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TRACE METAL CHARACTERIZATION IN AQUATIC ENVIRONMENTS BY ANODIC STRIPPING VOLTAMMETRY

H. E. Allen, W. R. Matson, and K. H. Mancy

Generally it is accepted that trace metals such as Cu, Zn, Cd, Co, Cr, Ni, and Mo play a significant role in biologically mediated reactions in the aquatic environment. In trace quantities many of these metal ions are essential micronutrients for enzymatic transformations, but in high concentrations they may be inhibitory or toxic to biological systems. The controlling role of metal ions on the ecological balance and productivity of fresh waters has been emphasized by several authors (1) (2) (3) (4). For example, molybdenum, considered an essential micronutrient for nitrogen fixation and the formation of the plant enzyme nitrate reductase, controls the primary productivity of Castle Lake, Calif. (1).

The trace metals in the aquatic environment also may serve as "markers" in the identification of water masses. The distribution and relative abundance of metal ions may offer valuable information on the geochemical history and pollutional characteristics of natural waters. The exchange of metal ions between the hydrosphere and the biosphere, lithosphere, and atmosphere must be considered in studying metals in natural waters. Therefore, trace-metal analysis is important in most water pollution characterization programs.

The availability of a trace metal to a biological system depends on the oxidation state, degree of hydration, and organic complexation of the metal ion. Shapiro (4) emphasized this point in his studies on the availability of iron as an algal nutrient, when he showed that the availability of iron to the biological system depends on the degree of complexation of iron with yellow organic acids extracted from lake water. He concluded that in biological systems it is important to differentiate between the analytical concentration of metal ions in solution and the metal ions available to the biota.

Trace metals in the aquatic environment are frequently in the part-per-billion range or lower (10^{-8}–$10^{-10}M$), which places them below the sensitivity limit of most analytical procedures. (A summary of the sensitivity limits of various analytical procedures is given in Table I.) Except by activation analysis and anodic stripping voltammetry, direct determinations of metal ions cannot be made without concentrating the water samples. Sample pretreatment, i.e., separation or concentration by various procedures, usually modifies the physicochemical characteristics of the species under investigation.

Although activation analysis offers the high sensitivity required for trace-metal analysis, its use is limited by the availability of reactor facilities; furthermore, it is an elemental analysis procedure that offers no information

H. E. Allen, W. R. Matson, and K. H. Mancy are, respectively, Chemist, Bureau of Commercial Fisheries, U. S. Department of the Interior, Assistant Professor, and Associate Professor, Department of Environmental Health, School of Public Health, University of Michigan, Ann Arbor, Mich.

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TABLE I.—Sensitivity of Some Analytical Methods for the Determination of Trace Metals

Method of Analysis	Sensitivity
Molecular absorption spectrophotometry	10^{-5}–$10^{-8}M$
Molecular fluorescence spectrophotometry	10^{-7}–$10^{-8}M$
Atomic absorption spectrophotometry	10^{-6}–$10^{-7}M$
Atomic fluorescence spectrophotometry	10^{-7}–$10^{-8}M$
Optical and emission spectroscopy	10^{-5}–$10^{-6}M$
Neutron activation analysis	10^{-9}–$10^{-10}M$
Potentiometry with metal specific glass or membrane electrodes	10^{-4}–$10^{-5}M$
Classical polarography	10^{-5}–$10^{-6}M$
Derivative polarography	10^{-6}–$10^{-7}M$
Square-wave and linear-sweep voltammetry	10^{-7}–$10^{-8}M$
Anodic stripping voltammetry with hanging mercury drop electrodes	10^{-7}–$10^{-9}M$
Anodic stripping voltammetry with thin film or solid electrodes	10^{-9}–$10^{-10}M$

about oxidation state or degree and type of complexation.

Perhaps the best method for trace-metal characterization is anodic stripping voltammetry, which potentially is capable of performing *in situ* analysis of free and complexed metal ions in natural waters. Stripping voltammetry, in general, consists of a deposition step in which the desired component is deposited cathodically or anodically as a solid or an amalgam, and a stripping step (reverse electrolysis) in which the components are determined.

Theory

Ordinarily, the deposition step is performed at controlled potential in a uniformly stirred solution. The deposition under reproducible stirring conditions follows the first order kinetic expression:

$$Q_t = Q_o(1 - e^{-kt}) \quad \ldots\ldots 1$$

where Q_t = number of coulombs in the stripping peak at any time, Q_o = number of coulombs equivalent to the total metal ion in the sample solution, t = deposition time (sec), and k = rate constant. The rate constant, k, is equal to:

$$k = \frac{DA}{V\delta} \quad \ldots\ldots 2$$

where: D = diffusion constant of electroactive species in the test solution, sq cm/sec, A = electrode surface area, sq cm, V = volume of the solution, cu cm, and δ = effective thickness of diffusion layer (cm).

Ordinarily partial deposition of a sample is sufficient for analysis. Under conditions where the rate constant is not reproducible for different samples, extension of the plating increases the accuracy of the determination. With a long deposition time, the expression e^{-kt} approaches zero; therefore slight changes in k which may occur between analyses under adverse working conditions, e.g., on board research vessels, have little effect on the precision of the results. The deposition step can be arranged to segregate the species present as well as deposit a reproducible fraction of the sample.

Quantitative determination of the deposited materials is made in the stripping step, most commonly by a chronoamperometric technique with a linear potential sweep. Commercial polarographic equipment employing operational amplifiers may be used for slow potential sweep rates, in the order of 2 to 100 mv/sec. A characteristic stripping curve is shown in Figure 1. When the proper electrode is used under controlled conditions, the concentration of metals in solution is linearly proportional to the peak current, and qualitative identification of the metal ions in solution is obtained from peak potential values (5). These relationships for a hanging mercury drop electrode (HMDE) are approxi-

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mated by the Randles-Sevcik equation (6):

$$i_p = [K z^{3/2} A D^{1/2} \nu^{1/2}] C_o \quad \ldots\ldots 3$$

where: i_p = peak current for a given geometry and plating time, amp, z = number of electrons involved in the electrochemical step, ν = rate of voltage scan, v/sec, and C_o = concentration of metal in the sample.

The concentration of metal in the sample also may be determined coulometrically. The peak potential, E_p, is related to the polarographic half-wave potential, $E_{1/2}$, by

$$E_p = E_{1/2} - 1.1RT/zF \quad \ldots\ldots 4$$

where F = Faraday. This means that E_p will occur at a potential, $0.028/z$ volt more cathodic than $E_{1/2}$ at 25°C.

Electrode Types

Three main types of electrodes have been used in stripping analysis: HMDE's of the Kemula (7) and Gerischer (8) types, solid metal electrodes (9), and mercury thin-film electrodes (10) (11).

The HMDE's offer high overvoltage for hydrogen evolution, and usually insure a constant activity in the metal deposited in the amalgam. Because of their thickness, however, the deposited metal must diffuse out of the mercury during the stripping step; this diffusion results in broadened peaks. Solid electrodes are rugged and have a greater anodic range than HMDE's, but their surfaces are difficult to reproduce and the formation of mixed activity deposits limits their use in complex systems. Because the problems of diffusion in the mercury are negligible in thin-film mercury electrodes, sensitivity and resolution are increased, and the hydrogen overvoltage is comparable to that for the HMDE. However, the mercury film may sag on metal amalgam electrodes, and the formation of bimetallic association

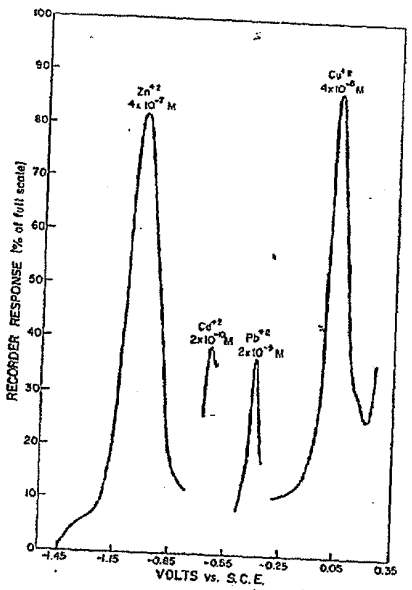

FIGURE 1.—Anodic stripping voltammagram showing the sensitivity and range of the method. Full-scale ranges were 100 μa (Zn^{+2}), 2 μa (Cd^{+2}), 5 μa (Pb^{+2}), and 20 μa (Cu^{+2}).

compounds, e.g., Ni-Zn or Co-Zn, is enhanced.

The working electrode used in the present study was a composite mercury-graphite electrode (CMGE), which is composed of small droplets of mercury electroplated on a graphite surface impregnated with paraffin. The graphite serves as an inert support and the dispersed mercury is more durable than a mercury film on metal. This electrode system offers high sensitivity and reproducibility, and a ruggedness that makes it very suitable for field work.

Roe and Toni (10) derived and tested the anodic stripping equation for a mercury-film electrode in a stirred solution. Within the limits of their approximation the authors proved that at constant stirring rate with a known deposition time (t_d) the peak current is directly proportional

to the metal ion concentration in solution,

$$i_p = \left[zFAl\frac{\phi}{e}\nu \right] C_R \ldots\ldots 5$$

where l is the thickness of the mercury film, ϕ is equal to zF/RT, and e is the base of Napierian logarithms. The peak current is directly proportional to the potential scan rate; in this characteristic the electrode differs from the HMDE, in which the peak current depends on $\nu^{1/2}$, as shown in Equation 3. The peak potential equation for the mercury-film electrode was given as follows (10):

$$E_p = E^\circ + \frac{e}{\phi}\log\frac{\delta l\nu\phi}{D} \ldots\ldots 6$$

where E° is the standard electrode potential (which is equal to $E_{1/2}$ in many systems) and δ is the thickness of a boundary diffusion layer at the solution-electrode interface. In contrast to that in Equation 4, the peak potential depends on the logarithm of the scan rate. Experimental variation in δ and l will have little effect on E_p, which generally is cathodic to E°.

Qualitative and quantitative information on free and combined metal ions and metal-binding ligands and their distribution can be gained by varying the sample pretreatment and the anodic stripping procedures. A flow chart showing various analytical procedures is given in Figure 2. Total metal content can be determined by digestion of the sample before anodic stripping analysis, and filtration separates dissolved from particulate fractions on the basis of variations in particle size.

Complexation

Metal ions in natural waters may be complexed with simple inorganic ligands such as water, halides, carbonate, and sulfate, or they may be tied up with complex organic ligands such as amino acids, organic acids, vitamins, porphyrins, humic acids, and tannins. It is possible to exchange the metal in many complexes by additions of acid (H^+) or metal cations; the freed metal ions subsequently may be determined by anodic stripping voltammetry (Figure 2).

The metal-complexing ability of natural waters, which is a measurable

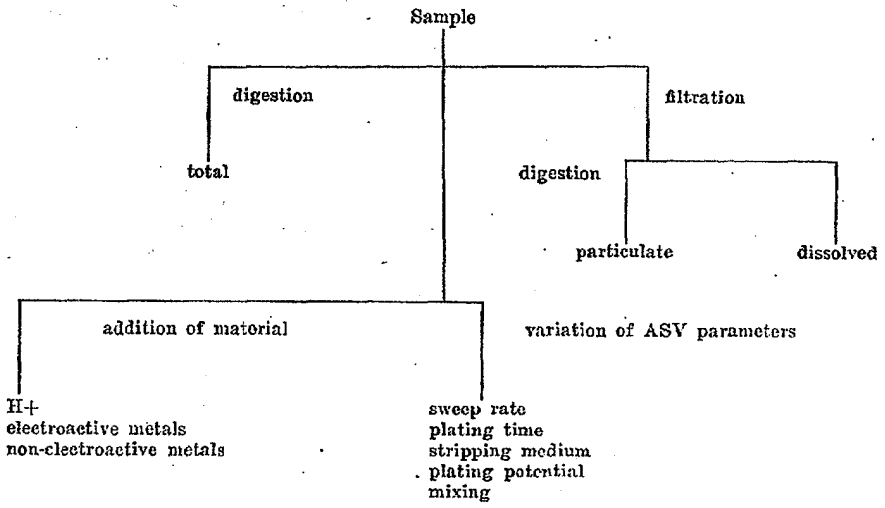

FIGURE 2.—Possible variations in procedures for anodic stripping voltammetric determination of metal ions in natural waters.

characteristic, depends on the type and concentration of simple or complex ligands. Quantitative and qualitative information on metal-binding ligands can be obtained by a complexometric titration procedure in which an electroactive metal ion is used as the titrant. In this technique the stepwise metal-ligand complex formation can be followed and the stoichiometric end points can be detected by anodic stripping. Similarly, the rates of metal-ligand dissociation on titration with a strong acid can be determined.

The analytical feasibility of anodic stripping voltammetry can be extended greatly by varying the deposition time, the potential sweep rate, the stripping medium, and the mixing regime. These variations can be used to advantage to characterize free and complexed metal ions in the aqueous environment.

Experimental Design

The anodic stripping voltammetric cell and electrodes used in the present study are shown in Figure 3. The CMGE was prepared by the electrodeposition of mercury (with vigorous stirring) at −400 mv vs. Ag/AgCl, onto spectrographic grade graphite electrodes impregnated with paraffin (11). A platinum counter electrode and a Ag/AgCl reference electrode were in electrolytic contact with the test solution through leached Vycor* plugs. The cell was a 3- × 1-in. (7.62- × 2.54-cm) quartz vial with a Teflon plug for support of the electrodes. A Teflon tube with a platinum wire insert for rigidity was used to bubble nitrogen for deaeration and mixing of the test solution.

A previously described multiple anodic stripping unit (12), with Heath operational amplifier modules, was used to provide the necessary voltammetric deposition and stripping modes

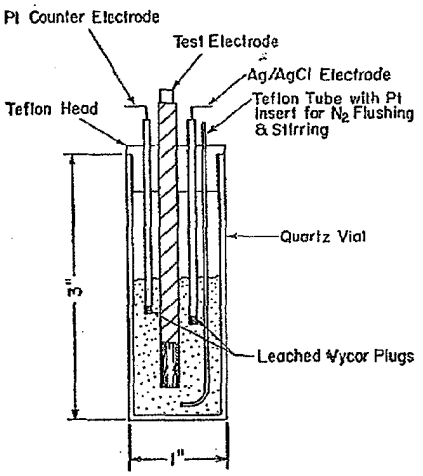

FIGURE 3.—Anodic stripping voltammetric cell. (In. × 2.54 = cm.)

for simultaneous use of eight anodic stripping cells. Each CMGE had an effective area of about 1.3 sq cm and a half-time for deposition of 15 min for a 10-ml sample. By using similar electrode and cell designs a sensitivity of 10^{-10} M (0.02 ppb) for lead can be achieved with a linear anodic sweep of 20 mv/sec (5) (11). A typical stripping curve for Zn, Cd, Pb, and Cu in a lake-water sample based on the use of a CMGE is shown in Figure 1.

Analysis for Trace Metals

The analytical feasibility of anodic stripping voltammetry has been illustrated by the analysis of a number of lake- and river-water samples for their free and complexed (acid-exchangeable) metal content. Samples were collected at the surface from the lower Rouge and Detroit Rivers, at the surface and bottom (15 m) from the central basin of Lake Erie 10 miles (16 km) northeast of Sandusky, Ohio; and at 10 m from Lake Michigan near Waukegan, Ill., and Ludington, Mich. The samples were refrigerated and brought to the laboratory for analysis. The water samples were analyzed before and 30 min after acidi-

* Mention of products and manufacturers is for identification only and does not imply endorsement by the Bureau of Commercial Fisheries.

TABLE II.—Trace Metal Concentrations in Various Natural and Waste-Waters Determined by Anodic Stripping Voltammetry

Sample	Location	Concentration (μg/l)				
		Free			Acid Exchangeable	
		Cd	Pb	Cu	Pb	Cu
1	Rouge River 0.5 mile (0.8 km) above Ford Motor Co. turning basin	<0.1	1.1	2	15	27
2	Rouge River turning basin	7.4	2.2	14	37	108
3	Rouge River mouth	1.5	0.4	8	11	19
4	Detroit River, Trenton Channel	0.8	0.4	18	5	28
5	Detroit River, Livingston Channel	1.9	0.4	11	6	29
6	Lake Erie, central basin, surface water	—	—	—	1.8	6.8
7	Lake Erie, central basin, bottom water	0.3	0.07	0.5	1.6	1.8
8	Lake Michigan, Waukegan, Ill.	1.0	0.2	0.8	3.3	19
9	Lake Michigan, Ludington, Mich.	—	—	—	0.6	0.4

fication to pH 2 with perchloric acid, at a plating time of 15 min. Although detailed analysis of so few data is not possible, some inferences may be drawn from the results (Table II). Free and acid-exchangeable metals were much higher in the Rouge River below the point of introduction of industrial wastes (sample 2) than above (sample 1). Concentrations of acid-exchangeable metals were lower at the mouth of the Rouge River (sample 3) than above most of the pollutional sources. This low concentration may be due to the presence in the river of large amounts of ferric hydroxide, which act as scavengers for trace metal ions. It was to be expected that large quantities of trace metals would be lost quickly to bottom deposits by such precipitation mechanisms.

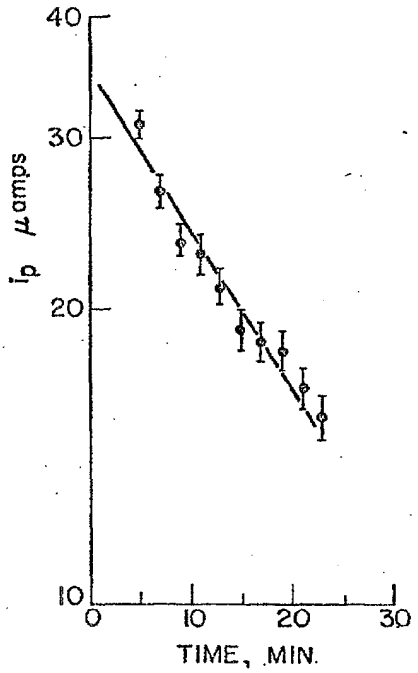

FIGURE 4.—Decrease of cupric ion added to Rouge River water (0.13 μg Cu^{+2} added to a 10-ml sample).

The difference in acid-exchangeable copper in Lake Erie between the surface (sample 6, 6.8 ppb) and bottom (sample 7, 1.8 ppb) may be due to the concentration of copper by phytoplankton in the surface water or the removal of copper from the bottom of the analyses of sample 9, from the relatively pure water in northern Lake Michigan, and sample 8, collected near Waukegan, Ill., were dramatically different. Acid-exchangeable copper and lead were about 50- and 5-fold waters by the sediments. The results higher, respectively, in the sample collected from the southern portion of the lake.

ration (μg/l)

	Acid Exchangeable	
Cu	Pb	Cu
2	15	27
14	37	108
8	11	19
18	5	28
11	6	29
—	1.8	6.8
0.5	1.6	1.8
0.8	3.3	19
—	0.6	0.4

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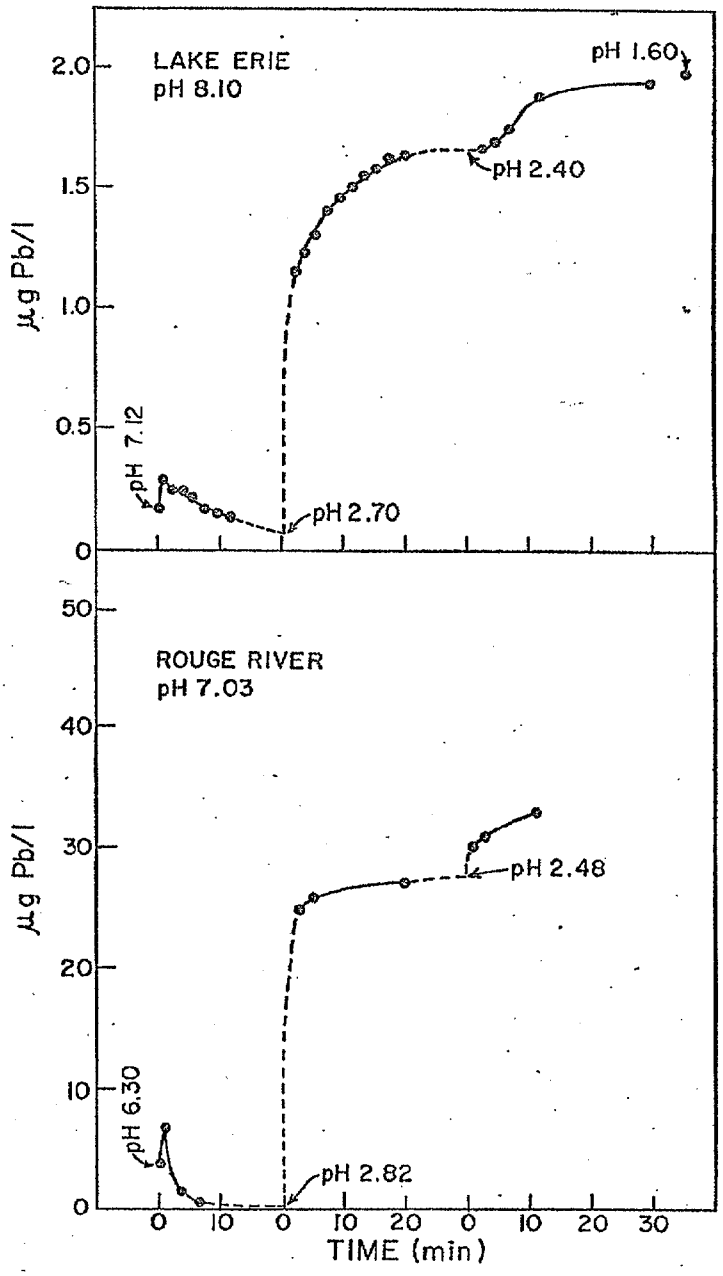

FIGURE 5.—Release of lead in water from Lake Erie and the Rouge River after the addition of acid.

Characterization of Complexes

Anodic stripping voltammetry is extremely useful for the study of kinetics of complexation reactions. Figure 4 shows the reduction of free copper in a sample after 0.13 μg of Cu^{+2} was added to a 10-ml sample of Rouge River water containing excess ligand. This sample was collected near an outfall of a Detroit wastewater treatment plant. Analyses were performed at 2-min intervals at plating times of 1 min. The complexation of copper followed first-order kinetics with a rate constant of 0.031/min. The rate constant for the complexation of a metal with naturally present ligands or the ratio of two rate constants would be extremely useful in the characterization of ligand types present in natural waters.

The acid exchange rates for lead in water samples from the Rouge River and from Lake Erie are shown in Figure 5. The Rouge River sample had an initial pH of 7.30 and contained 1.3 mg Fe/l. Upon acidification of the sample to a pH of 6.30, the lead signal rapidly increased and then slowly decreased. The changes in the lead concentration were attributed to dissolution of a portion of the ferric hydroxide followed by its reformation, which exerted a slow scavanging action on the lead. The newly formed ferric hydroxide had a scavening efficiency greater than that of ferric hydroxide originally present, possibly because a locally high acid concentration caused dissolution of ferric hydroxide, followed by a reestablishment of equilibrium.

Further additions of acid were accompanied by a rapid release of lead at pH 2.82 and pH 2.48. Perturbation of the system by acid additions yielded an instantaneous release of the trace metal, followed by slow acid exchange rates. Such transient responses to acid additions are characteristics of the metal-binding ability of a given water sample.

The release of metal from the Lake Erie surface sample was much slower and was characteristic of exchange of metal from a more stable complex. Only an extremely small amount of lead was released by acidification when the pH of Lake Erie water was changed from 2.40 to 1.60. This increase was due almost exclusively to lead in the acid—most of the lead in complexes would have been exchanged by pH 2.40. This amount of acid was used to acidify the water samples from Rouge River, Lake Erie, and other samples listed in Table II.

Titration of a ligand excess of natural or pollutional origin also can be done by additions of spikes of various metal ions such as Zn, Cu, In, Bi, Pb, and Tl (13). The rates of complex formation or complex exchange with specific metal ions can be used as diagnostic criteria for the identification of labile and nonlabile complex compounds.

Conclusion

Anodic stripping voltammetry is a valuable analytical procedure highly applicable to the characterization of metals in the aquatic environment. The technique extends the detection limits far below the sensitivity of other analytical procedures and permits the analysis of trace metals in natural waters without prior concentration. Because of its freedom from reagent contamination and its ability to distinguish between complexed and free metal ions, the method is considered very useful in studying the role of trace metals in biologically mediated reactions in aquatic ecosystems. The speed and selectivity of anodic stripping voltammetry facilitate the study of the metal-binding ability by ligands of natural or pollutional origin.

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