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MICROPROCESSOR-CONTROLLED ANODIC STRIPPING VOLTAMMETER FOR TRACE METAL ANALYSIS IN TAP WATER

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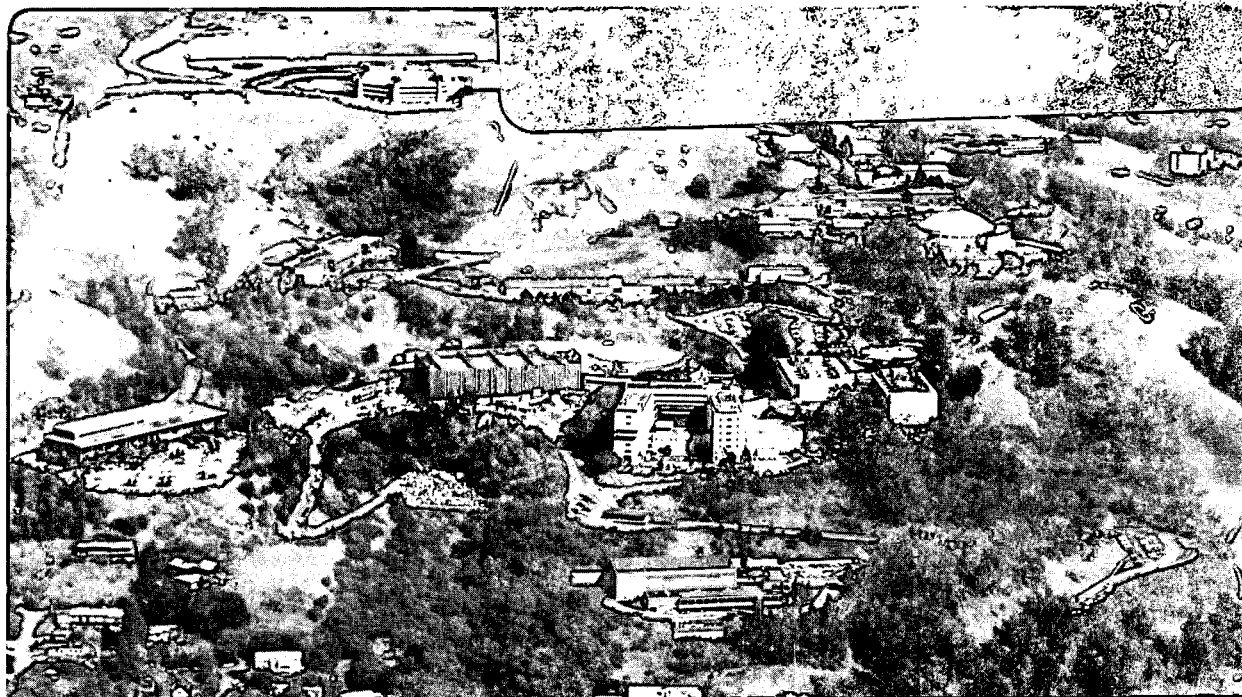
Engineering & Technical Services Division

MICROPROCESSOR-CONTROLLED ANODIC STRIPPING
VOLTAMMETER FOR TRACE METAL ANALYSIS
IN TAP WATER

R.G. Clem, F.W. Park, F.A. Kirsten, S.L. Phillips,
and E.P. Binnall

June 1984

DISCLAIMER

MICROPROCESSOR-CONTROLLED ANODIC STRIPPING VOLTAMMETER
FOR TRACE METAL ANALYSIS IN TAP WATER

by

R.G. Clem, F.W. Park, F.A. Kirsten, S.L. Phillips
and E.P. Binnall

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Contract No. EPA-790-X-0507

Project Officer

Marvin C. Gardels
Drinking Water Research Division
Cincinnati, Ohio 45268

June 1984

DISCLAIMER

FOREWORD

The Environmental Protection Agency was created because of increasing public and government concern about the dangers of pollution to the health and welfare of the American people. Noxious air, foul water, and spoiled land are tragic testimony to the deterioration of our natural environment. The complexity of that environment and the interplay between its components require a concentrated and integrated attack on the problem.

Research and development is that necessary first step in problem solution and it involves defining the problem, measuring its impact, and searching for solutions. The Municipal Environmental Research Laboratory develops new and improved technology and systems for the prevention, treatment, and management of wastewater and solid and hazardous waste pollutant discharges from municipal and community sources, for the prevention and treatment of public drinking water supplies, and to minimize the adverse economic, social, health, and aesthetic effects of pollution. This publication is one of the products of that research; a most vital communications link between the researcher and the user community.

This study evaluated the feasibility of measuring trace metals in drinking water at the user's tap with the goal to relate the concentration to any corrosive effects of water on pipes and tanks. The anodic stripping voltammeter constructed for this purpose was used to establish the idea of a portable monitoring system for selected trace metals in drinking water, and was tested in Seattle, Washington. The result of this work should provide laboratories involved in measuring the quality of drinking water with the means to determine the need for water quality control programs to minimize health effects associated with the presence of trace metals that are the products of corrosion in water distribution systems, or that are inadvertently added to the drinking water during water treatment processes.

Francis T. Mayo, Director
Municipal Environmental Research Laboratory

ABSTRACT

The construction and use of a portable, microprocessor controlled anodic stripping voltammeter for on-site simultaneous metal analysis of copper, lead and cadmium in tap water is discussed. The instrumental system is comprised of a programmable controller which permits keying in analytical parameters such as sparge time and plating time; a rotating cell for efficient oxygen removal and amalgam formation; and, data handling via a minicomputer or analog pen recorder. Plating and stripping potentials are controlled by a digital potentiostat; stripping is done using a staircase waveform with measurement of the current after a one msec delay. In this way charging current effects are minimized. Results of tap water analysis showed 3±1 µg/L lead, 22±0.3 µg/L copper, and less than 0.2 µg/L cadmium for a Berkeley, California tap water, and 1-1000 µg/L Cu, 1 -2 µg/L Pb for ten samples of Seattle, Washington tap water. Recommendations are given for a next generation instrument system.

This report was submitted in fulfillment of Contract No. EPA-790-X-0507 by the Lawrence Berkeley Laboratory under the partial sponsorship of the U.S. Environmental Protection Agency. The report covers the period from September 1976 to August 1982, and work was completed as of June 1978.

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SECTION 1

INTRODUCTION

Measurements of trace metal concentrations in drinking water are important for predicting harmful health effects on being ingested and for inferring the species likely to be present in a drinking water supply. The water resources for municipalities vary in both the type and concentration of dissolved metals; in untreated water these concentrations are generally significantly lower than the EPA Interim Primary Drinking Water Standards. However, chemicals used in water treatment contain trace metals as impurities, and may introduce these metals into the water at the treatment plant. Another potential source of metal contamination is corrosion and dissolution of metallic piping or tank interiors through which the treated waterpasses or is stored before use. Thus, there is a need to measure the concentration of dissolved metals at the user tap where the water is actually ingested (1-5).

Both electrochemical and spectroscopic methods are widely used to measure concentrations and species of metals in water (1,6,7). The method used here, anodic stripping voltammetry (ASV), offers a number of advantages including: (a) capability for simultaneous analyses of more than one metal; (b) sensitivity to concentration levels less than $1\mu g/L$; (c) portability of instrumentation; (d) identification of metal speciation at ambient concentrations; and, (e) ease of automation. The method is generally limited to metals which are soluble in mercury such as zinc, copper, tin, lead and cadmium, and which dissolve from amalgams prior to mercury dissolution (8-10).

Our central idea was to design and construct an automated ASV instrument wherein the cell, potentiostat, signal generator, data handling and display are a single system. This approach permitted optimization of many parameters such as deaeration time, staircase stripping voltage and calculation of concentrations. Thus a rapid method was developed for the simultaneous determination of Cd, Pb and Cu in drinking water at $\mu g/L$ levels. Commercially available instruments while adequate in many respects, lack one or more important features. Other instruments have separate cells and stirrers so that manual control is required. Whereas in this instrument, the cell is a portion of the system, so that cell rotation and deaeration are automatically controlled. Thin mercury films simultaneously deposited with the metals being analyzed are used here. Other instruments use hanging mercury drops which are less sensitive at equivalent plating times than thin film electrodes. This system also contains data handling to include storage of

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the stripping curves, automated calculation of the concentrations of each metal, and display of the stripping curves utilizing a built-in computer program.

This report describes the ASV instrumental system designed and constructed by the Lawrence Berkeley Laboratory. Calibration of the instrument with known metal concentrations is also discussed together with results of some analyses of tap water in Seattle, Washington and Berkeley, California. Selected background information is given on the anodic stripping electrochemistry of Cd, Pb, and Cu; the ASV method using mercury thin films plated onto graphite electrodes; ASV instrumentation electronics; and, computerized data handling using a minicomputer linked to the ASV. A photograph of the cell and microprocessor controlled digital potentiostat is shown in Fig. 1.

ANODIC STRIPPING VOLTAMMETRY AT MERCURY FILM ELECTRODES

Anodic stripping is the term applied to the analysis of µg/L quantities of mercury soluble metals such as cadmium and lead using thin films formed by depositing mercury onto carbon electrodes.

The first step involves electroplating from a solution of the sample using convective mass transfer (e.g., stirring) during which time the metals being determined are concentrated in the Hg film. This deposition step is not exhaustive (non-stoichiometric); only 2% to 3% of the total amount in the water sample may be deposited. The applied potential is sufficiently negative so that the electrodeposition rate is limited only by the rate of mass transfer of the dissolved metals from the bulk of the solution to the electrode surface.

After a set time such as 5 or 10 min., stirring is stopped and the solution becomes quiet. During this quiescent period, any concentration gradient within the Hg film is essentially eliminated because deposition is almost negligible, and the plated metals diffuse through the film from regions of high concentrations to lower concentrations. A quiescent time of 5 sec. was used here, mostly to permit the solution to become quiet.

The third step is anodic stripping of the metals from the amalgam by application of a linearly increasing positive potential (10-17). At potentials near the Nernstian value for a particular metal, the metal begins to dissolve (strip) giving rise to typically peak-shaped curves at more positive potentials. A peak is obtained for each metal; thus a current-voltage curve can consist of more than one peak. Usually, this peak height is measured and related to the metal concentration in the solution through calibration data. Peak areas have also been used as a measure of concentration.

Much instrumental research has been directed toward lowering the background current, mainly to reduce effects of the double-layer charging current. Anodic stripping using pulse polarography, or measuring the faradaic current by means of a staircase-shaped linearly increasing anodic potential (16) are two approaches. We have used the latter procedure.

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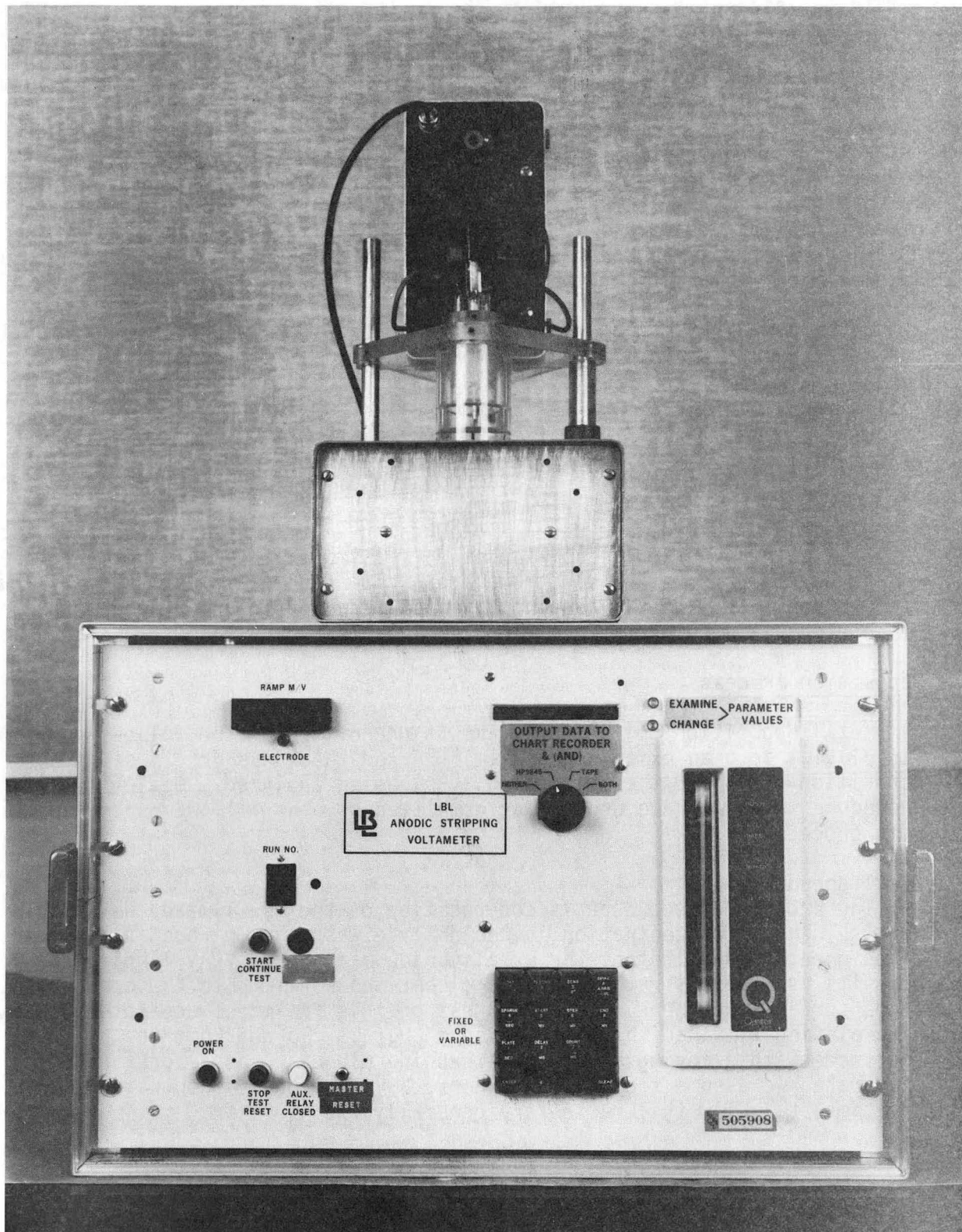
Figure 1.   Photograph of anodic stripping system.

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In the staircase procedure used here, the potential is made increasingly positive in 5 mv steps; the anodic current is measured after a 1-msec delay for each step to permit the charging current to decay so that the current is essentially faradaic. This faradaic current is measured for 400 msec before stepping to the next voltage increment.

For data handling, the digitized current-voltage curves are stored in ASV memory, then disposed to magnetic tape for permanent storage. Optionally, a digital/analog converter permits readout onto a strip-chart recorder. However, the data can also be stored on magnetic tapes or floppy disks using a Hewlett-Packard 9845 computer for subsequent machine calculation and graphic display. This is the preferred approach.

The electrolysis step involves metal plating followed by dissolution in the mercury film to form an amalgam under conditions of constant applied potential from a stirred solution. Rotating electrodes or cells (17), are also used to stir the solution. The magnitude of the potential applied by the potentiostat is sufficiently negative to cause the highest possible plating rate of the dissolved metals. Under these conditions, the concentration of metal being determined is maintained zero at the solution-film interface.

Obtaining reproducible results depends on a number of factors such as: constant stirring rate; deposition of only a small amount of the metal present in solution; constant electrode area; a plated metal flux (faradaic current) proportional to the concentration of metal in solution; and, absence of intermetallic compound formation within the mercury film.

Deposition Process

Metal deposition to form amalgams is one of two of the following options: (1) plating into an existing Hg film of fixed thickness or (2) simultaneous deposition of Hg and the metal (e.g., Pb) being analyzed. Option (2) is the procedure which we have used. For completeness, the following describes both procedures.

Simultaneous Deposition--
The procedure used here is codeposition of the Hg film and Hg-soluble metals. The Hg concentration in the analyte was usually about a thousand times greater than that of the metals being measured. Very likely the Hg deposits as droplets rather than as a continuous film onto the carbon electrode surface used here. The thickness of this "film" of droplets increases with plating time, so that deposition of Hg, Cd, Pb and Cu takes place at an electrode with a moving boundary (expanding plane). For a constant deposition rate, we assume the film thickness, ℓ, is directly proportional to plating time, t. Film thicknesses are generally 1 to 1000 nm.

The concentration gradient of metals dissolved within the Hg film is flat, or very nearly so, assuming continual deposition of an amalgam with a constant composition.

Plating Into Existing Film--
   Amalgamation using this optional procedure results in a concentration gradient within the Hg film. The gradient during plating is estimated as follows:

   The initial-boundary value problem for the film electrode may be formulated in terms of Fick's law equation for diffusion between two parallel planes (9,18).

$$\frac{\partial C_R}{\partial t} = D_R \frac{\partial^2 C_R}{\partial x^2}$$ (1)

Here, C_R is the concentration of amalgam-forming substance within the film; t is the time; D_R is the diffusion coefficient; and x is the linear distance within the electrode. For the planar mercury film electrode, the bounds on x are the solid-mercury interface defined by x = 0, and the mercury-solution interface at x = ℓ. The electrode then has a finite film thickness, ℓ.

   Initially, we assume the mercury film is free of amalgam-forming substances so that

$$t = 0, \quad 0 < x < \ell: \quad C_R = 0$$ (2)

The boundary conditions required to solve Equation 1 are:

$$t > 0, \quad x = 0: \quad D_R \left(\frac{\partial C_R}{\partial x} \right) = 0$$ (3)

$$x = \ell: \quad D_R \left(\frac{\partial C_R}{\partial x} \right) = F(t)$$ (4)

where F(t) is any function of time. For anodic stripping analysis, F(t) = F_0, a constant: F_0 is the flux of amalgam-forming metal.

   In Equation 3, we prescribe that there is no material flux at the solid-mercury interface; while at the mercury-solution interface Equation 4 relates the flux to the cathodic plating current, F(t).

   The desired concentration-distance-time relation describing the gradients within the mercury film may be obtained by application of the Laplace transform to Equations 1-4. In transform notation, the solution of the resulting ordinary differential equation is:

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$$\overline{C}_R = \frac{f(s)}{\sqrt{s\,D_R}} \left\{ \frac{\cosh\,(x\sqrt{s/D_R})}{\sinh\,(\ell\sqrt{s/D_R})} \right\} \tag{5}$$

where $f(s)$ is the Laplace transform of $F(t)$ in Equation 4. A very general solution to Equation 5 may be obtained by noting that for the constant-flux boundary condition, $F(t) = F_0$ so that $f(s) = F_0/s$. Equation 5 then becomes:

$$\overline{C}'_R = \frac{F_0}{s\sqrt{sD_R}} \left\{ \frac{\cosh\,(x\sqrt{s/D_R})}{\sinh\,(\ell\sqrt{s/D_R})} \right\} \tag{6}$$

where C'_R is the transform of the concentration when the material flux at the electrode surface is constant. The quantity C'_R may be obtained from the solution to the steady-study flux condition given in Carslaw and Jaeger (19) for the comparable heat-transfer case. In terms of electrochemical parameters, the solution is

$$C_R\,(x,t) = \frac{\ell F_0}{D_R} \left\{ \frac{D_R t}{\ell^2} + \frac{3(x/\ell)^2 - 1}{6} - \frac{2}{\pi^2} \sum_{n=1}^{\infty} \frac{(-1)^n}{n^2}\, \exp\,[-n^2\pi^2 D_R t/\ell^2]\cos[n\pi x/\ell] \right\} \tag{7}$$

Figure 2 is a plot of Equation 7 for distances within the film, $0 < (\,/\ell) < 1.0$ for values of $D_R t/\ell^2$ equal to 0.1, 0.25, 0.5, and 1.0. It is seen that each curve corresponding to various plating times has a similar shape, and reflects the increasing amalgam concentration as a function of time. At long times or for thin films Equation 7 approximates to:

$$C_R = \frac{\ell F_0}{D_R} \left[\frac{D_R t}{\ell^2} + \frac{3x^2 - \ell^2}{6\ell^2} \right] \tag{8}$$
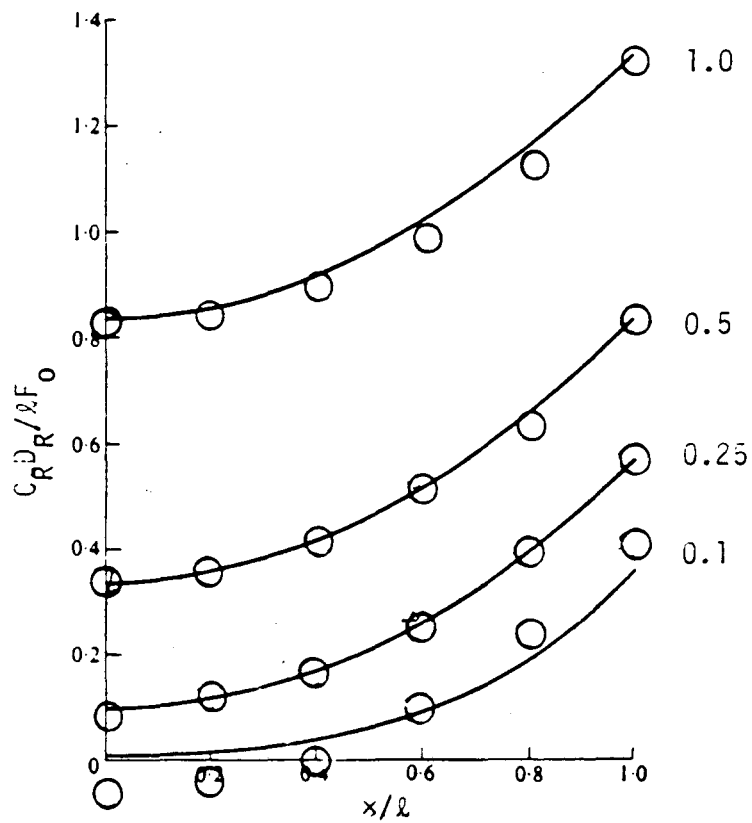
Figure 2. Concentration gradients in fixed Hg
film for constant flux (stirring).

Values of parameter Dt/ℓ^2 shown for
each curve, 0.1-1.0. Circles show
Equation 8 approximation.

Quiescent Period

Following the plating step, during which amalgam accumulates at the electrode, rocking of the cell stops. There is a 5 sec interval during which the solution becomes quiet. Stripping subsequently takes place from a mercury film now homogeneous in concentration of Cd, Pb and Cu. However, Equation 7, which holds for plating into a fixed Hg film, shows that a concentration gradient exists for the amalgamated metals. Thus, if a fixed film is used, time should be allotted to permit the film to become homogeneous in metal distribution. Otherwise stripping will take place from a film wherein the concentration changes with time. This may lead to nonreproducible results.

The concentration of metal as amalgam in a mercury film electrode is approximated by the following equation:

$$C_R = \frac{i_L t}{A \ell n F} \tag{9}$$

which is the first term in Equation 7. In Equation 9

$$
\begin{aligned}
i_L &= \text{deposition current, } \mu A \\
t &= \text{deposition time, sec} \\
A &= \text{Hg film area, } cm^2 \\
\ell &= \text{thickness of Hg film, } \mu m \\
n &= \text{number of electrons in deposition step} \\
F &= \text{Faraday (96,500 coulombs)} \\
C_R &= \text{concentration of metal in film, moles/}cm^3
\end{aligned}
$$

The deposition current, i_L, is proportional to the quantity of metal dissolved in the solution.

Anodic Stripping with Linearly Increasing Potential

In the method used here, stripping takes place from an unstirred solution, after the quiescent period, under conditions of a linearly increasing staircase anodic potential. The staircase stripping waveform is shown in Figure 3 (20). The stripping peak current is approximated by

$$i_p = 1.1157 \times 10^6 \, (2)^2 \, A C_R \, \ell \, v \tag{11}$$

where v is the rate of voltage scan. In our method using codeposition of Hg, Cd, Pb and Cu, the final voltage is +0.350 v. vs. S.C.E. so that the Hg

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0.5s.

5 mv.
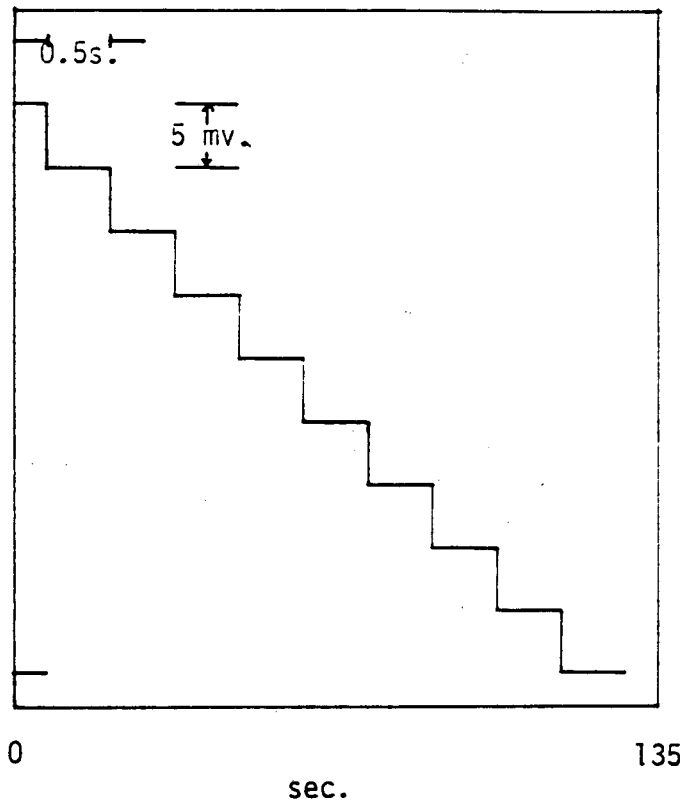
0   135
                              sec.
Figure 3. Staircase stripping voltage
              waveform. Not to scale.

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film is stripped from the carbon electrode surface. The Hg film may or may not be stripped when a pre-plated existing film is used. A more exact relation than Equation 11 might be derived using the work reported in Reference 20.

ANODIC STRIPPING ELECTROCHEMISTRY

When water quality monitoring results are reported, it is common practice to measure the total concentration of a metal. However, the importance of metal speciation in terms of bioavailability and sorption has been recognized for more than a decade (21). In addition, metal species exist that may not be measured by ASV.

The electrochemistry of Cd, Pb and Cu under anodic stripping conditions is important from the standpoint of nonreducible species, and the quantity of metal actually measured. It is well established that electroinactive complexes of these metals exist in natural waters; thus, the total concentration is higher than that determined by ASV. For example, the anodic stripping of Pb in organic-free seawater gave peak currents smaller than predicted because of the electrochemical inactivity of the $PbOH^+$ species (22). See also the analysis of tap water in Madison, WI (23).

An acetate buffer with pH 4.5 to 4.8 was selected as optimum for simultaneous determination of Cd, Pb and Cu. In this supporting electrolyte, a plating voltage of -1.0 volts ensures instantaneous deposition. Peak potentials are expected as follows: Cd, -0.65 v.; Pb, -0.45 v.; Cu. -0.3 v. See, for example, Reference 24.

In summary, ASV has been applied to measure Pb, Cu, Cd and other metals at ug/L levels in a variety of water samples. Continuous analysis using ASV has been developed; computer-controlled instrumentation is used. It must be borne in mind that not all species are electroactive and, therefore, measurable by ASV; however, electroactivity is used to determine species and lability of metal complexes at ug/L levels (10).

Reviews of applications of anodic stripping to analysis of trace metals in natural waters are published in alternate years by Analytical Chemistry (10) and yearly by the Journal of the Water Pollution Control Federation (25). The monitoring of water for a larger number of important parameters is discussed in the EPA publication "Water Quality Monitoring in Distribution Systems" (2), and in Reference 1.

SECTION 2

CONCLUSIONS AND RECOMMENDATIONS

In summary, a portable microprocessor-controlled ASV system was designed and constructed for on-site analysis of Cu, Pb, and Cd in tap water. The instrumental parameters such as sparge time and plating time are keyed into the processor, and analysis then done automatically. The ASV system was applied to the analysis of one sample of the Lawrence Berkeley Laboratory tap water, and 10 samples of tap water from Seattle, Washington.

An ASV system offers a number of advantages for on-site analysis of metals including portability, ruggedness, ease of temporary installation and data handling. In addition, this work identifies areas where the ASV can be improved for constructing a newer system.

Based on the experience gained from the tap water analysis with the instrument described in this report, a next generation ASV might include the following:

1. A cell that incorporates self-cleaning capabilities. Carbon electrodes with electro-deposited mercury films tend to age with use, and give spurious peaks as well as increased background current during the stripping step. This aging causes a loss in sensitivity, and could also result in erroneous analyses by showing peaks for metals that are not actually present in detectable amounts. Currently, cleaning is done manually by periodically rubbing the surface gently with filter paper.

2. Methods for removing large quantities of dissolved copper. Plated copper interferes in two ways: first by forming intermetallic compounds with cadmium, which reduces the anodic peak height for Cd; and, secondly by masking the lead and cadmium peaks. Large concentrations of dissolved copper (estimated at >800 µg/L) interfered in this way with measurement of Pb and Cd in the samples of Seattle water. Copper plates more easily than either Pb or Cd, so that one approach to this problem might be a preanalysis step involving deposition of Cu with a dual-working electrode system. See, for example, reference 29.

3. Methods for measuring the total concentration of dissolved metals. Metals form more than one complex in natural waters: some of these complexes are not measured by ASV. A pre-ASV step such as ozonolysis might be effective in freeing metals from electroinactive species.

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4. Programming of the ASV system so that the readout will be in μg/L of the metals being measured. Currently, the output signal is either in analog form on a strip chart recorder, or in digital form on magnetic tape; both must be further processed by manual or computer·methods (e.g., HP9845).

5. Redesign of the electrolytic cell and electrode system. The present system was developed from research and works well; however, the reference electrode requires attention to be certain the salt bridge is filled with KCl solution. A new design would be capable of automated sampling, and would have redesigned reference and working electrodes.

SECTION 3

INSTRUMENTATION SYSTEM COMPONENTS

The ASV system constructed here was designed to: automate settings for the analytical procedure; acquire data for relating peak height or area to metal concentration in standards and water samples; and, store current-voltage data for subsequent calculations. The system is comprised mainly of the following: a rotating cell containing the water sample, electrodes and inlet for the sparge gas; digital potentiostat for voltage control during plating and stepwise stripping; microprocessor controller for automating the procedure; and, a pen recorder or magnetic tape for data storage and calculation. See Fig. 4. Provision is also made for transferring measured data to an external Hewlett-Packard Model 9845B computer for subsequent analysis.

ROTATING CELL

A cylindrically-shaped rotating cell machined from Lucite is used for quick oxygen removal during the sparging step, and for a high rate of metal preconcentration during the metal deposition (Fig. 5). Only 60 seconds is required for effective oxygen removal from 15 mL of solution.

During sparging, the cell is rotated automatically in a clockwise direction for 0.9 seconds; a counter-clockwise pulse is then imparted for a duration of 0.1 seconds. The clockwise rotation is at a speed sufficient to build up by centrifugal force a film of solution on the sides of the rotating cell. In this way a large surface area is presented to the sparge gas thereby accelerating the deaeration step. During the counter-clockwise pulse, the film is partially collapsed; it then reforms with a fresh surface presented to the sparge gas. Under these conditions, the dissolved oxygen concentration is lowered sufficiently so that the background current due to oxygen reduction does not interfere with the analysis procedure. Nitrogen or argon was used for deaeration.

After sparging, the microprocessor stops the cell rotation, and the solution drains completely from the walls to the solution level of the cell because a Lucite surface is not wetted by water. Then agitation (stirring) is begun during which time amalgam is accumulated in the plating, preconcentration, step.

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ELECTRO CHEMICAL CELL

AE

RE

WE

DIGITAL POTENTIOSTAT

STIRRING MOTOR

SPARGING GAS RESERVOIR

MOTOR CONTROL

MICROCOMPUTER

START/STOP
  CELL ROTATION
  PLATING
  STRIPPING
  OXYGEN SPARGE

DELAY TIMES
DATA STORAGE

STRIP CHART RECORDER

DATA PROCESSING

CASSETTE RECORDER
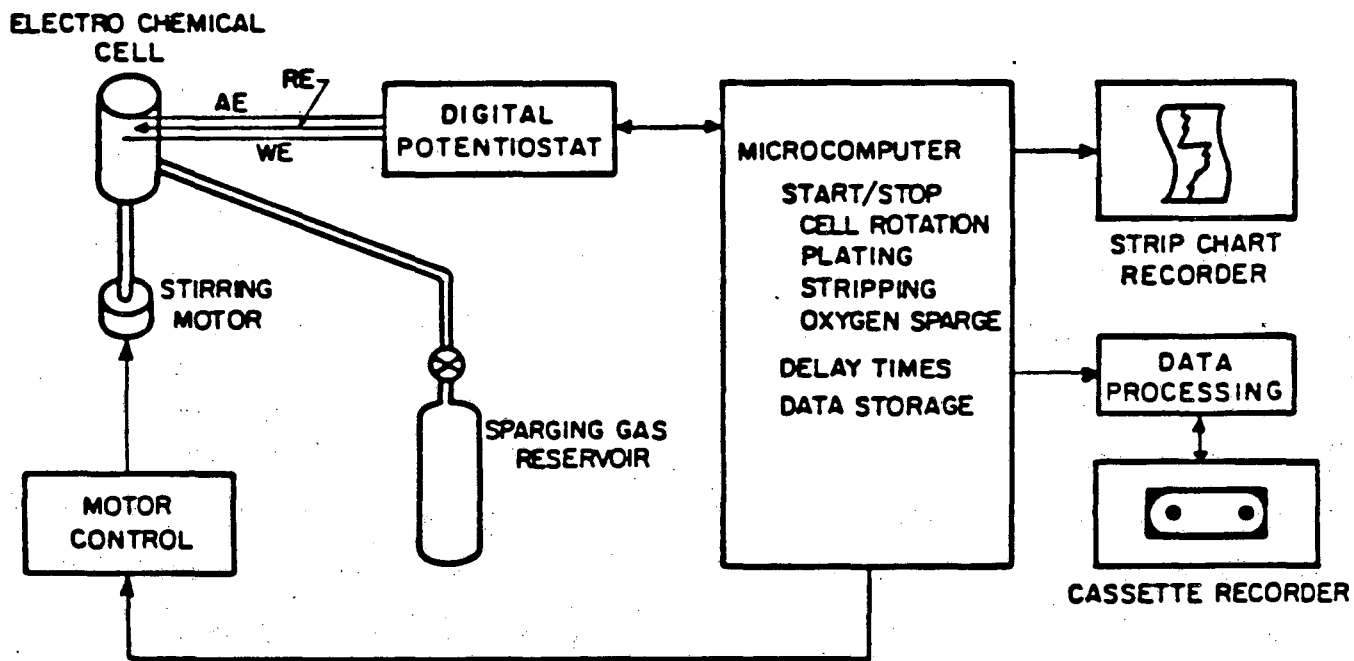
XBL 818-6204

Fig. 4. Schematic diagram of ASV system.

SCE

AE

Gas Inlet

Cell Top Mounting

Hg Film Graphite Electrode

Cell Fitting

Cell Rotator
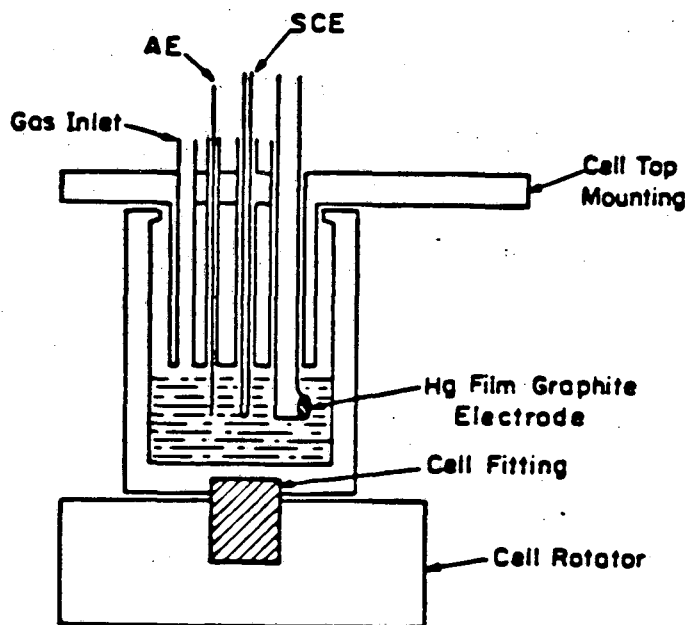
XBL 814-5567

Fig. 5. Rotating cell.

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Stirring is produced in the rotated cell during plating by controlled periodic reversal of the direction of rotation of the cell every second. During stirring the rotational speed is much less than during sparging. The effect is a horizontal rocking motion similar to that in a household washing machine. The graphite working electrode is placed on a radius of the cell and is positioned to face the cell wall. Turning the electrode through 180° so that it faces the center of the cell results in a marked decrease in the rate of amalgam accumulation because of a substantially lowered stirring rate. This means that the electrode, once positioned and locked into place with the set screw, should not be moved until the analysis is completed.

A low flow rate of nitrogen is maintained during the plating step to prevent infusion of air into the cell and thereby maintain a low background current.

During stripping, the cell is stationary so that stripping takes place in a quiet solution.

DIGITAL POTENTIOSTAT

Figure 6 is a circuit diagram of the essential features of the digital potentiostat designed and constructed for application to anodic stripping analysis. The two main functions are: (1) controlling the potential between the Hg-film working electrode (WE) and saturated calomel reference electrode (RE) during the plating step; and, (2) monitoring the current necessary to maintain this voltage during the stripping process. The current measured at each stripping voltage is the data from which the metal concentrations are measured.

The potentiostat includes two constant-current sources. One of these is a 0.1 ma negative current source, which is permanently connected to the cell. The other is a 1.0 ma source of positive current, which is switched into and out of the cell circuit by means of the current switch. When transistor Q4 of the current switch is ON (Q3 is OFF), diode D2 is caused to conduct, and diode D3 is reverse-biased. In this condition, the positive current from the 1 ma source is isolated from the cell, and the negative 0.1 ma current source drains charge from the cell. When transistor Q3 is turned on by a signal from the flip-flop, Q4 is turned OFF. This causes the 1 ma current to deposit charge into the cell via diode D3. During this time, the net current into the cell is a positive 0.9 ma.

The voltage across the cell is regulated by controlling the dwell time of the current switch; this is in turn controlled by the feedback loop consisting primarily of the voltage comparator and the J-K flip-flop. The voltage comparator compares the reference electrode potential with the potential commanded by the signal "VOLT DAC" in Fig. 6. The result of this comparison controls the gating of 1.0 μs pulses through the flip-flop. These pulses then turn the current switch on and off, causing pulses of positive current to be injected into the cell. The comparator causes pulses to be gated at a sufficient rate so that the cell potential is made equal to the commanded potential.
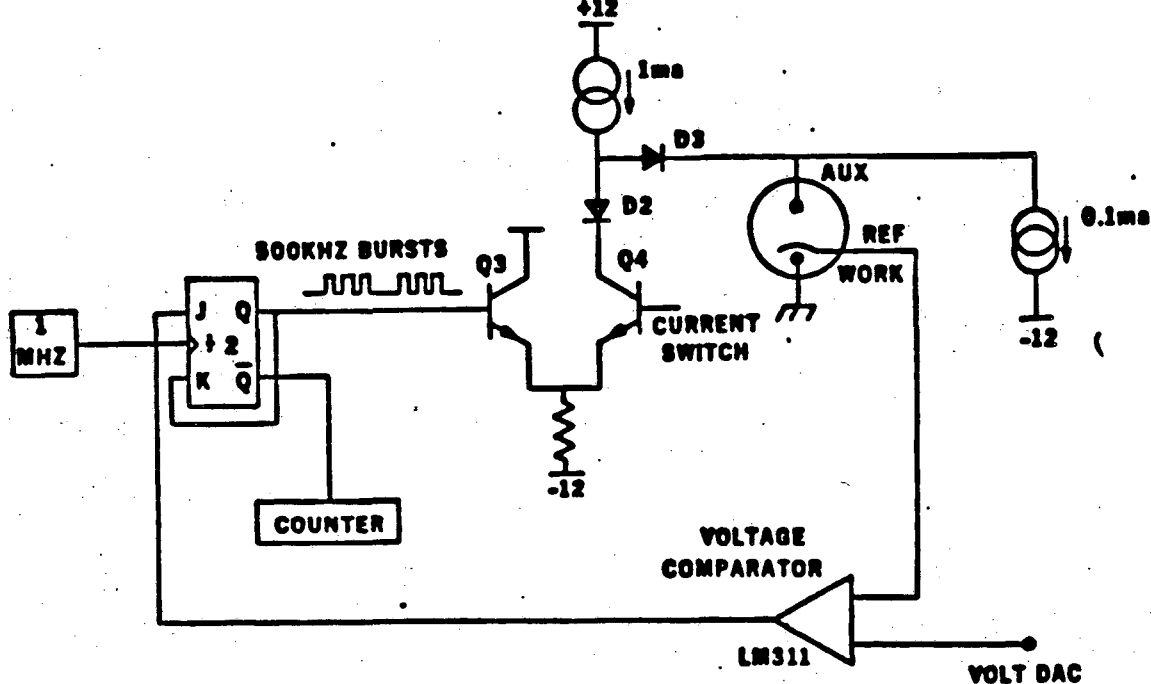
Fig. 6. Digital potentiostat. The voltage on the REF electrode
is controlled to be equal to the VOLT DAC input voltage
by this circuit.

Since each pulse deposits a fixed quanta of charge into the cell, the
charge required to maintain the potential at each step of the staircase
waveform used during stripping is measured simply by counting the number of
pulses gated by the flip-flop, and subtracting from this the number of
pulses required just to balance the negative 0.1 ma current source. The
average cell current is then this charge divided by the time duration of the
step.

MICROCOMPUTER CONTROLLER

A microcomputer controller was designed and built to control the opera-
tion of the instrument. It is based on an Intel 8080A 8-bit microprocessor.
The main operating program is written in the BASIC language. Certain sub-
routines are coded in 8080 assembly language and called by the BASIC program.
The use of BASIC simplifies the writing of the program, while providing more
than adequate speed of execution. The BASIC program and the assembly lan-
guage routines are permanently resident in the instrument in ROM (Read-Only
Memory). When the instrument is turned on, the BASIC program is copied from
ROM into RAM (Read-Write Memory) for execution. A simple BASIC interpreter*
also permanently resident in ROM, executes the BASIC code.

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*The ROM-based BASIC interpreter was developed at Lawrence Livermore National
Laboratory. It is described in Reference 26.

The microcomputer exercises control of the instrument at four levels.
First, it provides detailed control within the major functions (sparging,
stripping, etc.). For example, the timing and stepping of the commanded
potentiostat potential, described above, is under microprocessor control.
Secondly, it exercises overall sequence control by initiating the major
functions in the proper sequence, and by controlling their durations.
Thirdly, it provides an operator interface by which he may influence certain
parameters of the functions as described below. Finally, it controls the
acquisition, storing and outputting of the data from the stripping operation.

Sequence Controller

Certain parameters are used within the program to control operational
characteristics of the instrument, and to identify the recorded data. These
parameters are preset to default values stored in the program whenever power
is turned ON or when the MASTER RESET button is pushed. Subsequently, they
may be altered by the operator if desired. The parameters and their default
values are listed in Table 1. The values of the parameters actually used in
running a measurement are output with the data from the measurement, and thus
become part of the permanent record.

Operator Interface

The values of the parameters listed in Table 1 can be examined and/or
modified by the operator to effect special measurement sequences. If he
does not modify them, the standard, default sequence is used.

The operator interacts with the microprocessor by using the 16-key key-
board. The keyboard can be seen in the lower center of the front panel, as
shown in Fig. 1. The keys are used both to select the parameter and to
alter the values. To view the present value of the parameter on the display
(upper center of front panel), the correspondingly labeled key is pressed.
At this point, the value can be changed. As an example, the plating time
can be changed from 420 seconds to 20 seconds as follows.

(1)   Press the key marked PLATE; the display will then show PLATE
        420S" (assuming that is the current value).

(2)   Press the key marked "ENTER"; the display now shows "PLATE 0S".

(3)   Press in turn the keys "2" and "0"; the display will now show
        "PLATE 20S".

(4)   Press ENTER again; the new value is now entered in the program.

Following this, the value for plating time will remain 20 seconds either
until it is changed again; until the power is turned OFF and then ON again;

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or until the MASTER RESET button is pushed. In addition, the operator must choose the output medium. The switch in the upper center of the front panel permits directing output to the internal tape cartridge recorder, to an external Hewlett-Packard 9845 computer, or to neither. Regardless of the setting of this switch, the results of the stripping operation can be plotted on a strip-chart recorder, if it is connected to the appropriate connector on the rear of the instrument.

With this accomplished, the remaining interaction is to push the button marked START CONTINUE TEST. The instrument will then go through the complete sparging, plating and stripping sequence automatically, and will send the data to the appropriate medium at the conclusion of the measurement. A measurement sequence may be stopped at any time by pushing the STOP TEST RESET button (parameter values are preserved) or the MASTER RESET button (parameters revert to default values).

A flow chart of the complete sequence of operations, including those of the Hewlett-Packard 9845 computer used for data analysis is shown in Fig. 7.

TABLE 1. PARAMETERS, SIGNIFICANCES, AND DEFAULT VALUES

Parameter Name	Default Value	Significance
SPARGE	60 s	Length of sparge cycle
START	- 1000 mV	Voltage of first step of stripping cycle
END	350 mV	Voltage of last step of stripping cycle
STEP	5 mV	Voltage steps for stripping
PLATE	420 s	Length of plating cycle
DELAY	1 ms	Delay between each voltage step and start of current measurement for that step
COUNT	400 ms	Length of time data accumulated during each step of stripping cycle
RCDR	3	Power of 2 scale factor for strip-chart output of stripping data
DAY	0	Serial number of day of test (0-9999)
TEST NO.	0	Serial number of test (0-9999)
SPIKE A	0 μL	Numerical information on first standard addition
SPIKE B	0 μL	Numerical information on second standard addition

Data Handling

The ASV output signal of analytical interest is the Faradaic current as a function of applied potential. During the stripping sequence, this signal may be recorded on a strip-chart recorder or an X-Y recorder. The output signal sent to the recorder is an analog voltage proportional to the number of counts accumulated by the counter (see Fig. 6) during each voltage step of the stripping cycle. The results of recording the ASV output signal in this way are shown in Figs. 8-12. In each curve, the concentration of the selected metal is indicated by the height of the peaks that occur at the characteristic voltage for that metal. The "staircase" form of the curves is due to the stepping of the stripping voltage in discrete increments.

Data in digital form can also be recorded on an internal digital cartridge recorder, or it can be transmitted by cable to an auxiliary computer for analysis and storage. In the next section, the use of a Hewlett-Packard 9845B computer for this purpose is described.
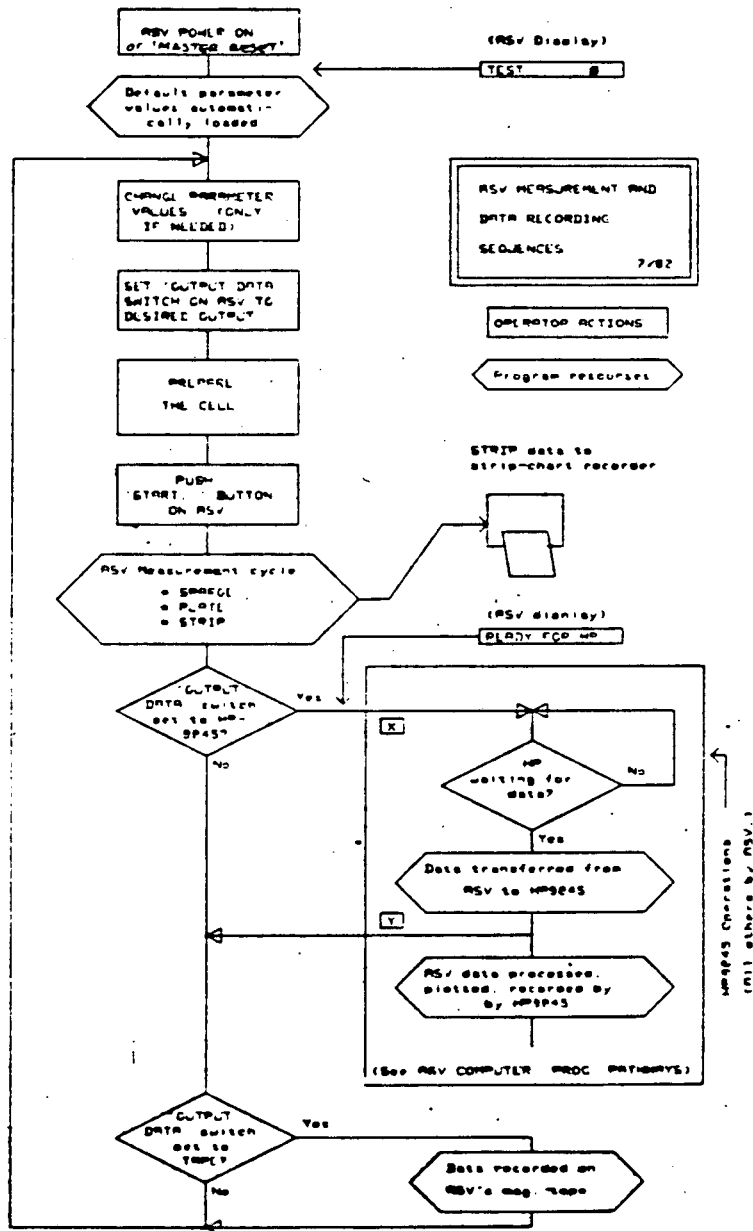
Fig. 7. Flow chart for sequence of steps.

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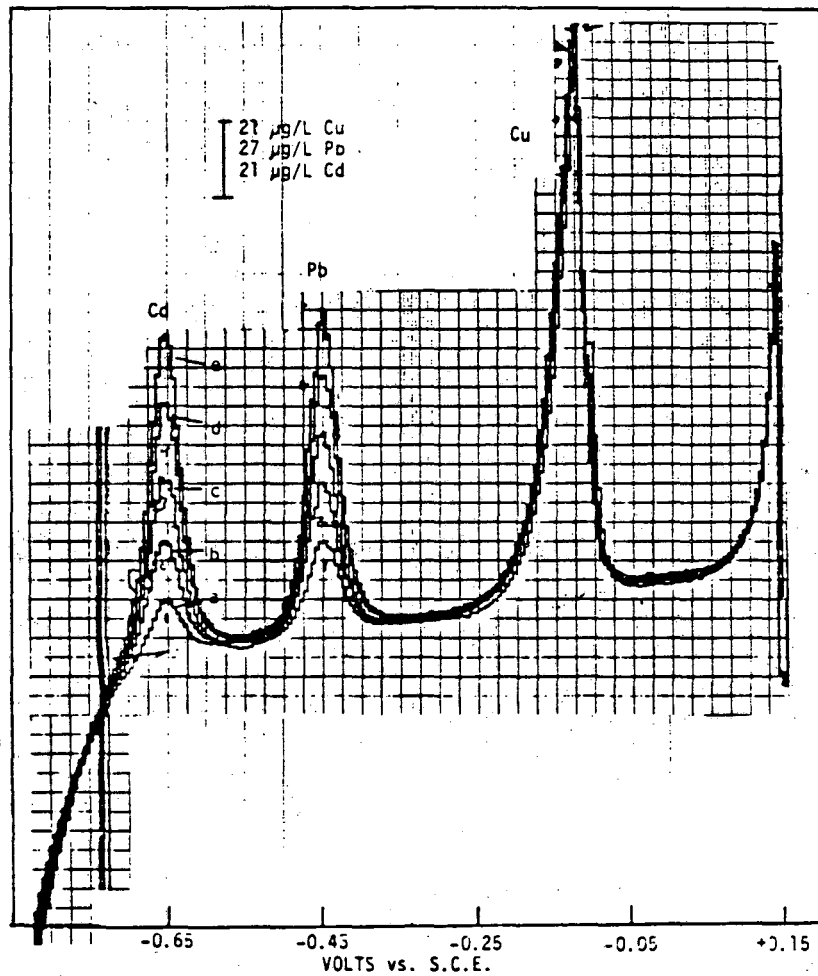
Figure 8. Variation in stripping peak height with Cd and Pb
concentrations in 0.1M NaCl, 0.05M acetate, 2 mg/L Hg

a) 16.7μg/L Cd, 13.3μg/L Pb, 146.5μg/L Cu 2.
b) 33.4 μg/L Cd, 26.6 μg/L Pd, 146.5μg/L Cu;
c) 30.2μg/L Cd, 39.9μg/L Pb, 146.5μg/L Cu;
d) 66.8μg/L Cd, 53.2μg/L Pb, 146.5μg/L Cu;
e) 83.5μg/L Cd; 66.5μg/L Pb, 146.5μg/L Cu.

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VOLTS vs. S.C.E.
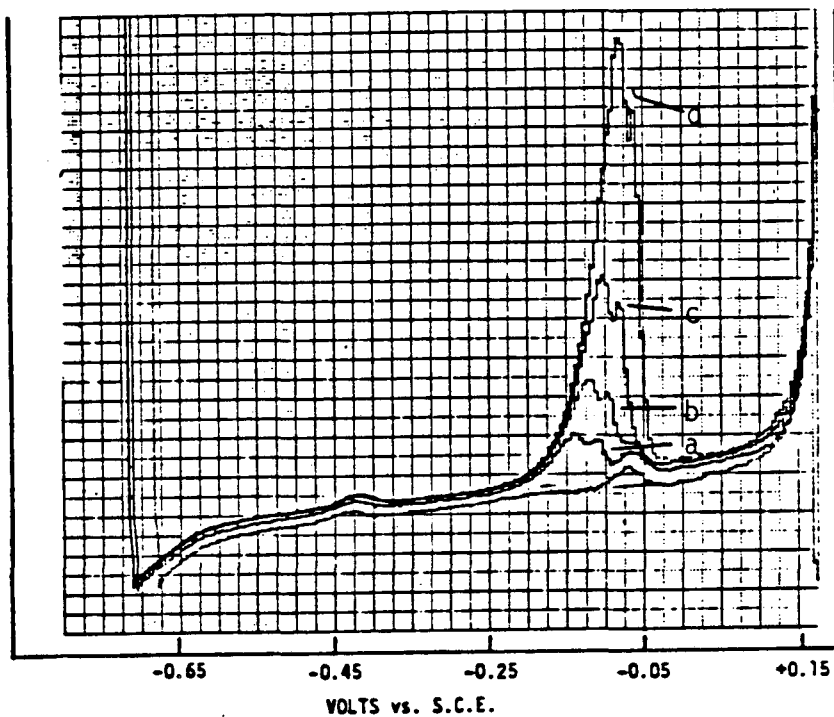
Figure 9. Change in peak height with added Cu. O;   a) 18.3µg/L;
b) 36.6µg/L;   c) 73.2µg/L;   d) 145.4µg/L.
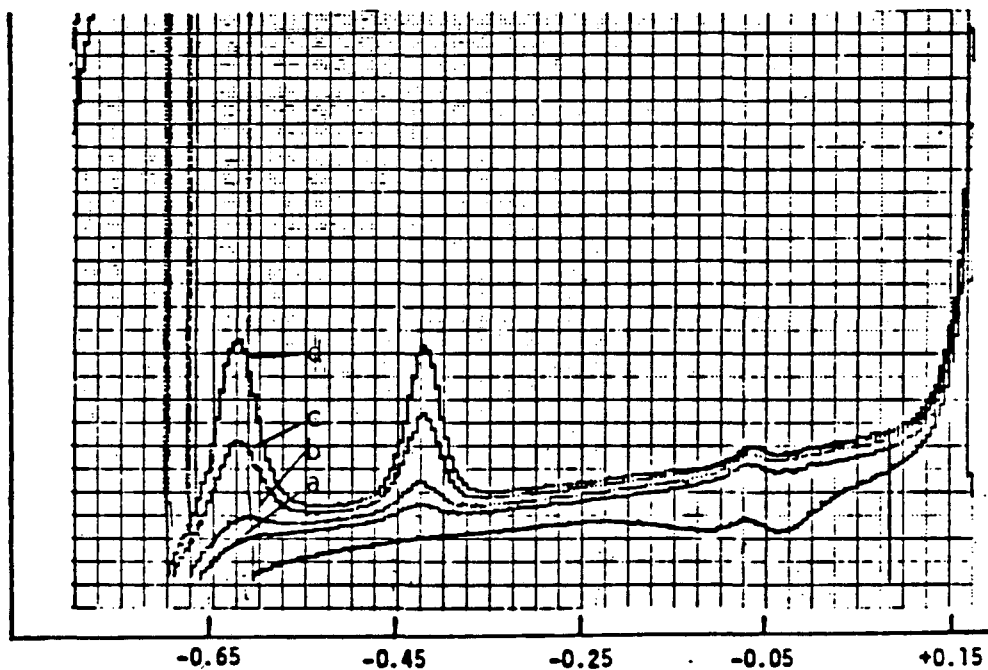
Figure 10. Change in peak height with Cd and Pb: a) 3.3µg/L Pb,
4.2µg/L Cd;   b) 6.6µg/L Pb, 8.4µg/L Cd;   c) 23.1µg/L Pb,
29.4µg/L Cd;   d) 36.3µg/L Pb, 46.2µg/L Cd.

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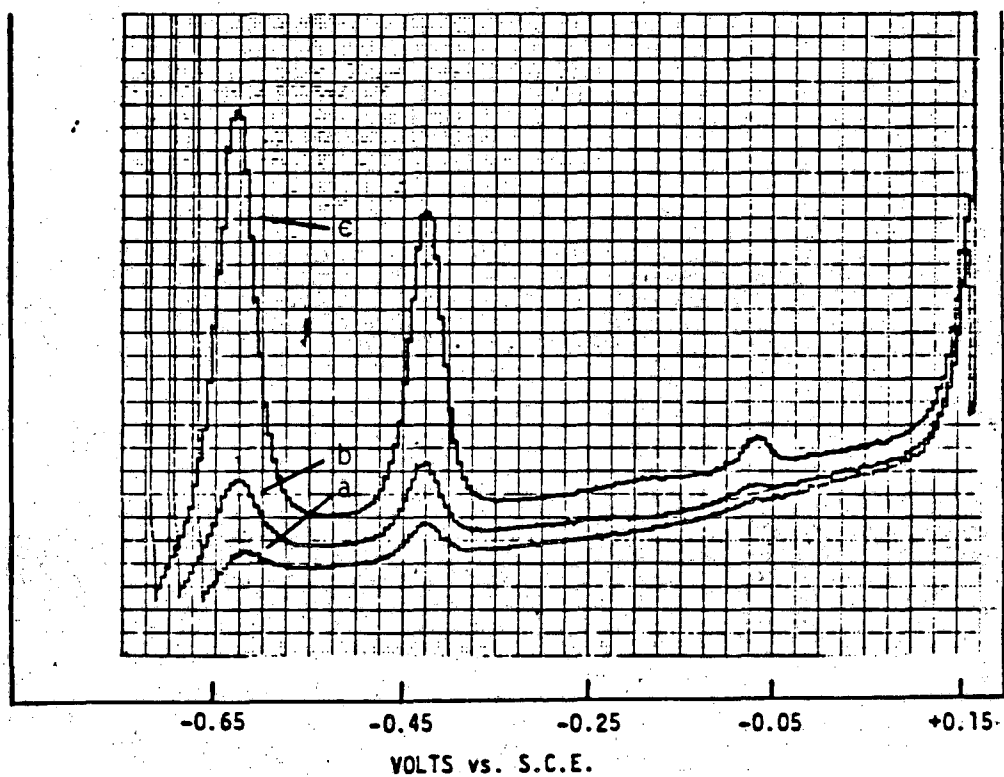
Figure 11. Variation in stripping peak height with plating time:
a) 105 sec; b) 270 sec; c) 840 sec 46.2μg/L Cd+ 36.3μg/L Pb.

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-0.65   -0.45   -0.25   -0.05   +0.15

VOLTS vs. S.C.E.

Figure 12. Peak height change with Cd, Pb, Cu concentration:
a) Blank; b) 36.6µg/L Cu, 8.2µg/L Cd, 6.6µg/L Pb;
c) 73.2µg/L Cu, 16.4µg/L Cd, 13.23µg/L Pb; d) 109.8µg/L Cu,
33.6µg/L Cd, 26.4µg/L Pb; e) 128.1µg/L Cu, 49.2µg/L Cd,
39.6µg/L Pb.

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SECTION 4

AUXILIARY COMPUTER SYSTEM

As described above, the ASV instrument measures the value of cell current for each step of voltage during the stripping operation. While the stripping function is proceeding, these data can be plotted on a strip-chart or an X-Y recorder. From such recordings, the concentrations of metals in the solution can be determined, for example, by manually measuring the amplitudes of the peaks, or by manually integrating the areas under the peaks. In order to obtain the concentrations automatically, provision has been made to connect an auxiliary computer to the ASV. The auxiliary system is programmed to process the data and to obtain numerical values for the metal concentrations. It can also permanently record the data on magnetic tape for archival purposes.

The auxiliary computer used in this project is a Hewlett-Packard model 9845B. This type was used because it had already been chosen for use in the Water Quality Monitoring Van (27) project. The program written for the HP 9845B for supporting the ASV has two major segments. One is used for transferring the data from the ASV to the HP9845 and recording it on the HP 9845's internal tape cartridge; the other performs an analysis of the data.
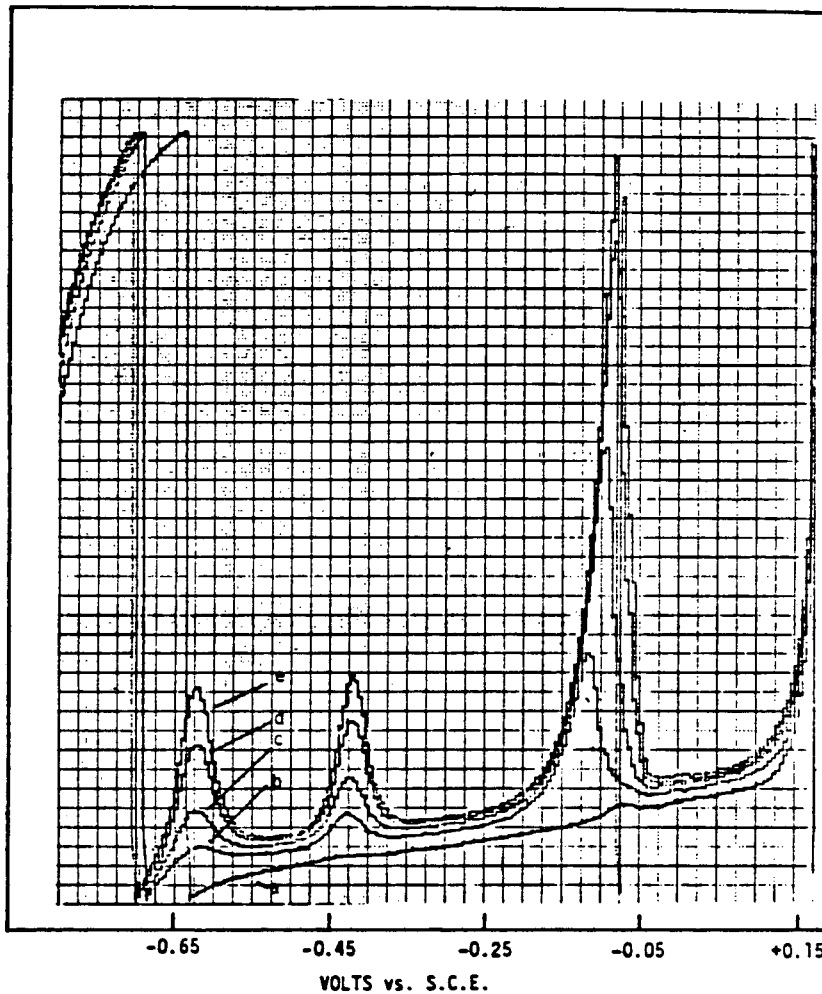
AUTOMATED DATA TRANSFER

Electrical connection between the ASV and the HP9845B is made by means of a bus connection based on the RS232 standard (28). When the bus is connected, transfer of data will automatically take place at the end of the stripping operation if: 1) the "OUTPUT DATA" knob on the front panel of the ASV is in the HP9845" or the "BOTH" position; 2) the program in the HP9845 has been started and is waiting for data. This situation is shown graphically in the flow chart of Fig. 7. Once started, the transfer of data takes about 30 seconds. The HP9845 computer program then causes the data to be recorded on its internal digital cartridge recorder.

In addition to the data, the values of all parameters listed in Table 1 are recorded. Also, the HP9845 program permits the user to enter additional information--e.g., comments on the conditions of the measurement; remarks on the amounts of metal added, if any; etc.

After the complete set of data has been transferred, the ASV is released to commence another measurement, if that is desired.

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At any time that data are not actually being transferred, the user has the option to command the HP9845 to perform an analysis of data from a selected measurement that had previously been recorded. Results of several analyses are shown in Figs. 13-16.

The first step in the analysis program is to "normalize" the data. A constant is subtracted from each datum (number of counts at a step of stripping voltage--cf Fig. 6) such that one part of the curve will have the value zero. Then an appropriate scale factor is chosen, and the 'normalized' curve is plotted.

The next step is to calculate a background curve. The background curve is the curve that, it is assumed, would have been the curve plotted in the first step if no metals were present in the solution. If this assumption is correct, the presence of metals is the cause of any difference between the 'normalized' curve and the background curve. The background curve is itself calculated by fitting a composite of a fifth-degree polynomial and a straight line segment through a set of selected points on the 'normalized' curve. These points, indicated by '1', '2', '3' and '4' on Figs. 13-16, are within ranges of stripping voltage where we do not expect peaks from lead, cadmium or copper to occur. The fifth-order polynomial is fitted through points from regions 2, 3 and 4. The straight line is fitted through points from regions 1 and 2. The voltage limits for these ranges are printed on the same page as the curve.

The third step is to integrate the areas subtended by the background and 'normalized' curves in the three pre-selected regions where we expect the peaks due to presence of metals to occur. The three areas are represented on the graphs by 'Cu', 'Cd', and 'Pb'. The voltages at the limits of these three areas are indicated under the line "INTEGRATION LIMITS (MV)".

The forth and final step is to multiply the three areas so obtained by calibration constants, and to print the results. The results are not necessarily in practical units (e.g., mg/mL); these are derived by the process of performing standard additions as described in a later section.

As shown in Figs. 13-16, which are copies of output generated by the HP9845 computer program, certain information regarding the measurement is printed along with a plot of both the 'normalized' and background curves. The printed information includes values of certain of the parameters used by the ASV in making the measurement, comments added by the operator of the HP9845, and constants used by the HP9845 program in performing the analysis.

The HP9845 program also contains the provision for the user to adjust both the voltage limits used in fitting the background curve, and the voltage limits used in integrating the peaks. These values may need to be adjusted as measurement conditions--such as the pH of the solution--vary.

`,f NUMBER 39   ASV RUN WAS ON DEC 11,1981
_OPPER CONC.= 0PP3   LEAD CONC.= 0PP3.   CADMIUM CONC.= 0PP3
COMMENT:REPEAT OF TEST 30 (BLANK)
LIMITS FOR GRAPH ARE: Xmin   Xmax   Ymin   Ymax
                       -500   .1000   0   40000
VOLTAGE LIMITS FOR BACKGROUND FITTING REGIONS ARE:
   REGION   1   2   3   4
   START (MV)   -50   200   320   720
   END(MV)   0   330   560   840
A POLYNOMIAL OF DEGREE 5 IS FIT USING 48 POINTS FROM REGIONS 2 THRU 4
REGRESSION COEFF = +70077.5767   POLYNOMIAL COEFFS.:-1.29E+00, +2.71E+00, -2.1
0E-02, +7.54E-05, +1.89E-08, -2.34E-11,
STRAIGHT LINE IS FIT USING 24 POINTS FROM REGIONS 1 THRU 2
THE STRAIGHT LINE IS +9.9410E+02 + +1.3019E-01 + X. REGR. COEFF. =   .2785
INTEGRATION LIMITS (MV)
  COPPER-   50 220   LEAD- 350 400   CADMIUM- 590 690
  COPPER, LEAD, CADMIUM (Counts) = 24751,   4089,   8680,

RESULTS++++++++
     COPPER   33; LEAD   4; CADMIUM   :   9
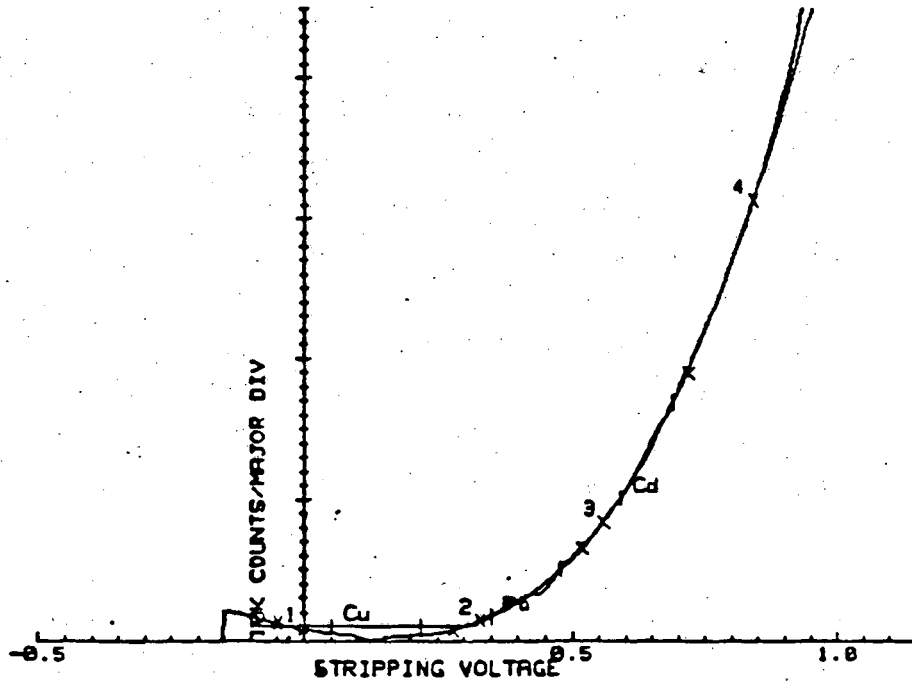
Figure 13. 0.1 M NaCl, 0.01 M acetic acid, 0.01 M sodium acetate, pH4.7,
          300 second plating time.

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COPPER CONC.= 0PPB   LEAD CONC.=25uL OF 8   CADMIUM CONC.=25uL O
COMMENT:300 SEC PLATING TIME
LIMITS FOR GRAPH ARE: Xmin   Xmax   Ymin   Ymax
                      -500   .1000   0   50000
VOLTAGE LIMITS FOR BACKGROUND FITTING REGIONS ARE:
   REGION   1   2   3   4
   START (MV)   -50   280   520   720
   END(MV)   0   330   560   840
A POLYNOMIAL OF DEGREE 5 IS FIT USING 40 POINTS FROM REGIONS 2 THRU 4
REGRESSION COEFF = +24665.1729   POLYNOMIAL COEFFS.:+8.84E-01, +6.15E+01, -2.9
5E-01, +6.44E-04, -5.23E-07, +1.74E-10,
STRAIGHT LINE IS FIT USING 24 POINTS FROM REGIONS 1 THRU 2
THE STRAIGHT LINE IS +7.3197E+03 + -6.0561E+00 * X. REGR. COEFF. =   538.6518
INTEGRATION LIMITS (MV)
   COPPER-   50 220   LEAD- 350 400   CADMIUM- 590 690
   COPPER, LEAD, CADMIUM (Counts) = 23166,   42831,   50617,

RESULTS++++++++
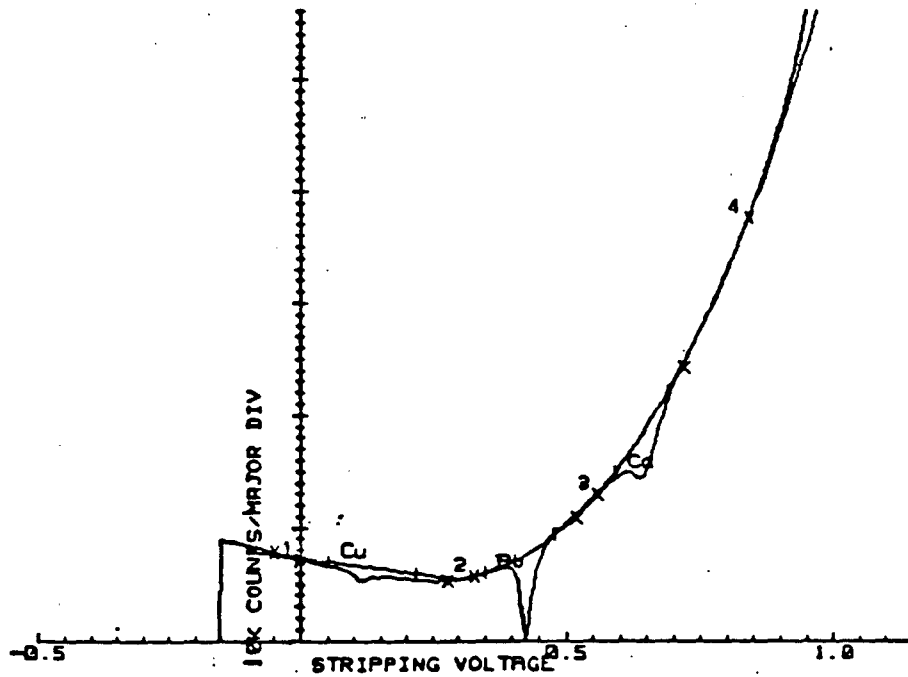   COPPER   81; LEAD   41; CADMIUM   51

Figure 14. Added 25 µL each of Pb and Cd solutions to 15 mL solution,
          300 second plating time.

```
TEST NUMBER 41                                    ASV RUN WAS ON DEC 11,1961
COPPER CONC.= 0PPB          LEAD CONC.=50uL OF 8   CADMIUM CONC.=50uL O
COMMENT:300 SEC PLATING TIME
LIMITS FOR GRAPH ARE: Xmin    Xmax    Ymin    Ymax
                      -500    1000     0      70000
VOLTAGE LIMITS FOR BACKGROUND FITTING REGIONS ARE:
   REGION          1       2       3       4
   START (MV)     -50     200     520     720
   END(MV)         0      330     560     840
A POLYNOMIAL OF DEGREE  5 IS FIT USING  40 POINTS FROM REGIONS 2 THRU 4
REGRESSION COEFF = +19390.1947    POLYNOMIAL COEFFS.:+4.11E+00, +1.96E+02, -5.1
7E-01, +2.80E-03, -1.90E-06, +7.89E-10,
STRAIGHT LINE IS FIT USING  24 POINTS FROM REGIONS 1 THRU 2
THE STRAIGHT LINE IS +2.1884E+04 + -1.7440E+01 * X. REGR. COEFF. =   2274.5965
INTEGRATION LIMITS (MV)
   COPPER-   50   220   LEAD-   350   460   CADMIUM-  590  690
   COPPER, LEAD, CADMIUM (Counts) = 24652,    184976,    118402,

RESULTS++++++++
     COPPER          33; LEAD           100; CADMIUM          118
```
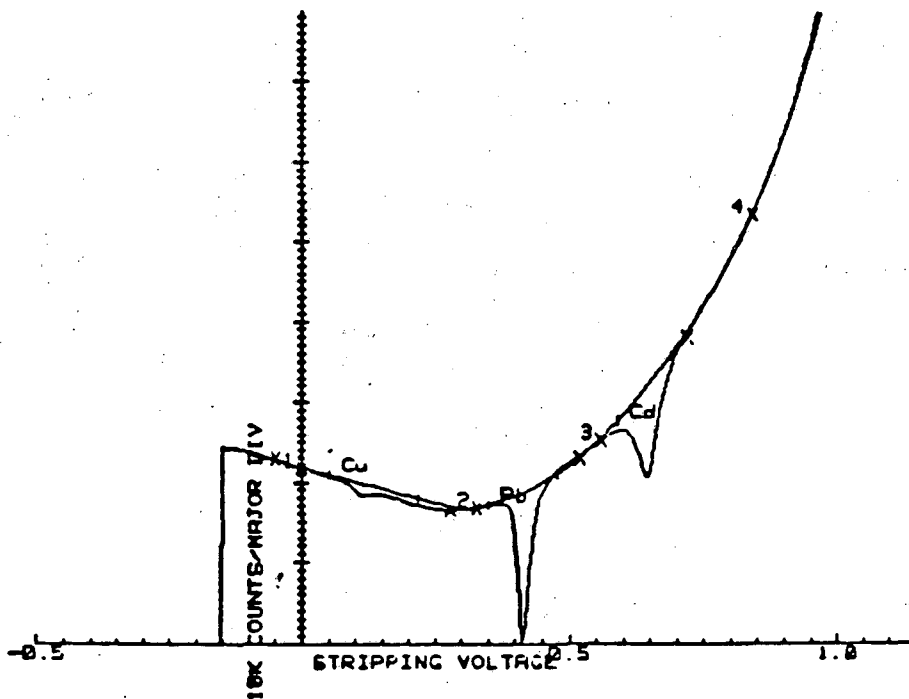

Figure 15. Added 50 µL each of Pb and Cd solutions to 15 mL; 300 second
plating time.

```
TEST NUMBER 33                                          ASV RUN WAS ON DEC 10,1981
COPPER CONC.= 0PPB          LEAD CONC.--100uL           CADMIUM CONC.= 6PPB
COMMENT:1.00mL LEAD STD=100ug  LEAD
LIMITS FOR GRAPH ARE: Xmin      Xmax      Ymin      Ymax
                      -500      1000       0        70000
VOLTAGE LIMITS FOR BACKGROUND FITTING REGIONS ARE:
    REGION          1           2           3           4
    START (MV)     -50         200         520         720
    END(MV)         0          330         560         840
A POLYNOMIAL OF DEGREE  5 IS FIT USING  48 POINTS FROM REGIONS 2 THRU 4
REGRESSION COEFF = +223263.8384    POLYNOMIAL COEFFS.:+7.90E+00, +3.43E+02, -1.7
2E+00, +3.07E-03, -3.90E-06, +1.51E-09,
STRAIGHT LINE IS FIT USING  24 POINTS FROM REGIONS 1 THRU 2
THE STRAIGHT LINE IS +2.7732E+04 + -8.9934E+00 + X. REGR. COEFF. =   15261.3255
INTEGRATION LIMITS (MV)
    COPPER-   50  220   LEAD-  350  480   CADMIUM-  590  690
    COPPER, LEAD, CADMIUM (Counts) = 7281,     165964,      10972,

RESULTS·······
    COPPER            10;  LEAD           150;  CADMIUM            19
```
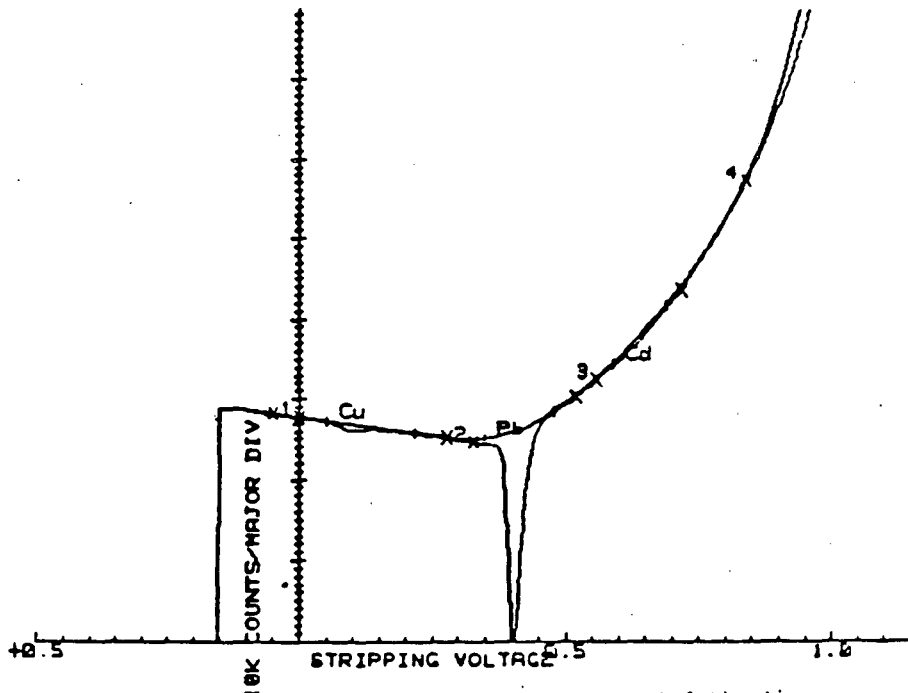

Figure 76. Added 100 µL Pb solution to 15 mL; 300 second plating time.

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SECTION 5

CALIBRATION PROCEDURE

Reagent grade sodium acetate (NaOAc) contains both copper and lead; concentrations can exceed 1 ppm. Cadmium is not present in significant amounts. It is essential that these concentrations be reduced; otherwise they add to the background level thereby reducing the lower limit of detection, e.g., by increasing the uncertainty of measurements.

Fortunately, the levels are reduced by the following recrystallization procedure. Sufficient sodium acetate is weighed out to form a saturated solution in 100 mL of water at $100^{\circ}C$. Following dissolution, the beaker is removed from the hot plate, ammonia gas is passed into the solution at a rapid rate through a clean glass tube which is over 7 mm in diameter. Small glass tubes will become completely plugged with NaOAc crystals. The ammonia treatment is continued until the solution cools to room temperature. The beaker is then placed in an ice bath and ammonia passed through until the solution temperature drops to about $10^{\circ}C$. The resulting acetate crystals are immediately removed by filtration through a medium porosity filter glass funnel. The crystals are washed with a small amount of ice cold water; the beaker and crystals are dried under vacuum over concentrated sulfuric acid with occasional washing of the crystals.

One recrystallization usually suffices to reduce the lead level below the detection limit of the analytical procedure. This purification procedure probably works because lead is converted to soluble PbO_2^{2-} and copper to the ammonia complex. Both are incompatible with the sodium acetate crystal habit, and do not co-precipitate.

Standard stock solutions of Cd, Pb and Cu for calibration purposes were prepared according to Standard Methods, 15th Edition (1). For cadmium, 123.3 mg of pure metal were dissolved in 5 mL HCl + 20 mL H_2O. The resulting solution was diluted to 1000 mL with quartz distilled water (1 mL = 123µgCd), and stored in a cleaned polyethylene bottle. Standard Pb was prepared by dissolving 1.598 g of $Pb(NO_3)_2$ in 25 mL of water to which about 1 mL HNO_3 was added. On dilution to 1000 mL, 1 mL=1.00 mg Pb. Similarly, 111.9 mg Cu foil was added to a 250 mL beaker, and dissolved in a mixture of 3 mL H_2O plus 3 mL HNO_3. Following dissolution, 1 mL H_2SO_4 was added, and the solution heated on a hot plate—but not to dryness. The resulting solution was cooled and diluted to 1000 mL:1 mL = 112µg Cu. The mercury solution was prepared by dissolving 1.1 g of triply distilled Hg in hot 5 mL HNO_3, cooling and diluting to 1000 mL.

The resulting solution contained 1.1 mg/mL (1100 ppm). The Cd, Pb and Cu stock solutions were diluted as needed to prepare fresh solutions containing 0.00247 µg/µL Cd, 0.0020µg/µL Pb and 0.011µg/µL Cu.

Generally, 25µL of the Hg solution was pipetted into 15 mL of the solution to be analyzed to give a final concentration of 27µg/15 mL (1.8ppm).

Calibration was done by pipetting 25-50 microliter aliquots of Cd, Pb and Cu solutions into 15 mL of quartz-distilled water containing 0.1 M NaCl and 0.01 HOAc, 0.01 M NaOAc (pH 4.7). Table 2 contains typical calibration data for Cd, Pb and Cu in this solution, covering the concentration range 13-147 µg/L.

Manual

Stripping curves were output to a Hewlett-Packard Model 7044A X-Y recorder after being converted into analog form. Figure 8 contains a series of ASV curves for 13.3-66.5µg/L Pb, 16.7-83.5µg/L Cd, and a constant concentration of 146.5µg/L Cu. The Cd peaks are at -0.6 v., Pb at -0.40 v. and Cu -0.1 v. vs. S.C.E. Figure 9 is a calibration series for Cu covering the range 18.3-145.4µg/L. As shown, the blank contained about 15µg/L of Cu, and 1-2 µg/L Pb. Figure 9 also shows a shift in peak potential with added Cu, and the appearance and merging of two Cu peaks. Nonetheless, peak heights could be linearly related to added Cu by measuring the peak height and correcting for the blank. See Figure 17.

Data were obtained showing the variation in peak height with Cd and Pb concentration (Fig. 18, 19), and the variation in peak height with plating time for a mixture of Cd and Pb (Fig. 20). Peak heights versus concentration were also measured for different concentrations of Cu, Pb and Cd.

The calibration data are given in Tables 3 and 4 and are plotted in Figs. 17-19. The zero values were obtained by superimposing the blank on the curves obtained for added Cd, Pb and Cu. This was especially important for Cd where there is a steep rise as the voltage is made anodic during the stripping process. See Fig. 8 as an example of a typical anodic stripping scan for three metals.

The calibration data in the tables for Cu, Pb and Cd were fit to linear equations, as follows:

Peak height $= -2.432 + 1.071$ [Cd] $r^2 = 0.994$
Peak height $= -0.114 + 1.231$ [Pb] $r^2 = 0.967$
Peak height $= -7.956 + 0.995$ [Cu] $r^2 = 0.938$

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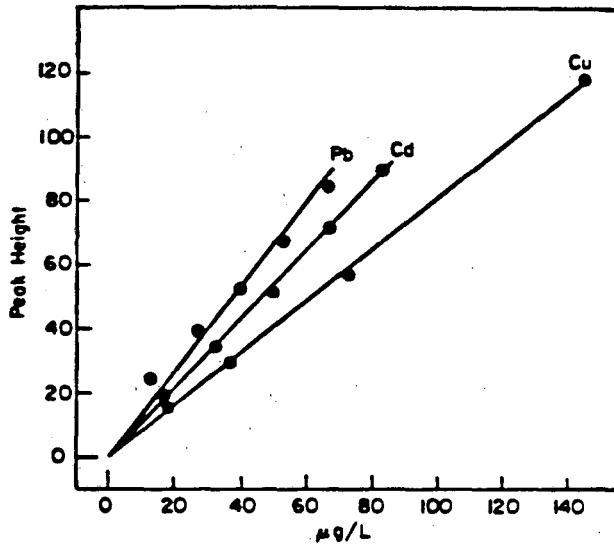
Figure 17.   Peak height versus added metal
concentration for mixtures of Cu, Pb and Cd.
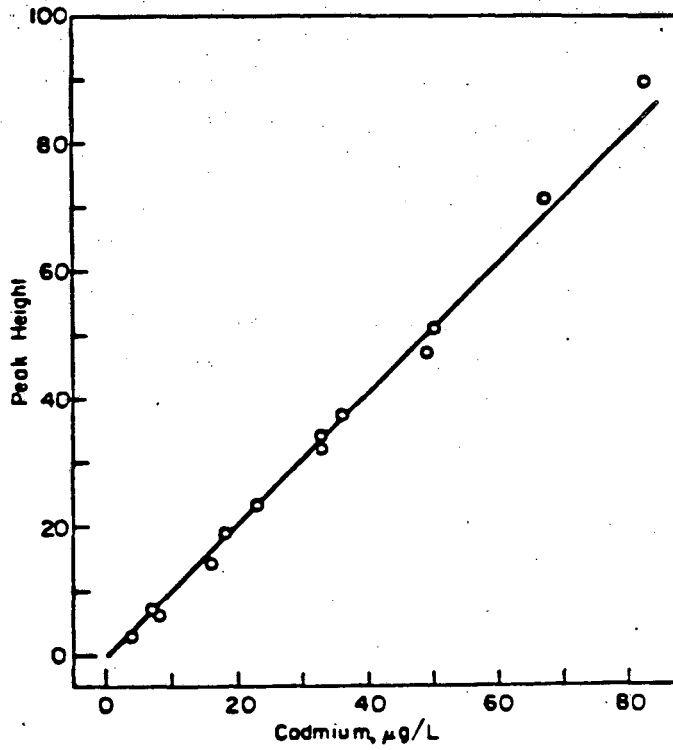

Figure 18.   Peak height versus added Cd.
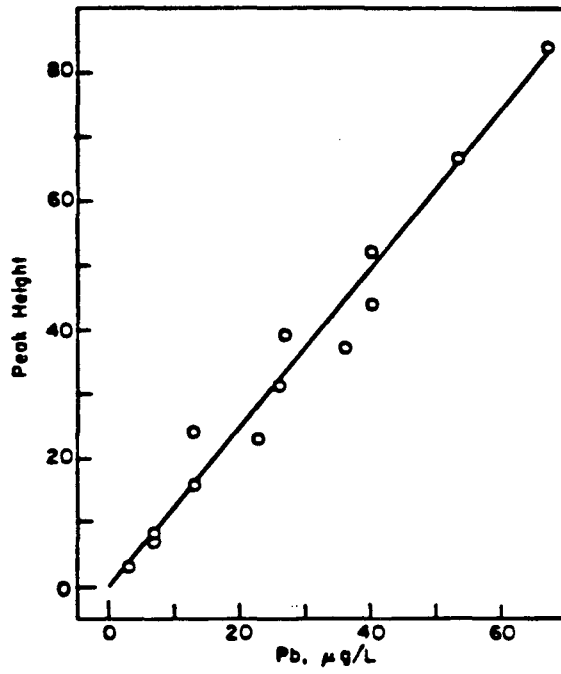
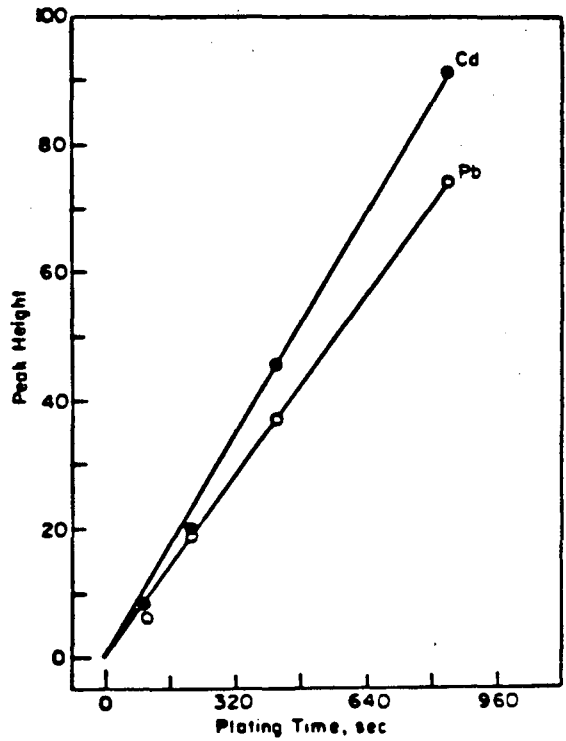Figure 19.   Peak height versus added Pb

Figure 20.   Effect of plating time
on Cd and Pb peak heights.

TABLE 2. Variation in Stripping Peak Height with Concentration for Varying
Mixture of Cd, Pb and Cu in 0.1 M NaCl, acetate buffer

Peak Height (units)

µg/L	Cd	Pb	Cu
146.5	---	---	125,150,152,160,160
13.3	---	24	---
26.6	---	---	---
39.9	---	52	---
53.2	---	67	---
66.5	---	84	---
16.7	19	---	---
33.4	34	---	---
50.1	51	---	---
66.8	71	---	---
83.5	89	---	---

TABLE 3. Variation in Peak Height with Concentration for Individual
Solutions of Cu, Pb and Cd in 0.1 M NaCl, acetate buffer

Peak Height (units)

µg/L	Cd	Pb	Cu
18.3	---	---	15
36.6	---	---	29
73.2	---	---	56
145.4	---	---	118
4.2	3	---	---
8.4	8	---	---
29.4	26	---	---
46.2	46	---	---
3.3	---	3	---
6.6	---	7	---
23.1	---	23	---
36.3	---	37	---

TABLE 4. Variation in Stripping Peak Height with Concentration for Mixture of Cd, Pb and Cu in 0.1 $\underline{M}$, NaCl, acetate buffer.

Peak Height (units)

µg/L	Cd	Pb	Cu
8.2	6	---	---
16.4	14	---	---
32.8	32	---	---
49.2	47	---	---
6.6	---	8	---
13.2	---	16	---
26.4	---	31	---
39.6	---	44	---
36.6	---	---	40
73.2	---	---	93
109.8	---	---	147
128.1	---	---	---

Automated Data Handling

Standard stock solutions of Cd, Pb and Cu for calibration purposes were prepared. For Cd, 100.0 mg of pure metal was dissolved in 5 mL HCl + 20 mL H_2O. The resulting solution was diluted to 1000 mL with quartz distilled water (1 mL = 100 µg Cd), and stored in cleaned polyethylene bottles. Standard Pb was prepared by dissolving 159.9 mg of $Pb(NO_3)_2$ in 200 mL of water to which about 10 mL HNO_3 was added. On dilution to 100 mL, 1 mL = 100 µg Pb. Similarly, 200.0 mg Cu foil was added to a 250 mL beaker and dissolved in a mixture of 10 mL H_2O plus 5 mL HNO_3. Following dissolution, the solution was heated on a hot plate—but not to dryness. The solution was cooled and diluted to 1000 mL; 1 mL = 200 µg Cu. The mercury solution was prepared by dissolving 1.1 g of triply distilled Hg in hot 5 mL HNO_3, cooling and diluting to 1000 mL. The resulting solution contained 1.1 mg/mL (1100 ppm). The Cd, Pb and Cu stock solutions were diluted as needed. Generally, 25 µL of the Hg solution was pipetted into 15 mL of the solution to be analyzed, giving a final Hg concentration of 27 µg/15 mL (1.8 ppm).

The ASV-HP9845 system was tested by obtaining stripping curves for known concentrations of Pb and Cd over the range 2.5 – 10.0 µg/15 mL. Peak areas were automatically calculated and printed in the "RESULTS" section for each run: for example, the blank (Fig. 13) was calculated as containing 33 units of Cu, 4 units of Pb and 9 units of Cd. These factors are converted to µg by multiplying the 0.0676 µg/unit for Pb and 0.0595 µg/unit for Cd. Plots of peak area versus added metal content for both Cd and Pb are shown in Figs. 21 and 22.

Summary of Data Handling

A software program was written for the HP9845 to permit automated processing of ASV data. The stored data are printed as net peak areas ("RESULTS") for each metal, and in graphical form as stripping curves. See Figures 13-16. Calibration data shows satisfactory linearity over the range of concentrations used here for Pb, Cd and Cu using laboratory solutions. Linearity was also obtained for the variation in peak height with added µL volumes of known amounts of each metal.

For manual analysis, readout was on a strip chart recorder. The estimated uncertainty for concentrations <3 µg/L is about ± 1 peak height unit; this could introduce an error of 33% for peak heights which are manually measured. At low concentrations (~ <5 µg/L), the better approach to measuring peak heights is computer calculation of the difference between the background level and each peak height.
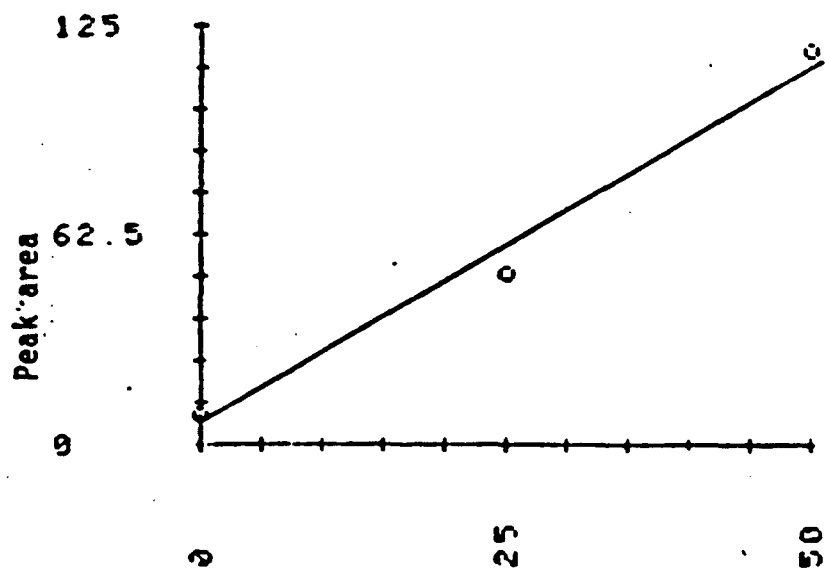
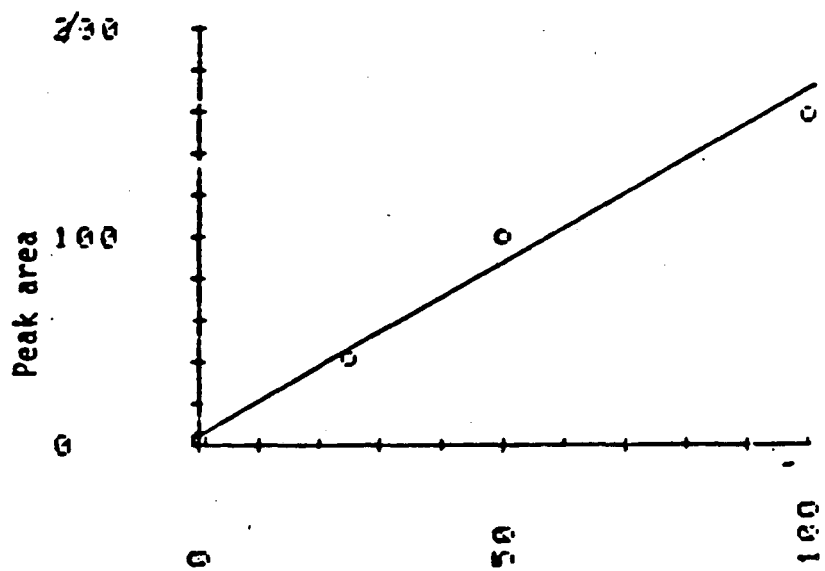Figure 21. Stripping peak area versus added Cd.

Figure 22. Stripping peak area versus added Pb.

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SECTION 6

TAP WATER ANALYSIS

Codeposition of mercury and metal from the water sample is recommended in this procedure; thus the mercuric ion concentration used is of importance. In an experiment employing Pb deposition, in which the mercuric ion was added over the range of 1 ppm to 20 ppm, a gradual increase in sensitivity of the trace lead ASV peak height with mercuric ion concentration, was observed. However, at mercury levels much greater than 2 ppm, precision suffered.

For example, precision on the order of ±120% ppm was attained; the precision at 2 ppm can be as good as 0.5 . Mercuric ion concentration of 2 to 4 ppm is recommended to obtain the maximum precision. It is likely that the reduced precision at high mercuric ion concentrations results from the dislodgement of the plated mercury droplets from the graphite substrate by the stirring action of the Lucite container.

All measurements were made with a styrene-impregnated graphite electrode which had been irradiated using a cobalt-60 source. The reference electrode was a saturated calomel electrode; connection was made to the rotating cell via a salt bridge. A platinum wire served as the counter electrode. In practice, 15 mL of water was added to the cell for all analyses.

The microprocessor was programmed for a 60 sec deaeration time for oxygen sparging, and 420-sec preconcentration plating step. The plating potential was -1.0 v. Stripping current-voltage curves were recorded on a Hewlett-Packard Model 7044 X-Y recorder for the Berkeley tap water samples.

A sample of Berkeley tap water was obtained by running the water for one to two minutes, then collecting 500 mL in a polyethylene bottle which had been cleaned and rinsed with tap water. Hydrochloric acid was added to pH 1, and the solution was permitted to equilibrate for about 48 hours. The sample was then discarded, and an additional 500 mL collected in the same manner. After 48 hours, 15 mL were added to the rotating cell, and ammonia treated sodium acetate was added dropwise to pH 4.7. Then 25µL of 0.0025 M mercury nitrate solution were pipetted in and background anodic stripping curves obtained. Known µL concentrations of Cd, Cu and Pb standards were pipetted in, and stripping curves again obtained. The peak heights were measured on an X-Y recorder, and the concentrations of the

three metals in the tap water were determined by the method of standard additions. See Figure 23. Any cadmium in the water was below the limits of detectability of the procedure used. Analysis by atomic absorption did not detect any cadmium. See Table 4.

Table 5a. Analysis of Municipal Water from Seattle, Washington;

Sample Designation	AA Values, ppb		ASV Values, ppb	
	Cu	Pb	Cu	Pb
NE 24 105NE	1000	10	---	---
7914 NE 26	680	<10	550	1.3
9850 Belfair Rd, Standing	950	<10	1100	N.D.*
9850 Belfair Rd., Running	510	<10	800	N.D.*
Taylor Creek Well 7/4	<6	<10	2.6	N.D.
Taylor Creek Well 7/13	<6	<10	1.4	N.D.
EPA Samples				
Jones Res. Running	---	---	12.4	2.3
Jones Res. Standing	---	---	1800	N.D.*
Park Pl. Standing/1st run	---	---	1000	N.D.*
Park Pl. Standing/2nd run	---	---	1000	N.D.*

Table 5b. Analysis of Tap Water from Berkeley, California

	ASV Values, µg/L		
	Cu	Pb	Cd
Tap Water Sample	22	3	<0.2

N.D.   =   Not detected
N.D.* =   Non detection likely due to solid phase amalgam formation.
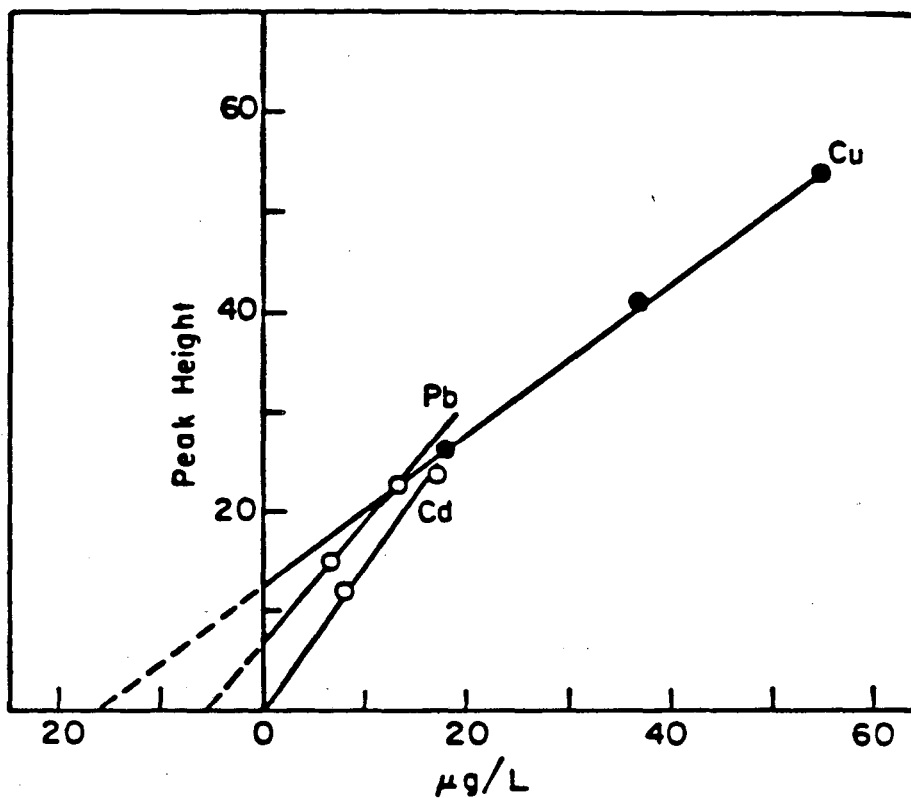
XBL818-6202

Figure 23.   Tap water, Lawrence Berkeley Laboratory, March 26, 1980.
     a)   15m: acidified tap water, 1 drop saturated NaCl solution
           4 drops 5 $\underline{M}$ NaOAc (purified), ph 4.7, 25μL 0.005 $\underline{M}$ Hg
           $(NO_3)_2$.
     b)   18.3μg/L Cu;
     c)   36.6μg/L Cu;
     d)   54.9μg/L Cu;
     e)   8.3μg/L Cd, 6.7μg/L Pb, 54.9μg/L Cu;
     f)   16.6μg/L Cd, 13.4μg/L Pb, 54.9μg/L Cu.

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