zirino and Healy (1970a)		
Position	Zinc, meter	Zinc, μg/l.	Position	Depth, meter	Zinc, μg/l.
30° 27′N			08° 41.0′N		
122° 02′W	10	4.5	83° 24.1′W	0	4.3
	300	4.3		20	0.5
	600	5.6		50	2.4
	1000	3.3		80	2.6
	2000	3.3		200	1.0
	3500	1.6			
			08° 58.0′N		
30° 19′W			85° 57.4′W	0	1.1
124° 03′W	10	4.0		20	ND[a]
	400	1.7		50	3.2
	750	1.4		300	0.4
	1500	1.4		1000	ND[a]
	2800	4.4		3000	1.2
30° 36′W			10° 18.0′N		
123° 55′W	10	3.3	86° 48.0′W	500	2.6
	400	1.7		1000	0.7
	750	1.2		3000	1.4
	1000	1.0		3400	0.8
	1500	1.2		4000	1.3
	2800	0.5		4800	0.8

[a] Not detectable at 0.2-μg/l. level.

Table III. Trace Metal Data from Natural Waters—High Altitude Lakes and Rivers

	Zn		Cd		Pb		Cu	
	Concn, µg/l.	E_p, V	Concn, µg/l.	E_p, V	Concn, µg/l.	E_p, V	Concn, µg/l.	E_p, V
Trinity River, Shasta-Trinity Natl. Forest, Calif.[a]	0.3	−0.955	0.2	−0.555	2.5	−0.370	2.2	+0.07
Sulphur Springs, Kittitas County, Wash.	3.2	−0.933	added	−0.525	1.8	−0.340	[b]	[b]
Park Lake, Kittitas County, Wash.[c]	4.3	−0.945	1.0	−0.525	1.0	−0.325	0.2	+0.070
Rachel Lake, Kittitas County, Wash.	0.4	−0.950	0.2	−0.550	<0.2	−0.350	0.6	+0.070
Roosevelt Lake, Okanogan County, Wash.	1.6	−0.935	0.3	−0.530	1.6	−0.350	1.3	+0.090

[a] Unidentified peak at −0.170.
[b] Not possible to determine because of a −0.25-V shift in the mercury dissolution.
[c] Unidentified peak at −0.165.

of the three metals showed no decrease with time when measured at intervals over a 1-hr period.

The presence of ligands which form inert complexes with a substantial fraction of the metals to be measured leads to peak currents which cannot be directly interpreted as concentrations by single spike methods. Matson (1968) has made a detailed study of the effects of natural ligand systems on trace metal peak currents obtained with the CGME. The principles discussed in that work are also applicable to differential voltammetry with the HMDE.

Although a direct comparison between the results obtained by voltammetry and other methods has not been made, in Table II, Zn data obtained by the differential voltammetric analysis of unfiltered water samples from the eastern tropical Pacific Ocean (Zirino and Healy, 1971) may be compared to the Zn values obtained for the northeast Pacific by neutron activation after oxidation of the seawater samples with a peroxidisulfuric–sulfuric acid mixture (Slowey, 1966).

The data in Table III present values obtained from samples collected from relatively uncontaminated fresh water from high-altitude lakes and rivers. The values were obtained by the single spike technique, with CO_2–H_2CO_3 as the supporting electrolyte. They agree well with the values of Durum et al. (1960) for waters from similar sources. Although there are only a few distinct variations in concentration levels, the potential shifts indicate there exist characteristic complexing agents at each locality. The influence of these agents would be an interesting subject for future study.

Conclusions

Differential anodic stripping voltammetry is a useful tool for the study of certain trace metals in natural waters. The increased sensitivity gained by the differential electrode method permits the use of slow-voltage scan rates and produces clear current peaks above a low, level background. The electrodes are almost insensitive to ship's motion and the technique is useful in the field. The addition of CO_2 to the purging gas provides both pH control and electrolyte so that determinations can be made on both saline and fresh samples without other reagent addition. Increasing the acidity of the sample decreases adsorption of metals on surfaces and for Zn, Cu, and Pb, enhances the peak current by reducing complexation of these metals with weak acid anions.

The use of pH-controlled DASV with short plating times is a sensitive, nondestructive technique. Because the activity of the metal ions in the sample is controlled by the nature of the medium, there are many possibilities for examining the trace metal environment in the hydrosphere.

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The technique of anodic stripping voltammetry has been made applicable to the direct analysis of Zn, Cd, Pb, and Cu in natural waters. The state and concentration of these ions were studied in the parts-per-billion range in fresh, saline, and artificial media. The sensitivity of conventional stripping analysis has been enhanced by opposing two hanging mercury drop electrodes; this differential approach eliminates the large background current and allows maximum signal amplification.

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