UNIVERSITY OF WASHINGTON
SEATTLE, WASHINGTON 98195

TO: Department of Energy

TYPE OF SUPPORT REQUESTED: Second year funding of Contract Number
EY-76-S-06-2225, TA 48

TITLE OF PROJECT: Trace Metal Characterization and Speciation
in Geothermal Effluent by Multiple Scanning
Anodic Stripping Voltammetry and Atomic
Absorption Analysis

PRINCIPAL INVESTIGATOR: Bruce R. Kowalski, Associate Professor
Laboratory for Chemometrics
Department of Chemistry BG-10
University of Washington
Seattle, Washington 98195

AMOUNT REQUESTED: \$40,865

DESIRED PERIOD: September 1, 1979 - August 31, 1980

UNIVERSITY OFFICE TO BE
CONTACTED REGARDING GRANT
OR CONTRACT NEGOTIATION: Grant and Contract Services
Rm 1 Administration Building, AD-24
University of Washington
Seattle, Washington 98195
Telephone: (206) 543-4043

DATE: May 25, 1979

Bruce R. Kowalski, Professor

Alvin L. Kwiram, Chairman
Department of Chemistry

Joe S. Creager, Associate Dean
College of Arts & Sciences

OFFICIAL AUTHORIZED TO
GIVE UNIVERSITY APPROVAL:

MASTER

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Department of Energy, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

Donald R. Baldwin, Director
Grant and Contract Services
1 Administration Building, AD-24

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

BUDGET
Estimated Requirements
September 1, 1979 - August 31, 1980

1. Personnel Costs		<u>\$20,472</u>
Research Associate		
12 months @ \$1,200/month	\$14,400	
Graduate Research Assistant		
6 months @ \$537/month	3,222	
Employee Benefits	2,850	
2. Equipment		-0-
3. Travel (Domestic)		<u>\$ 3,500</u>
A. Attendance at 1 scientific meeting		
(2 people, transportation and per diem)	\$ 1,500	
B. Sampling Trips (Washington and Oregon)		
10 trips to 3 sites	2,000	
(Use of University car at \$50 per trip is planned.)		
4. Miscellaneous Supplies and Services		<u>\$ 7,200</u>
Maintenance and Computer Supplies for PDP-11	\$ 550	
Reagent Chemicals, Gases and Ion Exchange Resins	2,200	
Laboratory Glassware for Trace Analysis	1,000	
ASV Electrode Materials	300	
Machine Shop Services	500	
Electronics Shop Services	450	
Maintenance for Atomic Absorption Unit	1,000	
Publication Costs	600	
Computer Center Costs	600	
5. Indirect Costs		<u>\$ 9,693</u>
55% of Salaries and Wages		
TOTAL PROJECT COSTS		<u>\$40,865</u>

PREFACE

This proposal has been funded since September 1, 1978. During this time, construction and testing of the ASV instrument has been completed and the instrument has been applied to a number of model systems to test a new method of speciation in dilute solutions (sub nanogram/ml). Results from these test cases agree with studies in the literature that used a wide range of methods but at higher concentrations. The manuscript submitted here as Appendix A gives a complete account of this work.

As a result of the principal investigator's consulting connection with the Lawrence Livermore Laboratory, a sample of geothermal effluent from the Imperial Valley Geothermal project (DOE) was obtained and analyzed. The chemical composition of the hyper saline brine sample was not at all similar to samples proposed for analysis under this contract but, on the other hand, represented a severe test of the new method. The results of the first "real sample" study also can be found in Appendix A.

At this point in the overall experimental design, we are quite ahead of schedule. The student responsible for the work found in Appendix A has received his doctorate and taken a position on the faculty at the University of California, Berkeley. Our instrument development goals have been met and no further work will be done in that direction.

Second year funding is requested so that the speciation methodology can be applied to the selected sites in the Pacific Northwest. For the remainder of the current funding period, construction of

sampling equipment is the focus. As sites become accessible, the sampling program will begin. Second year funding will allow sampling to continue until about December, 1979. Analysis will begin with the acquisition of the first samples (approximately in September) and will continue throughout the second year funding period.

The change in personnel is required as one student has graduated, another will only be available on a half-time basis, and an experimental electrochemist is required to perform the analysis. Summer support for the principal investigator is not required.

TRACE METAL CHARACTERIZATION AND SPECIATION
IN GEOTHERMAL EFFLUENT
BY MULTIPLE SCANNING ANODIC STRIPPING VOLTAMMETRY
AND ATOMIC ABSORPTION ANALYSIS

ABSTRACT

Geothermal power production has recently become important as a possible long-term energy source, particularly in the western United States. Recent studies have shown geothermal power plants to have a significant environmental impact on the ground water of the area. The heavy metals arsenic and mercury are special problems, as both are concentrated by flora and fauna exposed to the effluent waters. Because the toxicity of these and the other metallic pollutants present in geothermal effluent depends on the chemical form, or speciation, of the particular metal, any serious study of the environmental impact of a geothermal development should include studies of trace metal speciation, in addition to trace metal concentration.

This proposal details a method for determining metal speciation in dilute waters. The method, based on ion-exchange and backed by atomic absorption spectrometry and multiple scanning anodic stripping voltammetry, classifies metals as labile cations, labile anions, organically bound inert cations/anions or inorganically bound inert cations/anions. Special laboratory studies will be performed on mercury, arsenic and selenium speciation in synthetic geothermal water. The method will be applied to three known geothermal areas in Washington and Oregon, with emphasis on the speciation of mercury, arsenic and selenium in these waters. Other trace metal concentrations and speciations will also be determined.

The method is a new concept based on up-to-date knowledge on metal speciation. It uses a new technique (multiple scanning anodic stripping voltammetry - MSASV) for some of the heavy metal determinations. It is expected that the work will furnish important results on:

(1) the viability of ion-exchange sampling for trace metals in speciation work;

(2) arsenic, mercury, and selenium speciation in thermal waters;

(3) the suitability of MSASV to trace analysis in real systems;

(4) the concentration and speciation of trace metals in the three geothermally important areas in Washington and Oregon as a function of time.

INTRODUCTION

Recent events have brought both trace metal analysis and geothermal energy exploitation to the foreground in their respective areas of science. The Minimata poisonings (1) shown later to be caused by methyl mercury chloride (2), focused attention upon the effects that a trace component of the water can have, especially when it is concentrated in the food chain. Other work (3) has shown that many metals present in trace amounts also have far greater effects than was first suspected, and are thus worthy of detailed study.

Geothermal energy was long thought to be "clean", i.e., non-polluting. However, recent reports (4,5) cast doubt on this belief. Axtmann (6) found that the geothermal plant at Wakenai, New Zealand released about as much H_2S and SO_2 as a power plant, and released substantial quantities of As and Hg. These elements are now found in elevated amounts in the flora and fauna of the area. Other elements also have been implicated in geothermal "pollution", including U, Rn, and Se (4,7). Thus, the whole area of geothermal effluent deserves careful study. Because the metal's chemical form directly affects its chemical properties and its ultimate toxicity, this information is of great importance in determining the overall effect of the metal on the surroundings. The well-known differences in toxicity and behavior of Hg^{2+} and CH_3Hg^+ are a good example.

The problem, though, is that chemical form is difficult to determine. Most trace methods simply cannot tell the form of the metal. In fact, their results seldom even agree to better than an order of magnitude (8). A new approach is needed. We are proposing a new method based on the new technique of multiple scanning anodic stripping voltammetry (MSASV) and on atomic absorption spectrometry. Preliminary studies (9) using multiple scan voltammetry techniques indicate that it is far more sensitive and precise than conventional anodic or cathodic stripping techniques. We intend to use the sensitivity and precision of MSASV to analyze geothermal effluent for the major metallic components, as well as the trace heavy metals Hg, As, and Se. Our technique, when combined with ion exchange sampling, will provide information on the chemical form, or speciation, of these elements in the geothermal effluent. Additional analyses by both MSASV and AA will determine the concentration of the other trace heavy metals present in the geothermal water, notably Cu, Zn, and Pb. The ion exchange sampling system has been designed to preserve speciation information and to avoid the usual difficulties inherent in the analysis of trace impurities in nature waters.

BACKGROUND

The techniques of ion exchange and atomic absorption are rather well established. Because of this, and in view of the fact that many excellent reviews are available in the literature for each technique, only very brief summaries will be given here.

Ion Exchange In ion exchange techniques (10), the exchanger is usually an organic polymer with special, metal-binding groups (11) or an organic molecule chemically attached to an inorganic base such as silica (12). The basic principle of the ion exchange method is the selective interaction of some types of ions (or only one type of ion, in some cases) with the resin, thus effecting a separation by differential migration of ions. The exchanger can work either on an acid-base or a chelation principle. Typically, chelating resins tend to be more selective toward metal ions (13). Glass-based chelating resins can be tailored to the metals to be separated, thus allowing extreme selectivity (14). These, also, are among the most rapid exchangers available. A particularly suitable resin for both cation and anion collection has recently been described (15,16).

Advantages of a selective ion exchange system are numerous. A concentration factor is easily achieved by using a small amount of eluent. Some resins, like the one above (15), reject the more common groups I and II metal cations, thus easing AA analysis by lessening the matrix effects which such elements may cause. Most important, the ion exchange can be selective to a particular form of a metal at a given pH; i.e., a broad-spectrum anion exchanger passes cations, but holds anions. Subsequent analysis

thus reveals the exchangeable anionic constituents of the solution by this method. By combining exchange resins with complex-hydrolyzing methods and with sensitive and precise methods of analysis, a large number of metals can be analyzed accurately, and information about each metal's form can also be furnished.

Atomic Absorption One method now famous for its sensitivity and precision is atomic absorption analysis (17). Flame (e.g., 18) and nonflame (e.g., 19) methods are common. The method is reliable, fairly rapid, and precise. Applications of AA to water analysis abound (e.g., 20).

Briefly, this method consists of the following: metals, atomized by some means (e.g., a flame) are introduced into a beam of essentially monochromatic light emitted from the element whose concentration is sought. The attenuation of the beam is related to the number of atoms in the beam, and thus to the amount of that substance in the sample undergoing analysis. With simple preconcentration methods, such as ion exchange or solvent extraction, the method is suitable in the ng/ml range (19).

Anodic Stripping Voltammetry Another method ideally suited to water analysis is considerably more recent: stripping voltammetry (SV). SV, encompassing both anodic stripping voltammetry (ASV) and cathodic stripping voltammetry (CSV), is an electrochemical technique suited to the analysis of electroactive heavy metal ions in water (20). Basically, the method consists of an electrolysis step, where the species to be analyzed is deposited on the electrode, and a stripping step, where the species is

forced off the electrode. A plot of current vs. applied potential yields a peak for each species at its stripping potential. One such plot is shown in Figure I. For each peak, the peak height is proportional to the concentration of analyte producing the peak. Anodic stripping voltammetry is commonly used for metals in water, because only "labile" (free or loosely complexed metals) will deposit during the electrolysis step. This difference generates information about the chemical form of the metals in solution. Various waveforms, including linear scan (21), a.c. scan (22), differential pulse (23,24) and staircase stripping (25) have been employed in ASV. The latter two are favored at present. Although many kinds of electrodes can be used, present opinion favors the glassy carbon thin film electrode (26) due to its sensitivity (23), resolution (27), and useful lifetime (28). ASV has attracted attention lately because of its ability to determine heavy metal complexation in very dilute solutions. Stumm (29) has recently determined stability constants for Cu, Zn, Cd, and Pb species in natural water. The sensitivity of modern ASV rivals flameless AA, but ASV has demonstrated better precision (29,30).

Recent work by Florence (31,32,33) has demonstrated the utility of ASV in speciation studies of sea water. Florence demonstrated that heavy metal speciation directly influences the efficiency of extraction by chelating resins or by the usual extractant for AA, ammonium pyrrolidinedithiocarbamate (32). He found that heavy metals could not always be extracted with 100% efficiency. ASV, however, was able to determine these metals in

all cases with good precision. Chakrabarti (34) has also found ASV suitable for speciation studies on Pb, Cu, Cd, and Zn in natural waters.

Multiple Scanning Anodic Stripping Voltammetry Many recent advances in ASV have not yet been applied to natural systems. One is the development of multiple scanning anodic stripping voltammetry (MSASV). MSASV (9,35,36,37) uses the same electrodes and potential scan methods as conventional ASV but differs in that, after the reduction step, several rapid potential scans are run in succession, and the currents produced are added by computer. This is illustrated in Figure I. The background (charging) current is obtained by repeating these scans after the deposited material is removed at a suitably high anodic potential. The true faradic current is then calculated by subtraction of the normalized total background current from the normalized total signal currents. This is shown in Figure II. Conventional ASV is not usually able to produce true faradic currents free from background currents (36).

In the MSASV method, rapid anodic potential scans are performed, each with a duration of less than a second. Most of the oxidized material will remain near the electrode in the diffusion layer and will be replated when the electrode is returned to the deposition value after the scan. Repeated scans and reductions force metal ions into and out of the mercury film, and allow multiple contributions to the signal current by each ion. In theory, any waveform may be used, but work reported at present uses only linear scan stripping (9) or differential pulse strip-

ping (36). Stripping voltammetry theory predicts that high scan rates will generate large faradic currents, but it also predicts that these high scan rates will generate large charging currents (38). By experimentally measuring these currents (36), or by using sophisticated real time digital filtering techniques (39) to monitor them, the computerized MSASV system can compensate for the charging currents and thus generate only true faradic current.

At present, MSASV is in its infancy. Only three papers have appeared, and these only describe the computerized system (9,35, 36) and illustrate some of the features of the method. All used direct charging current compensation. The advantages of MSASV are apparent from these papers, however. It has improved precision and sensitivity over conventional ASV because of the removal of the charging currents, and is much faster than conventional ASV because both deposition and analysis times are shorter. With MSASV, analyses take minutes; with ASV, they could take hours. Digital filter compensation techniques (39,40) should take even less time, as they do not require the measurement of background currents as with the present form of MSASV. The MSASV technique, therefore, offers the advantages of conventional ASV (sensitivity, few matrix effects, metal speciation) with additional advantages (improved sensitivity and precision, rapid analysis).

We are presently involved in constructing an MSASV unit using a PDP-11 minicomputer dedicated to a PAR-174 potentiostat, with a high-speed synchronous rotator and vitreous carbon electrode. A versatile laboratory interface is being constructed,

and plans are underway to study the Kallman filter (39,40) as well as direct measurement to compensate for charging currents. Only one paper has appeared using the Kallman filter for real-time calculation of ASV parameters (39). The MSASV unit is supported by a grant from the Office of Naval Research. When the unit is finished and ready, it will represent the state of the art in MSASV and ASV units.

GEOTHERMAL DEVELOPMENT

In recent years, developmental studies have been initiated by many countries possessing geothermal power potential. The United States is one of these countries. Considerable time and money, both public and private, have gone into prospecting and evaluating new geothermal resource areas, mainly in the western and southwestern United States. Both geophysical and geochemical prospecting have been emphasized to supplement geological mapping of promising regions. These two prospecting methods have been refined over the past few years. Both are relatively expensive and time consuming, however. Because of the time and cost factors, only a limited number of chemical analyses can be run on each prospective geothermal site. Typically, analysis for dissolved SiO_2 and the cations Ca^{2+} , K^+ , and Na^+ are performed. These species are used as empirical indicators of the subsurface temperature in a liquid system because their solubilities (or the solubility of material from which they come) are determined by the temperature and pressure in the fluid reservoir beneath the ground (41,42,43). They are, in effect, geochemical "thermometers", accurate enough to allow considerable savings in time and money when a decision on a drill site is needed, as they are useful in eliminating less desirable sites (43). They are occasionally in error; however, due to underground mixing, or to variations in the other species in the water, particularly the anions, HCO_3^- , CO_3^{2-} , SO_4^{2-} , and F^- (44,45). Heavy metal ions also influence the "temperature" by altering the various equilibria (46,47).

Trace Metals in Geothermal Effluent

Although most of the major constituents are analyzed in a thorough study of a potential geothermal source, the minor constituents are generally neglected. Few groups have the time or equipment needed to investigate species with very small concentrations, e.g., Se, As, Cd, Hg, Pb, Cu, Zn. The analysis of water for these elements in sub ppm concentrations is difficult and does not appear at first glance to be of significant use, in view of the tiny amounts of these species. These trace contaminants, however, are of considerable importance in determining the overall environmental impact and potential cost of a geothermal development. The concentration of the major species, especially Cl^- , Na^+ , Ca^{2+} , and others, are critical in determining the uses of the geothermal effluent. They also determine the corrosion characteristics of the geothermal fluid, and thus the overall cleanup and maintenance costs involved in a geothermal plant (6). Trace contaminants may also cause significant problems, in spite of their low concentration. The trace contaminants are frequently toxic and many are efficiently concentrated by flora and fauna exposed to the effluent, or through their food sources (6). Synergistic effects (48,49), where one species (possibly a trace species) greatly affects the toxicity of a second species (possibly a major component) have been suggested. The various species probably will not concentrate to the extent that acute toxicity is evident, but they can be expected to occur at levels much higher than those found in the effluent. These levels can have deleterious effects on human health, as recent studies have

indicated (50). Examples include the effects of Cd on kidney and heart function (51). The levels of trace contaminants, their toxicity and their propensity toward bioconcentration are factors that need to be included in any environmental impact evaluation of a geothermal source development.

Trace contaminants can also have direct effects on the economics of power plant maintenance, by directly affecting the oxidizing properties of the geothermal water. Many of the transition metals are present in trace amounts in natural waters. The fact that many are excellent catalysts for many reactions involving oxygen (52), as well as the high temperature-high pressure conditions inherent in many designs utilizing geothermal fluid (53) make them important. Thus, trace metal contaminants are a factor in determining the down time of the geothermal power plant and in the relative frequency of replacement of equipment exposed to the geothermal fluid.

A third consideration involves the relative scarcity of these trace contaminants and their cost. A few, notably Ag, Au, Hg, and Cu, are relatively rare metals, and are therefore rather expensive. Others, such as As, Zn, and Pb, are more common, but as sources of high-grade ore are depleted, they will also become more costly. In some cases, the levels of trace metals are high enough now to merit collection of the metal with subsequent sale of the concentrate (54). Only measurement of the various trace contaminants would tell whether the extraction of these metals might be a profitable by-product of the geothermal venture.

In all of the discussion on trace contaminants above, one

factor not yet discussed is the overall determinator of the impact of the trace metal; its potential toxicity, catalytic and corrosion-assisting properties, and its ease in economic isolation: the actual chemical form of the individual trace metal. The chemical form, or speciation of the trace metal (or any metal, in fact) is the primary factor in determining the chemical properties of that metal. Two well-known examples are the differences in toxicity and stability of CH_3Hg^+ and Hg_2^{2+} ions (55,56), or As(III) and As(V) (57). The speciation of the various trace contaminants determines their overall importance, and is critical information in determining their potential effects, both in water quality and in turbine corrosion, as well as in potential treatment methods. In this respect, a knowledge of trace metal concentration and speciation, included with concentrations of major components (and, where possible, their speciation) would greatly assist in evaluating the potential of a prospective geothermal well. Since source conditions, and frequently the concentrations of the various species change when the geothermal source is exploited, a monitoring system that also gave information on speciation would be highly desirable. This is especially true in many of the geothermal areas now under study. Many are in water-deficient areas, such as Nevada, Idaho, and Eastern Oregon, where the development of multiple-use geothermal plants is actively being sought (58). Water from these plants, when built, would be used for irrigation or as water for cattle. Because of the danger of bioconcentration of the toxic elements usually present only as traces, the determination of the concentration and speciation of these elements in each of the various

wells is urgent. The extra costs that may be incurred in water may render the projects unfeasible. We propose to perform such a study, on a limited basis, by studying the concentration and speciation of the trace elements in three areas with geothermal potential. Special effort will be given to ones which strongly influence water quality, As, Hg, and Se. We wish to demonstrate both the feasibility of these determinations, and concurrently to generate data that we feel is of considerable value in any determination of the direction of those geothermal ventures. In addition, the work will be potentially significant for other areas involving the generation of waste water in the winning of energy, e.g., oil shale mining.

PROPOSED RESEARCH

The proposed research has two phases. The first phase consists of a detailed laboratory study of representative synthetic geothermal fluids. During this phase, we will examine the effects of pH, pE, and various metal ion activities on the speciation of As, Se, and Hg. The second phase consists of a time-based field study of three known geothermal sites in Washington and Oregon, where the laboratory results will be applied to determine metal concentration and speciation in natural geothermal waters.

Laboratory Speciation Studies

Various schemes showing metal speciation as a function of pH and pE have been published (59), but these rely on thermodynamic dissociation constants and solubilities from which the diagrams have been calculated. Experimental verification of these diagrams is generally lacking, in view of the low concentrations of metals which are present, and the extreme difficulty with which metal speciation is determined by classical means. We plan to construct diagrams relating speciation to various easily measured parameters such as pH, pE, and various other concentrations of potential ligands such as S^{2-} , Cl^{-} , CO_3^{2-} , and SO_4^{2-} . The diagrams will be generated with the aid of the MSASV technique, for the metals amenable to electroanalysis. We also plan to run atomic absorption determinations as checks throughout the procedure, and to use atomic absorption as a primary means of measurement for those trace metals not suited to electrochemical analysis. Various methods have been developed

for the metals Hg, As, and Se, using conventional ASV techniques. These elements are fairly easy to determine by atomic absorption (60,61) as well, although no speciation information is directly available by this method.

Speciation Studies on As, Se, and Hg

Previous work on arsenic by conventional ASV has shown that only As(III) is electroactive (62). Thus, by determining As(III) before and after a reduction, the relative amounts of As(III) and As(V) may be monitored. Such a measurement is a chemical determination of the pE of the solution, as the As(III)/As(V) ratio is determined by the oxidizing power of the solution (63), the amounts of each depending upon the relative stability of As(III) and As(V) species in that particular solution. The conventional ASV detection limit (62) for As(III) of 0.02 ng/ml (0.02ppb) on Au electrodes is at least as good as the atomic absorption detection limit of 1.0 ng/ml (61) using flameless atomic absorption methods, and MSASV is expected to be even more sensitive. Information on As speciation in natural waters is nonexistent. Although Raman studies of As_2O_3 solutions showed that the main species was $\text{As}(\text{OH})_3$ (63), the authors used high concentrations of As(III) to obtain data, and thus the behavior of trace amounts of As is unknown. One phase of the proposed research will be to study the speciation of As(III) in dilute solutions with various ligands including Cl^- , S^{2-} , SO_4^{2-} , and HCO_3^- . Such work is important, as As(III) is known to be concentrated in flora (6) as well as fauna (48), and has been implicated as a possible carcinogen of the esophagus and bladder (48).

Even less is known about selenium in natural waters. Se

analysis is usually ignored in view of the small concentrations of Se usually present. However, Se is effectively concentrated by plants both from soil and from water (66). It has been suggested that Se exists as H_2SeO_3 or HSeO_3^- in acidic water and as SeO_3^- or SeO_3^{2-} in basic water (7). Conventional ASV analysis of Se(IV) using Au electrodes is reported to have a detection limit of ~ 0.04 ng/ml (64,65), and to be most suitable for low concentrations, while the usual fluorescence method (67) for Se has approximately the same detection unit in ideal cases but is unable to distinguish the Se speciation. We propose to determine the speciation of Se in waters near pH 7, in the presence of the ligands Cl^- , SO_4^{2-} , and S^{2-} . This is important because selenium is an essential trace element in low concentrations. It is needed to prevent white muscle cell disease. In slightly higher concentrations, Se is quite toxic, causing kidney and liver degeneration as well as liver cancer (48).

Perhaps the most studied metal in terms of speciation is mercury, in view of its well-known toxicity (50). Several papers on the speciation of Hg have been published (59,68), most being thermodynamic work. A few model systems have also received attention, especially the $\text{HgS}|\text{S}^{2-}|\text{H}^+$ system (68). Uncertainty still exists as to the actual speciation of Hg in natural waters, as well as the transport of Hg in cinnabar and metacinnabar (68). Thermodynamic studies claim that only Hg^0 is stable in natural waters, while direct chemical studies (68) claim that HgS_2^{2-} is the predominant species. A major factor in this dispute is the inability of those techniques to allow an actual measurement of the native mercury in each of its forms; the proposed system

will allow this measurement. Thus, Hg^0 will pass through the ion exchange columns, and will not be electrochemically reduced at the MSASV electrode, while HgS_2^{2-} will be retained by the anionic resin, and will be reduced in acidic solution. By carefully controlling experimental parameters such as pH, pE, and ligand concentrations, we will be able to provide data on Hg concentrations and speciation in a variety of solutions. Conventional ASV detection limits for Hg are very good: In a KSCN supporting electrolyte as little as 10 pg of Hg (69,70) may be detected. Such sensitivity rivals flameless atomic absorption (60) and is achieved in about half of the time required for that technique (10-15 min, as opposed to 20-30 min). MSASV is expected to be more sensitive and even faster. Another report claims that CH_3HgCl may be detected at 0.5 ppb by conventional ASV using long deposition times (78.2 min). ASV can thus be used, along with either solvent extraction or ion exchange, to analyze and identify both inorganic and organic mercury.

Proposed Experimental Procedure

The work in the first phase will also emphasize the selection of suitable ion exchange columns for the proposed analysis scheme in Figure III. We plan to test chelating resins as well as the usual direct exchange resins, primarily because of the speed and selectivity that chelating resins show in trace metal exchange (16). Once the appropriate columns are selected, speciation studies will be initiated on Hg, Se, and As. The influence of pH and pE will be investigated in detail. Effects of the ligands on the trace metals naturally present in geothermal systems (Cl^- , SO_4^{2-} , S^{2-} , and HCO_3^-) will be determined.

Although ion exchange columns have seen only limited use in trace metal analysis of natural waters (primarily in x-ray fluorescence) (71,72), they possess several features which make them attractive for general trace metal analysis, and especially for trace metal speciation.

Because the ion exchanger actually interacts with the various species in solution, one is able to selectively absorb any one species or a given class of species, at least in theory. In practice, various separations can be achieved by tailoring the form of the exchanger to the separation, e.g., Hg^{2+} from other cations by R-SH (73), or by choosing the solvent characteristics so that only the elements of interest are eluted. A suitable weak base anion exchanger thus will only exchange with the anionic species present in the water, all other species pass freely, and the cationic species in the eluent from the anion exchanger may be absorbed onto a suitable cation exchanger. Unabsorbed species, such as organic complexes of metals and inorganic colloidal species pass both columns. Thus, analyses of each column provide information on the general form of each metal in solution, namely whether it is of anionic or cationic form in water. The eluent will be chemically altered (e.g., acid hydrolysis of all complexes, both inorganic and organic) and photochemically altered (photochemical destruction of organic complexes), and the resultant solution either analyzed directly or passed through another set of columns to absorb the newly liberated ions. Analyses of these yield information on the amounts of metal bound in neutral inorganic and organic complexes. The scheme of analysis is detailed in Figure III. This scheme

allows determination of metals in four classes:

- 1) labile (non-complexed or loosely bound) cations
- 2) labile anions
- 3) organically bound species not resin-bound anions and cations
- 4) inorganically bound species not resin-bound anions and cations

In favorable cases, ASV can be used to determine the amounts of ASV "labile" (+) and ASV "inert" specie in each class, giving as many as eight categories for the specie in water.

The approach combining ion exchange, AA, and MSASV, takes advantage of the favorable properties of modern ion exchanges. Metal speciation is a difficult task, particularly in the case of trace metals. All stresses (including changes in temperature, pH, pE, and pCO_2) change the overall equilibrium, and thus alter the amounts (and perhaps form) of the various specie in solution. Even storage of an unacidified sample changes the speciation, because metals are absorbed onto and desorbed from the container walls. This either forces field analysis, a task which is quite formidable in the case of trace analysis, or some method of "locking" the various metals into a fixed place until they can be analyzed under controlled conditions. This latter choice is exactly the purpose of the ion exchange resins. The resins "lock" the metals into one or more of four broad categories:

(+) Here, "labile" means reducible at the ASV electrode, and subsequently stripped out. Lability depends upon the dissociation constant of the complex and upon the plating potential used in the experiment.

cation, anion, organic complex, or inorganic complex. More categories could be imagined, but this would unnecessarily complicate the analysis. The resins also insure that no losses of metal occur on transport and storage, as the metals are found. Further, they eliminate the need to transport large volumes of water, thus allowing the collection of large numbers of samples, so that various sophisticated statistical techniques may be brought to bear on the system after the analyses are completed (74). They also can effectively eliminate matrix effects so common in trace metal analysis (e.g., in Se analysis by non-flame AA (19)) by discriminating against major constituents such as Na^+ . Their use thus improves precision by lowering the background caused by interfering metals. They also improve precision by concentrating the trace element to be analyzed. Further, by the correct choice of the eluting solution, each element of interest can be determined under predetermined optimum conditions, indicating another improvement in precision. One can use buffers which elute only the species of interest, and then adjust the solution conditions to obtain the best precision without fear of affecting the analysis of the other species present in the original natural water, as they are still held on the column. Sensitive analytical techniques like flameless AA and MSASV are still needed, however, because large sample volumes are needed to concentrate trace species by ion exchange. The method is versatile, as one can choose the resins to suit the particular types of species involved; thus, one may imagine, in addition to the application of the proposed system to geo-

thermal metal speciation, applications for the proposed scheme in the metal speciation of saline water, industrial waste water, as well as oil shale process effluent.

The proposed system also avoids two problems associated with trace metal speciation. The ion system will not drastically upset the water equilibrium by removing free ions from solution, and replacing them with more common (e.g., Cl^- or Na^+) ions. Experiments in sea water (32) show that complexed ions undergo very slow exchange and are not absorbed by chelating ion exchange resins. Because of this fact, an MSASV ion exchange-based scheme will be able to discriminate metal speciation, while other methods, based on analysis of radiotracer-spiked water, will not (32,75).

Another problem in trace metal analysis is the presence of trace impurities in the reagents. Occasionally, they are found in amounts greater than those present in the analyte. Ion exchange resins may be purified to ppb levels fairly easily (76). Such treatment insures that background levels of each element on the resins are small. After elution, the element to be analyzed has been concentrated dramatically, and the trace impurities present in modern ultrapure reagents (77) are not the problem that they would be without the preconcentration step.

Various methods of analysis are applicable to the scheme given above. For example, X-ray fluorescence (72) could be used directly. This has previously been the method of choice. We propose to use two very sensitive methods to analyze the eluent from the resins: flameless atomic absorption and anodic

stripping voltammetry. By using two sensitive methods, we will generate an internal check on the methods of analysis, and avoid the pitfalls associated with having the results of only one method of analysis on which to base conclusions. The study will therefore also serve as a direct comparison between the two methods, although with the preconcentration step, neither should be taxed too severely. It will, however, show the suitability of each to the ion exchange isolation/preconcentration/speciation scheme, and will therefore be of considerable later use. Only a few studies comparing AA and ASV have appeared (30), and they do not compare modern ASV with flameless AA.

Most lab work will be spent on observing the behavior of common trace metal contaminants found in geothermal waters, with special emphasis put on observing their interaction with common ligands also found in geothermal waters. Copper, mercury, arsenic, and selenium are of special interest in view of their known toxicity (48), and presence in geothermal waters (78). Ligands will include sulfate, chloride, bicarbonate, and fluoride, all common anions in geothermal waters (78). Some work is planned using organic ligands, such as glycine, but no thorough studies will be performed using these, as organic species apparently are uncommon in geothermal fluids (78).

Field Studies at Geothermal Sites

Field studies on three geothermal sites will encompass the second phase of work.

The first site chosen is Sulfur Hot Springs, Washington (48° 07' N, 121° 11.7' W). In view of its proximity to Seattle, its predicted subsurface temperature of 155-199° (79), and the

apparent lack of detailed chemical analysis of trace constituents in the spring, we feel it is an ideal testing ground for the method proposed here. The geology of the area is known (80), and the springs are of possible geothermal value, despite their location in a wilderness area (79). They are more suited to scientific study than the more familiar (and popular) Kennedy Hot Springs.

The second site is McCredie Hot Springs, Oregon ($43^{\circ} 40' N$, $122^{\circ} 14.1' W$). This is a potentially valuable geothermal site with subsurface temperatures of $\sim 160^{\circ}$ (79). Chemical analyses of this site have been done, but they are substantially incomplete (81,82). Because the area around this spring is water-deficient (83), this water would be desired for irrigation and other uses. The previously reported analyses (81,82) will serve as a check on our scheme. In addition, the ground water in the area is unusually high in arsenic (82).

The third site is the Hunter Hot Springs, Oregon ($42^{\circ} 12.0' N$, $120^{\circ} 21.6' W$). Analyses of the various springs in this area are incomplete, but the area has some geothermal potential (79), as liquid temperatures of $\sim 160^{\circ}$ have been observed. It is of interest to note that these springs are presently used to heat a spa in the area. These springs, however, are known (82) to contain As, Hg, and Se in moderate amounts. If other sites are of interest to the DOE, these could be added to or substituted for the ones mentioned above.

For each site, analyses will be made over a period of time, to determine the time variation, if any, of metal speciation. Such a determination is of more utility than a single analysis

based on one grab sample. The present plan is to make two analyses per month for ten months.

The sampling methods used will depend upon the actual site sampled. In all cases, modern E.P.A. sampling techniques developed for geothermal sources (84) will be used to minimize contamination and to insure representative sampling. Samples will be pressure-filtered under nitrogen at the site through 0.1 μ m filters, and passed through the ion exchange columns. Irradiation by portable u.v. light, and acidification will each be followed by passage through other ion exchange columns. For both the raw and filtered water, pH, pE, alkalinity, and temperature will be measured. Ion selective electrodes will be used to measure certain species (e.g., F^- , S^{2-}) in the filtered water before and after ion exchange, as a check on the procedure. Columns will then be cooled and transported to the laboratory for immediate analysis.

Time of Project

This project is expected to require three years. The first year will be spent on the development of the ion-exchange scheme. The next two years will be spent both on further laboratory speciation work, and on sampling the three sites.

Possible Extensions of Work

Further work on metal speciation using the ion exchange scheme above can easily be imagined. Radiotracer studies could be performed to study exchange rates in natural waters either geothermal or other waters. Attempts could also be made to implement the scheme in other areas where metal speciation is important, for example industrial or process effluent.

Facilities Available

We presently are constructing the multiple scanning ASV mentioned earlier. It consists of a PDP-11/05 processor with RX01 Disk Unit and 24K memory interfaced via a custom-designed interface unit to a modified PAR 174 potentiostat (on loan to us from the department). This instrument may not be continuously available, and we therefore are requesting the purchase of another potentiostat. A Pine Instruments Co. rotator is used to hold a glassy carbon electrode. Construction will be complete by January, 1977.

We also own a Perkin Elmer 303 atomic absorption unit, with a HGA 2000 carbon furnace, along with various hollow cathode lamps. This instrument is also being interfaced to the PDP-11. Our ion-selective electrode equipment consists of a Beckman 4500 digital pH meter, which is suitable for precise pX work.

We foresee a need for a potentiostat and an X-Y recorder. The ones we now use are on loan, and may not be available for the extended periods required for this project. We, therefore, have included them in our listing of estimated requirements.

We have also secured the services of Dr. Gary D. Christian of this department as a technical adviser. Dr. Christian is highly experienced in both electrochemical and spectroscopic techniques in trace analysis. A letter detailing this arrangement is included in the Appendix.

FIGURE I
VOLTAGE - TIME CURVE FOR MSASV

- (1) Electrolysis, or deposition, step.
- (2) Stripping step, with repeated rapid scans.
- (3) Cleaning step, to remove metals from electrode surface.
- (4) Background measurement step, for experimental charging current compensation.*

* MSASV using the Kalman filter method requires only steps (1) and (2).

FIGURE II
CURRENT-VOLTAGE CURVES FOR MSASV

- (1) Analytical Curves for each of four rapid scans. No background correction.
- (2) Background scans run after anodic polarization of electrode.
- (3) Curve resulting from normalized sum of curves in (1) corrected by removal of the normalized sum of curves in (2). Here, peak height is proportional to analyte concentration.

FIGURE III
PROPOSED ANALYSIS SCHEME

- (1) Here, water is untreated. All exchangeable complexes and free ions are absorbed on the columns. Others pass through.
- (2) Here, organic complexes are destroyed. Inert inorganic complexes pass through.
- (3) This process gives total ions present in water. All complexes are destroyed, and ions are absorbed onto the columns.
- (4) This sample serves as a check, and provides information on the effects of storing samples rather than using ion exchange.

* Later, the absorbed species are stripped from the columns and analyzed. The particulates are dissolved and analyzed as well.

REFERENCES

- (1) P. H. Abelson, Science, 169, 3 (1970).
- (2) L. T. Kurland, S. N. Faro and H. S. Siedler, World Neurologist, 1, 320 (1960).
- (3) "Environmental Geochemistry in Health and Disease", Geol. Soc. Amer. Memoir 123 (1971).
- (4) T. F. Gesell and J. A. S. Adams, Science, 189, 328 (1975).
- (5) R. C. Axtmann, Science, 189, 330 (1975).
- (6) R. C. Axtmann, Science, 187, 795 (1975).
- (7) Y. Uzumasa, Chemical Investigations of Hot Springs in Japan, Tsukiji Shokan, Tokyo (1965).
- (8) D. Hume, Ad. Chem. Ser. ACS, 147, 1 (1975).
- (9) D. Jagner and L. Kryger, Anal. Chim. Acta, 80, 255 (1975).
- (10) H. F. Walton, Anal. Chem., 48, 52R (1976).
- (11) T. Baltakmens, Anal. Chem., 47, 1147 (1975).
- (12) K. F. Sugawara, H. H. Weetall, and D. G. Shucker, Anal. Chem., 46, 489 (1974).
- (13) J. Inczédy, Analytical Applications of Ion Exchanges, A. Pall, trans., Pergamon, Oxford, 1966, pp. 346-396.
- (14) D. M. Hercules, L. E. Cox, S. Onisick, G. D. Nichols and J. C. Carver, Anal. Chem., 45, 1973 (1973).
- (15) D. B. Leyden and G. H. Luttrell, Anal. Chem., 47, 1612 (1975).
- (16) D. E. Leyden, G. H. Luttrell, W. K. Nonidez and D. B. Werho, Anal. Chem., 48, 67 (1976).
- (17) G. M. Hieftje, D. R. deOlivares, and T. R. Copeland, Anal. Chem., 48, 142R (1976).
- (18) G. Lunde and P. E. Paus, Anal. Lett., 7, 363 (1974).
- (19) E. L. Henn, Anal. Chem., 47, 428 (1975).
- (20) T. R. Copeland and R. K. Skogerboe, Anal. Chem., 46, 1257A (1974).
- (21) G. Colovos, G. S. Wilson, and J. Moyers, Anal. Chim. Acta, 64, 457 (1973).

- (22) W. L. Underkofler and I. Shain, Anal. Chem., 37, 2699 (1965).
- (23) T. R. Copeland, J. H. Christie, R. A. Osteryoung and R. K. Skogerboe, Anal. Chem., 45, 2171 (1973).
- (24) H. Blutstein and A. Bond, Anal. Chem., 48, 759 (1976).
- (25) V. Eisner, J. Turner and R. A. Osteryoung, ONR Tech Report No. 5, February, 1976.
- (26) T. M. Florence, J. Electroanal. Chem., 27, 273 (1970).
- (27) G. E. Bately and T. M. Florence, J. Electroanal. Chem., 55, 23 (1974).
- (28) T. M. Florence and Y. J. Farrar, J. Electroanal. Chem., 51, 191 (1974).
- (29) H. Bilinshi, R. Huston and W. Stumm, Anal. Chim. Acta, 84, 157 (1976).
- (30) R. F. Coleman, Anal. Chem., 46, 989A (1974).
- (31) T. M. Florence and G. E. Bately, Talanta, 22, 201 (1975).
- (32) T. M. Florence and G. E. Bately, Talanta, 23, 179 (1976).
- (33) G. E. Bately and T. M. Florence, Anal. Lett., 9, 379 (1976).
- (34) R. D. Guy, C. L. Chakrabarti and L. L. Schramm, Can. J. Chem., 53, 661 (1975).
- (35) L. Kryger, D. Jagner, H. J. Skov, Anal. Chim. Acta, 78, 241 (1975).
- (36) L. Kryger and D. Jagner, Anal. Chim. Acta, 78, 251 (1975).
- (37) Q. V. Thomas, L. Kryger and S. Perone, Anal. Chem., 48, 761 (1976).
- (38) W. T. DeVries and E. Van Dalen, J. Electroanal. Chem., 14, 315 (1967).
- (39) P. F. Seelig and H. N. Blount, Anal. Chem., 48, 252 (1976).
- (40) A. E. Bryson, Jr. and Y. C. Ho, Applied Optimal Control, Blaisdell, Waltham, Mass., 1969, Ch. 12.
- (41) R. O. Fournier and J. J. Rowe, Amer. J. Sci., 264, 685 (1966).
- (42) R. O. Fournier and A. H. Truesdell, Geochim. Cosmochim. Acta, 37, 1255 (1973).
- (43) D. E. White, Geothermics, special issue 2, V. 1, 58 (1970).

- (44) R. O. Fournier, D. E. White, and A. H. Truesdell, J. Res. U.S. Geol. Surv., 2, 259 (1974).
- (45) R. H. Mariner, T. S. Presser, and W. C. Evans, U.S. Geol. Surv. Open File Rept., 76-480, July, 1976.
- (46) A. J. Ellis, Bull. Volc. 29, 575 (1966).
- (47) A. J. Ellis, Geochim. Cosmochim. Acta, 32, 1356 (1968).
- (48) J. J. Dulka and T. H. Risby, Anal. Chem., 48, 640A (1976).
- (49) J. K. Buchard, J. Air Pollut. Control Assoc., 24, 1141 (1974).
- (50) L. Dunlap, Chem. Eng. News, 22, July, 5 (1971), among others.
- (51) J. W. Berg and F. Burbank, in Geochemical Environment in Relation to Health and Disease, H. C. Hopps and H. L. Cannon, Eds., Anal. N. Y. Acad. Sci., 199, 249 (1972).
- (52) T. Marshall and W. R. Braithwaite, in Geothermal Energy, H.C.H. Armstead, Ed., UNESCO, Paris, 1973, pp. 151-160.
- (53) B. Wood, in Geothermal Energy, H.C.H. Armstead, Ed., UNESCO, Paris, 1973, pp. 109-121.
- (54) B. Lindal, in Geothermal Energy, H.C.H. Armstead, Ed., UNESCO, Paris, 1973, pp. 135-148.
- (55) H. A. Schroeder, Science News, 100, 63 (1971).
- (56) E. R. Plunkett, Handbook of Industrial Toxicology, Chemical Rubber Publishing Co., New York, 1966.
- (57) The Merck Index, 8th Ed., P. G. Stecker, Ed., Merck and Co., Rahway, N. J., 1968.
- (58) W. Youngquist, Geothermal Energy, 4(5), 28 (1976).
- (59) J. D. Hem, U.S. Geol. Surv. Prof. Paper 713, 19 (1970), for example.
- (60) J. Olafsson, Anal. Chim. Acta, 68, 207 (1974), among many others.
- (61) K. C. Tam, Environ. Sci. Technol., 8, 734 (1974), among others.
- (62) G. Forsberg, J. W. O'Laughlin, R. G. Megargle, and S. R. Koirttyohann, Anal. Chem., 47, 1586 (1976).
- (63) T. M. Loehr and R. A. Plane, Inorg. Chem., 7, 1708 (1968).
- (64) R. W. Andrews and D. C. Johnson, Anal. Chem., 47, 294 (1975).

- (65) R. W. Andrews and D. C. Johnson, Anal. Chem., 48, 1056 (1976).
- (66) O. Beath, J. H. Draize, H. F. Eppson, C. S. Gilbert, O. C. McCreary, J. Amer. Pharm. Assoc., 23, 9497 (1934).
- (67) U. S. Dept. of the Interior, "Environmental Protection Agency Methods for Chemical Analysis of Water and Gases", 1970.
- (68) E. A. Jenne, U.S. Geol. Surv. Prof. Paper 713, 40 (1970).
- (69) M. Stulilcova and F. Vydra, J. Electroanal. Chem., 42, 127 (1973).
- (70) R. E. Allen, Ph.D. Dissertation, Iowa St. Univ., 1974.
- (71) F. C. Smith, J. M. Mathiesen, O. Masi, and T. M. Spittler, Amer. Lab., Dec., 1975.
- (72) F. C. Smith and J. M. Mathiesen, Finnigan Applications Tip QM40, Feb., 1975.
- (73) H. S. Miller and G. E. Kline, J. Amer. Chem. Soc., 73, 2741 (1951).
- (74) Our laboratory has a complete package (ARTHUR) developed for detailed statistical analysis.
- (75) J. P. Riley and D. Taylor, Anal. Chim. Acta, 40, 479 (1968).
- (76) E. D. Moorhead and P. H. Davis, Anal. Chem., 46, 1879 (1974).
- (77) D. E. Robertson, in Ultrapurity, Methods and Techniques, M. Zief and R. Speights, Eds., Dekker, New York, 1972, pp. 207-253.
- (78) "Data of Geochemistry", 6th Ed., Chapt. F, U.S. Geol. Surv. Prof. Paper 440-F, 1963.
- (79) J. L. Renner, D. E. White and D. L. Williams, U.S. Geol. Surv. Circular 726, 5 (1975).
- (80) Geologic Map of Glacier Pk. Quadrangle, Map 473, U.S. Geol. Surv., 1965.
- (81) R. H. Mariner, J. B. Rapp, L. M. Willey, and T. S. Presser, U.S. Geol. Surv. Open File Rept., March, 1974.
- (82) R. H. Mariner, T. S. Presser, J. B. Rapp, and L. M. Willey, U.S. Geol. Surv. Open File Rept., August, 1975.
- (83) "Summary Report of Oregon's Long-Range Requirements for Water", State Water Resources Board, Salem, Oregon, 1969.
- (84) Environmental Protection Agency Conference on Geothermal Monitoring, Las Vegas, 1975.

Bruce R. Kowalski is a Professor of Chemistry (effective 9/16/79) at the University of Washington. After receiving his Ph.D. from the University of Washington in 1969, he applied pattern recognition techniques to several areas of petroleum research for the Shell Development Company in Emeryville, California and Houston, Texas. In 1971 he joined the General Chemistry Division at the Lawrence Livermore Laboratory and in 1972 became an Assistant Professor at Colorado State University. He then moved to Seattle to the University of Washington where he has been since December, 1973. His research interests include the development and application of chemometric methods primarily for the analysis of analytical data and to the relationship between molecular structure and biological activity. Additionally, he is investigating the use of improved chelating agents for trace metal analysis.

FACULTY ACTIVITY SUMMARY

Professional Society or Governmental Service Activities

Society for Applied Spectroscopy, Chairman of Local Section

Executive Committee Member and Member at Large, Division of Computers in Chemistry,
American Chemical Society

Chemometrics Society Cofounder

Journal of Chemical Information and Computer Sciences, past Member of Advisory
Board

Advisor to Franklin Institute, Philadelphia, Pennsylvania

National Science Foundation, Member of Directorate for Research Applications

Analytical Letters, Assistant to the Editor, Chemometrics Section

Editorial Advisory Board of American Chemical Society Monograph Series

Consultant to Lawrence Livermore Laboratory (DOE)

Consultant to Boeing Company

MEMBERSHIPS

American Chemical Society

American Association for the Advancement of Science

The New York Academy of Sciences

The Society of Sigma Xi

The Society of Sigma Zeta

The Pattern Recognition Society

GOVERNMENTAL SERVICE

Host of Office of Naval Research Computers in Chemistry Meeting, May 20, 1976

BIBLIOGRAPHY

I. Research Publications

1. B. R. Kowalski and T. L. Isenhour, An Analytical Function for Describing Gamma-Ray Pulse-Height Distributions in NaI(Tl) Scintillators, *ANALYTICAL CHEMISTRY*, 40, 1186 (1968).
2. P. C. Jurs, B. R. Kowalski and T. L. Isenhour, Computerized Learning Machines Applied to Chemical Problems. Molecular Formula Determination from Low Resolution Mass Spectrometry, *ANALYTICAL CHEMISTRY*, 41, 21 (1969).
3. B. R. Kowalski and T. L. Isenhour, X-Ray Emission Analysis of High Atomic Number Elements: A New Excitation Source Using Monoenergetic 477 keV γ -Rays from the $^{10}\text{B}(n,\alpha)^7\text{mLi} \rightarrow ^7\text{Li}$ Reaction, *APPLIED SPECTROSCOPY*, 23, 1 (1969).
4. P. C. Jurs, B. R. Kowalski, T. L. Isenhour and C. N. Reilley, Computerized Learning Machines Applied to Chemical Problems. Investigation of Convergence Rate and Predictive Ability of Adaptive Binary Pattern Classifiers, *ANALYTICAL CHEMISTRY*, 41, 690 (1969).
5. B. R. Kowalski, P. C. Jurs, T. L. Isenhour and C. N. Reilley, Computerized Learning Machines Applied to Chemical Problems. Multicategory Pattern Classification by Least Squares, *ANALYTICAL CHEMISTRY*, 41, 695 (1969).
6. B. R. Kowalski, T. L. Isenhour and R. E. Sievers, Ultra-Trace Mass Spectrometric Metal Analysis Using Heptafluorodimethyl-octanedione Chelates, *ANALYTICAL CHEMISTRY*, 41, 998 (1969).
7. B. R. Kowalski, P. C. Jurs, T. L. Isenhour, and C. N. Reilley, Computerized Learning Machines Applied to Chemical Problems. Interpretation of Infrared Spectrometry Data, *ANALYTICAL CHEMISTRY*, 41, 1945 (1969).
8. P. C. Jurs, B. R. Kowalski, T. L. Isenhour and C. N. Reilley, An Investigation of Combined Patterns from Diverse Analytical Data Using Computerized Learning Machines, *ANALYTICAL CHEMISTRY*, 41, 1949 (1969).
9. P. C. Jurs, B. R. Kowalski, T. L. Isenhour and C. N. Reilley, Computerized Learning Machines Applied to Chemical Problems. Molecular Structure Parameters from Low Resolution Mass Spectrometry, *ANALYTICAL CHEMISTRY*, 42, 1387 (1970).
10. B. R. Kowalski, and C. A. Reilly, Nuclear Magnetic Resonance Spectral Interpretation by Pattern Recognition, *JOURNAL OF PHYSICAL CHEMISTRY*, 75, 1402 (1971).
11. B. R. Kowalski and C. F. Bender, PATTERN RECOGNITION: A Powerful Approach to Interpreting Chemical Data, *JOURNAL OF THE AMERICAN CHEMICAL SOCIETY*, 94, 5632 (1972).
12. B. R. Kowalski and C. F. Bender, The K-Nearest Neighbor Classification Rule (Pattern Recognition) Applied to Nuclear Magnetic Resonance Spectral Interpretation, *ANALYTICAL CHEMISTRY*, 44, 1405 (1972).
13. B. R. Kowalski, T. F. Schatzki and F. H. Stross, Classification of Archaeological Artifacts by Applying Pattern Recognition to Trace Element Data, *ANALYTICAL CHEMISTRY*, 44, 2176 (1972).

I. Research Publications (continued)

14. C. F. Bender and B. R. Kowalski, Construction of Optimum Variables for Spectral Interpretation (Pattern Recognition), ANALYTICAL CHEMISTRY, 45, 590 (1973).
15. B. R. Kowalski and C. F. Bender, PATTERN RECOGNITION: II. Linear and Nonlinear Methods for Displaying Chemical Data, JOURNAL OF THE AMERICAN CHEMICAL SOCIETY, 95, 686 (1973).
16. C. F. Bender, H. D. Shepherd, and B. R. Kowalski, Alternate Representation of Mass Spectra for the Spectral Identification Problem (Pattern Recognition), ANALYTICAL CHEMISTRY, 45, 1405 (1972).
17. B. R. Kowalski and C. F. Bender, The Hadamard Transform and Spectral Analysis by Pattern Recognition, ANALYTICAL CHEMISTRY, 45, 2334 (1973).
18. C. F. Bender and B. R. Kowalski, Multiclass Linear Classifier for Spectral Interpretation (Pattern Recognition), ANALYTICAL CHEMISTRY, 46, 294 (1974).
19. B. R. Kowalski, and C. F. Bender, The Application of Pattern Recognition to Screening Prospective Anti-Cancer Drugs. Adenocarcinoma 755 Biological Activity Test, JOURNAL OF THE AMERICAN CHEMICAL SOCIETY, 96, 916 (1974).
20. B. R. Kowalski, Pattern Recognition Techniques for Predicting Performance, CHEMICAL TECHNOLOGY, p. 300 (May, 1974).
21. B. R. Kowalski, Pattern Recognition, CANCER CHEMOTHERAPY REPORTS, Part 2, Vol 4, No. 4 (1974).
22. B. R. Kowalski and C. F. Bender, Solving Chemical Problems with Pattern Recognition, DIE NATURWISSENSCHAFTEN, 62, 10 (1975).
23. D. L. Duewer and B. R. Kowalski, Forensic Data Analysis by Pattern Recognition. Categorization of White Bond Papers by Elemental Composition, ANALYTICAL CHEMISTRY, 47, 526 (1975).
24. D. L. Duewer, B. R. Kowalski and T. F. Schatzki, Source Identification of Oil Spills by Pattern Recognition Analysis of Natural Elemental Composition, ANALYTICAL CHEMISTRY, 47, 1573 (1975).
25. J. R. Koskinen and B. R. Kowalski, Interactive Pattern Recognition in the Chemical Laboratory, J. CHEM INFOR & COMP SCI, 15, 119 (1975).
26. B. R. Kowalski, Measurement Analysis by Pattern Recognition, ANALYTICAL CHEMISTRY, 47, 1152A (1975).
27. B. R. Kowalski, Chemometrics: Views and Propositions, J. CHEM INFOR & COMP SCI, 15, 201 (1975).
28. B. R. Kowalski and C. F. Bender, An Orthogonal Feature-Selection Method, PATTERN RECOGNITION, 8, 1 (1976).
29. D. L. Duewer, B. R. Kowalski and J. L. Fasching, Improving the Reliability of Factor Analysis of Chemical Data by Utilizing the Measured Analytical Uncertainty, ANALYTICAL CHEMISTRY, 48, 2002 (1976).

I. Research Publications (continued)

30. B. E. H. Saxberg, D. S. Blom, and B. R. Kowalski, A Flexible Interactive Graphics System for Searching Atom Connectivity Matrices, J. CHEM. INFOR. & COMPT. SCI. 16, 233 (1976).
31. B. R. Kowalski and D. L. Duewer, Pattern Recognition Programs: Applications to Oil Identification, IEEE Proceedings on the Workshop on Pattern Recognition Applied to Oil Identification, Catalog No. 76CH1247-6C.
32. J. R. McGill and B. R. Kowalski, Recognizing Patterns in Trace Elements, JOURNAL OF APPLIED SPECTROSCOPY, 31, 87 (1977). Feature Article.
33. J. R. McGill and B. R. Kowalski, Intrinsic Dimensionality of Smell, ANALYTICAL CHEMISTRY, 49, 596 (1977).
34. J. R. McGill and B. R. Kowalski, Classification of Mass Spectra via Pattern Recognition, J. CHEM. INFOR. COMPT. SCI., 18, 52 (1978).
35. W. O. Kwan and B. R. Kowalski, Classification of Wines by Applying Pattern Recognition to Chemical Composition Data, JOURNAL OF FOOD SCIENCE, 43, 1320 (1978).
36. D. L. Duewer, B. R. Kowalski, K. J. Clayson and R. J. Roby, Elucidating the Structure of Some Clinical Data, COMPUTERS AND BIOMEDICAL RESEARCH, 11, 567 (1978).
37. B. E. H. Saxberg, D. L. Duewer, J. L. Booker, and B. R. Kowalski, Pattern Recognition and Blind Assay Techniques Applied to Forensic Separation of Whiskies, ANAL. CHIMICA ACTA, 103, 201 (1978).
38. W. O. Kwan and B. R. Kowalski, Mass Spectrometric Analysis of Iron Using a Clathrochelate as a Specific Reagent, CANADIAN JOURNAL OF SPECTROSCOPY, 23, 183 (1978).
39. J. C. Boyd, J. W. Lewis, J. J. Marr, A. M. Harper and B. R. Kowalski, Effect of Atypical Antibiotic Resistance on Microorganism Identification by Pattern Recognition, JOURNAL OF CLINCIAL MICROBIOLOGY, 8, 689 (1978).
40. B. R. Kowalski, Chemometrics, CHEMISTRY AND INDUSTRY, November 18, 1978, 882.
41. B. R. Kowalski, Analytical Chemistry: The Journal and the Science in the 1970's and Beyond, 50th Anniversary Issue, ANALYTICAL CHEMISTRY, 50, 1309A (1978).
42. M. Sjöström and B. R. Kowalski, A Comparison of Five Pattern Recognition Methods Based on the Classification Results From Six Real Data Bases, ANAL. CHIMICA ACTA, 112, 11, (1979).
43. J. L. Fasching, D. L. Duewer and B. R. Kowalski, A New Approach to Pattern Recognition Utilizing Uncertainties in Analytical Measurements, ANALYTICAL CHEMISTRY, in press.
44. J. D. S. Danielson, S. D. Brown, C. J. Appellof and B. R. Kowalski, A Low-Cost General-Purpose Data Acquisition and Control System for the PDP-11 Minicomputer, CHEMICAL, BIOCHEMICAL AND ENVIRONMENTAL INSTRUMENTATION, in press.
45. B. E. H. Saxberg and B. R. Kowalski, The Generalized Standard Addition Method, ANALYTICAL CHEMISTRY, in press.

I. Research Publications (continued)

46. S. D. Brown and B. R. Kowalski, Minicomputer-Controlled, Background-Subtracted Anodic Stripping Voltammetry: Evaluation of Parameters and Performance, ANAL. CHIMICA ACTA, in press.
47. A. M. Harper and B. R. Kowalski, Individualized Differences Scaling, The Analysis of Independent Sets of Measurements: Application to the Modelling of the Impact of Mine Activities on Water Quality, ANALYTICAL LETTERS, accepted for publication.
48. M. Moran and B. R. Kowalski, Image Analysis in Analytical Chemistry, Special Report Section, ANALYTICAL CHEMISTRY, accepted for publication.
49. R. W. Gerlach, B. R. Kowalski, and H. Wold, Partial Least Squares Path Modelling with Latent Variables, submitted to SCIENCE.
50. M. A. Sharaf, B. Weinstein, and B. R. Kowalski, Construction of Phylogentic Trees by Pattern Recognition Procedures, submitted to SCIENCE.
51. S. D. Brown and B. R. Kowalski, Pseudopolarographic Determination of Metal Complex Stability Constants in Dilute Solution by Rapid Scan Anodic Stripping Voltammetry, submitted to ANALYTICAL CHEMISTRY.
52. W. O. Kwan, R. K. Skogerboe and B. R. Kowalski, Pattern Recognition Analysis of Elemental Data: Wines of Vitis Vinefera Variety Pinot Noir from France and the United States, submitted to JOURNAL OF AGRICULTURAL AND FOOD CHEMISTRY.

II. Books, Chapters in Books, Monographs

1. T. L. Isenhour, B. R. Kowalski and R. E. Sievers, Ultratrace Metal Analysis by Mass Spectrometry of Volatile Metal β -Diketonates, in "Developments in Applied Spectroscopy", Vol. 8, Plenum Press, 1970.
2. B. R. Kowalski, Pattern Recognition in Chemical Research, in "Computers in Chemical and Biochemical Research", Vol. 2, Academic Press, C. E. Klopfenstein & C. L. Wilkins, Ed., 1974.
3. T. L. Isenhour, B. R. Kowalski, and P. C. Jurs, Applications of Pattern Recognition to Chemistry, in "Critical Reviews in Analytical Chemistry", Louis Meites, Ed., Vol. 4, Issue 1, page 1, 1974.
4. B. R. Kowalski, Measurement Analysis by Pattern Recognition, in "Modern Classics in Analytical Chemistry", Vol. 2, A. L. Beilby, Ed., American Chemical Society Collection.
5. B. R. Kowalski, Pattern Recognition Techniques, in "A History of Analytical Chemistry", H. A. Laitinen and G. W. Ewing, Ed., American Chemical Society, 1977.
6. G. Kirschner and B. R. Kowalski, The Application of Pattern Recognition to Drug Design, in "Drug Design", E. J. Ariëns, Ed., Academic Press, Vol. VIII, Chapt. 2, 1977.
7. Chemometrics: Theory and Application, B. R. Kowalski, Editor, American Chemical Society Symposium Series No. 52, 1977.

Chapters in Chemometrics: Theory and Application:

8. A. M. Harper, D. L. Duewer, B. R. Kowalski and J. L. Fasching, ARTHUR And Experimental Data Analysis: The Heuristic Use of a Polyalgorithm.
9. J. R. Koskinen and B. R. Kowalski, Analysis of the Electron Spin Resonance of Spin Labels Using Chemometric Methods.
10. B. R. Kowalski and S. Wold, Pattern Recognition in Chemistry, in "Handbook of Statistics", Vol II, in press.

APPENDIX A

Pseudopolarographic Determination of Metal Complex
Stability Constants in Dilute Solution
By Rapid Scan Anodic Stripping Voltammetry

Pseudopolarographic Determination of Metal Complex
Stability Constants in Dilute Solution
By Rapid Scan Anodic Stripping Voltammetry¹

by

Steven D. Brown*²

and

Bruce R. Kowalski

Department of Chemistry
University of Washington
Seattle, WA 98195

¹ Abstracted in part from the dissertation of S.D. Brown, submitted in partial fulfillment of requirements for the Ph.D. degree, University of Washington.

² Present Address: Department of Chemistry
University of California
Berkeley, CA 94720

BRIEF

A computer controlled anodic stripping voltameter is used to determine the ligand numbers and stability constants of metal complexes in very dilute solutions (ng/ml or less).

ABSTRACT

The theory of anodic stripping voltametry states that at any deposition potential, the deposition current will either be the limiting current or a fraction of the limiting current, depending on the deposition potential with respect to the metal desposition potential. By using a computer controlled anodic stripping voltmeter with automatic background correction, pseudopolarograms can be obtained by plotting the peak area vs the deposition potential for a series of stripping voltametric runs. With ASV as a method of amplification, the ligand number and stability constants are determined for metal complexes at concentration ranges expected of natural water systems. Results for lead and cadmium with chloride and carbonate are in excellent agreement with those of less sensitive methods used at higher concentrations. No complexation of lead and cadmium was found with glycine at pH = 4.68. The structure of arsenic (III) at 1.0 ng/ml in acidic solutions was determined to be $\text{As}(\text{OH})_3$ using a gold film electrode. Finally, the speciation of lead in a geothermal water was examined by pseudopolarography and a shift consistent with a PbCl^+ complex was observed.

The evaluation of the complexing properties of metals in solution has long been of interest to analytical chemists, who have developed a variety of techniques suited to the assignment of metal complexation in solution. These techniques, which include visible absorption spectrometry, isotopic exchange methods, and in a few cases, vibrational (Raman) spectroscopy as well as more exotic methods, have been used by a variety of groups to study the kinetics of ligand exchange.

For dilute solutions, in the millimolar range, however, these techniques lack the sensitivity needed to evaluate metal complexation. Polarographic techniques based on the shift of the half-wave potential ($E_{1/2}$) with ligand concentration were first used by Hevrowsky (1) and Lingane (2,3) to investigate metal complexation in dilute solution; these and similar determinations via ion-selective electrodes (4,5) do not extend to metal concentration ranges below about $10^{-5}M$. Thus, neither technique is directly applicable to evaluations of metal complexation at concentrations approximating those found in dilute natural waters, typically $10^{-8} - 10^{-10}M$.

In order to extend the sensitivity of polarography, a number of techniques have been employed, including differential pulse (6,7) and square wave polarography (8,9), various alternating current polarography-based techniques (10-12), and stripping voltammetry (13-18), but these techniques have not seen extensive use in studies of metal complexation in dilute natural waters.

Most recent work has been aimed at the classification of metal complexation in natural waters. A number of schemes (13-15) based on anodic stripping voltammetry have been developed to classify

metal complexes as "free" or "bound". Florence (16-18) has devised a system which classifies metal complexes as (1) free ions; (2) ASV labile complexes; (3) dissociable complexes; (4) non dissociable complexes. These systems have been called "coarse" speciation (19).

Direct identification of the metal complex in dilute solution via determination of the ligand number and complex stability constant has only been attempted quite recently, and most studies have used relatively large metal concentrations compared to levels found in dilute natural systems. This "fine" speciation (19) has not involved ASV, because many runs are needed to establish peak shifts, and ASV peak positions are known to be sensitive to factors such as ionic strength and scan rate (20).

Because metal reduction has been demonstrated to be sensitive to metal complexation through changes in the amount of metal deposited as a function of deposition potential (21), coupling reproducible plating at various potentials with a sensitive ASV technique will allow measurements of deposited metal charge (or, here, as peak currents derived from the ASV stripping peak) as a function of deposition potential. Two recent papers use linear scan ASV in this fashion (22,23) to obtain stability constants in dilute solutions. We report here the application of this technique to thin, glassy carbon-supported mercury and gold films using rotating disk electrodes and minicomputer-controlled background subtracted anodic stripping voltammetry. The system is capable of generating automated Q vs. E_d plots, called pseudopolarograms, with either linear scan or staircase stripping ASV. We also describe the theoretical basis of the technique.

THEORY

At any deposition potential E_d , the deposition current $i(t)$ is given by either the limiting current of the deposition process at the rotating disk electrode, or some fraction thereof. For constant plating time, the material deposited also will vary with E_d , and the individual stripping steps will merely analyze the material preconcentrated in the electrode.

For a rotating disk electrode, the instantaneous current $i(t)$ is given by:

$$i(t) = \frac{nFAD_{OX}}{\delta_{OX}} [C_{OX}^o - C_{OX}(0,t)] \quad (1)$$

where C_{OX}^o is the bulk concentration of analyte ion, $C_{OX}(0,t)$ is the surface concentration of analyte ion at time t , δ is the thickness of the diffusion layer, and the other symbols have their usual meaning.

De Vries and Van Dalen (24-26) have shown for thin mercury film electrodes the surface activity of the amalgam as a function of plating time is:

$$C_{RED}(0,t) = \frac{i(t)}{nFA} \left(\frac{t}{l} + \frac{1}{3D_{RED}} \right) \quad (2)$$

Here t is plating time and l is film thickness; this equation is suitable for $t \geq 20$ sec.

For an electrode process

$$i(t) = nFA\{k_{fh}C_{OX}(0,t)\gamma_O - k_{bh}C_{RED}(0,t)\gamma_R\} \quad (3)$$

where k_{fh} and k_{bh} are the forward and backward heterogeneous rate constants for the metal reduction. Combining equations 1-3 yields:

$$i(t) = nFAk_{fh}\gamma_{OX}\left(C_{OX}^o - \frac{i(t)\delta_{OX}}{nFAD_{OX}}\right) - k_{bh}\gamma_r i(t) \left(\frac{t}{l} + \frac{1}{3D_{RED}}\right) \quad (4)$$

Since we desire charge, we integrate (4) with respect to time to get:

$$Q = \frac{k_{fn}\delta_{OX}}{D_{OX}} (Q_{LIM} - Q)\gamma_{OX} - k_{bh}\left(\frac{t}{2l} + \frac{1}{3D_{RED}}\right)Q\gamma_r \quad (5)$$

$$\text{where } Q_{LIM} = \int_0^t i_{LIM} dt = \int_0^t \frac{nFAC_{OX}^o}{\delta_{OX}} D_{OX} dt \quad (6)$$

$$Q = \int_0^t i(t) dt \quad (7)$$

Rearrangement of (5), and substitution of

$$k_{fn} = k_{fh}^o e^{-\frac{\alpha nF}{RT} E_d} \quad (8)$$

$$\text{and } \frac{k_{bh}}{k_{fh}} = \exp\left\{\frac{nF}{RT} (E_d - E^o)\right\} \quad (9)$$

gives

$$E_d - E^o = \frac{RT}{nF} \ln \left[\left(\frac{Q_{LIM} - Q}{Q} \right) - \frac{D_{OX}}{\delta_{OX} k_f^o \gamma_{OX}} \exp(\alpha nF E_d / RT) \right] - \frac{RT}{nF} \ln \left(\frac{\delta_{OX}}{D_{OX}} - \frac{\gamma_{OX}}{\gamma_r} \right) - \frac{RT}{nF} \ln \left(\frac{1}{3D_{RED}} + \frac{t}{2l} \right) \quad (10)$$

where $\alpha(E_d)$ is the transfer coefficient for the reduction and k_f^o is the heterogeneous rate constant for reduction at E^o .

Equation 10 is the general equation for the pseudopolarographic reduction and stripping of a free model ion under quasi-reversible conditions. Various techniques including ASV (27) and stripping chronoamperometry (28) can be used to strip the metal ions out of the fiber and monitor the change, so this and subsequent equations

are left in terms of charge, rather than peak stripping current.

When $k_f^0 \rightarrow \infty$, the reaction at the electrode surface is reversible and equation 10 reduces to:

$$E_d - E^0 = \frac{RT}{nF} \ln \left(\frac{Q_{LIM}^{-Q}}{Q} \right) + \frac{RT}{nF} \ln \left(\frac{\delta_{OX} \gamma_{OX}}{D_{OX} \gamma_{RED}} \right) - \frac{RT}{nF} \ln \left(\frac{1}{3D_{RED}} + \frac{t}{2l} \right) \quad (11)$$

Equation 11 is similar to that obtained by Zirino and Kounaves (29), but differs from their result as we use the exact expression for C_r and integrate.

For complexes, we consider the equilibria:

where complex formation is presumed rapid and reversible, and the stability constant β_j is defined as:

$$\beta_j = \frac{[ML_j^{n+}]}{[M^{n+}][L]^j} \cdot \frac{\gamma_{ML_j}}{\gamma_M \gamma_L^j} \quad (13)$$

Using the method of DeFord and Hume (30), which presumes only M^{n+} is reducible, all $D_{OX} = D$, excess L , and all activity constants do not vary with distance from the electrode, equation 14 is obtained for a quasireversible system:

$$\begin{aligned} E_d = E^0 + \frac{RT}{nF} \ln \left[\left(\frac{Q_{LIM}^{-Q}}{Q} \right) + \frac{D}{k_f^0 \delta_{OX}} \sum_{j=0}^N \left(\frac{\beta_j [L]^j \gamma_L^j}{\gamma_{ML_j}} \right) e^{\frac{\alpha n F}{RT} E_d} \right] - \\ \frac{RT}{nF} \ln \left[\frac{\gamma_r D}{\delta_{OX}} \left(\frac{t}{2l} + \frac{1}{3D_{RED}} \right) \right] - \frac{RT}{nF} \ln \left[\sum_{j=0}^N \left(\frac{\beta_j [L]^j \gamma_L^j}{\gamma_{ML_j}} \right) \right] \end{aligned} \quad (14)$$

For reversible cases, this is reduced to:

$$E_d = E_o + \frac{RT}{nF} \ln \left(\frac{Q_{LIM} - Q}{Q} \right) - \frac{RT}{nF} \ln \frac{\gamma_r D}{\delta_{OX}} \left(\frac{t}{2l} + \frac{1}{3D_{RED}} \right) - \frac{RT}{nF} \ln \left[\sum_{j=0}^N \left(\frac{\beta_j (L)^j \gamma_i^j}{\gamma_{MLj}} \right) \right] \quad (15)$$

from which:

$$E_{1/2}^*, \text{ comp} = E_o - \frac{RT}{nF} \ln \frac{\gamma_r D}{\delta_{OX}} \left(\frac{t}{2l} + \frac{1}{3D_{RED}} \right) - \frac{RT}{nF} \ln \sum_{j=0}^N \left(\frac{\beta_j [L]^j \gamma_i^j}{\gamma_{MLj}} \right) \quad (16)$$

results. For constant values of l , δ_{OX} , γ_r and t :

$$\Delta E_{1/2}^* = (E_{1/2}^*, \text{ free} - E_{1/2}^*, \text{ comp}) = - \frac{RT}{nF} \ln \left(\frac{D}{D_{OX}} \cdot \gamma_M \right) + \frac{RT}{nF} \ln \left[\sum_{j=0}^N \left(\frac{\beta_j [L]^j \gamma_i^j}{\gamma_{MLj}} \right) \right] \quad (17)$$

or, for a single complex with $\gamma_M \approx \gamma_{ML}$, $D \approx D_{OX}$

$$\Delta E_{1/2}^* \approx \frac{RT}{nF} \ln \beta_j + j \frac{RT}{nF} \ln a_L \quad (18)$$

where a_L is the ligand activity.

Equation 17 is exactly analogous to that obtained by DeFord and Hume for polarographic reduction of metal complexes where many complexes are possible, and equation 18 is analogous to the Lingane equation (3), suited for analysis of single complex systems. Thus, plots of $\Delta E_{1/2}^*$ vs. A_L provide metal complexation information through analyses similar to those used in classical polarographic studies.

Here, because stripping peak heights are directly proportional to total charge (26), we use ASV peak heights in our evaluations of $E_{1/2}^*$.

Davison has examined (31) the limitations on conventional polarographic and voltammetric schemes used to monitor speciation, and finds for conventional ASV that, for a kinetic current equal to 10% of the limiting current:

$$Q = \frac{\beta^{3/2}[L]}{k_1^{1/2}} (1 + \beta[L])^{1/2} = \frac{9\delta}{D^{1/2}} \quad (17)$$

where k_1 is the second order rate constant for the rate of substitution of the active form of the metal, here M^{n+} . For $D = 10^{-5} \text{ cm}^2 \text{ sec}^{-1}$, Q values of $10^4 - 10^6$ result for δ between 10^{-4} and 10^{-2} cm . For ligand concentrations in the 10^{-3} M range, and for $k_1 = 10^9 \text{ l mol}^{-1} \text{ sec}^{-1}$, limiting β values of about 10^5 are obtained.

The same argument can be applied to the pseudopolarographic determination of stability constants, since the technique relies on the measurement of charge passed during the plating period. There are some differences, however. Because plating times should be kept short, to avoid altering the composition of the solution, normal ASV with long plating times cannot be used, as serious metal depletion results. With the ASV method using background subtraction, sensitivities are such that a five minute plating period allows detection of pg/ml levels of metals (27); this allows the observation of small kinetic currents, approximately 1% of the diffusion current in the absence of complexer. The β values easily observable would then extend to about 10^{-6} for ligand concentrations in the 10^{-3} M range. The precision of the determination suffers slightly here, though, with kinetic currents on the order of 1% of the diffusion currents, because

the entire pseudo-polarogram is simply reduced in height proportionally, making the error in determining the half-wave potential somewhat larger. The possibility of decreasing the rotation rate, thus increasing δ , also exists.

EXPERIMENTAL

Equipment and Apparatus

The rapid-scan, background-subtracted ASV apparatus described in reference 27 was used for these studies. Modifications were made to the software to allow a sequence of scans to be performed automatically, with each run differing by a fixed value in the plating potential, but otherwise having identical parameters. Runs were stored sequentially on the disk to allow easy processing.

Measurements of pH were made with a Beckman 4500 digital pH meter, calibrated with pH 4.008 solution.

Electrodes and Cell

Both mercury and gold film electrodes were used in this study, the gold electrode being used for studies of arsenic speciation. Preparation of the electrodes has been discussed (27). A saturated KNO_3 bridge was used between the S.C.E. reference electrode and test solution to avoid contamination of the solution with trace amounts of complexer. The cell (27) was cleaned thoroughly with 5N citric acid between runs to avoid any transfer of complexer. This is particularly necessary in the case of arsenic, as arsenic species strongly absorb on the cell, and later interfere.

remained, after which the solution was allowed to become quiescent before the scan. A single scan, using either the linear ramp or staircase waveform, was then performed, using multiple point averaging (typically 16 points). Stirring at the cleaning potential was then performed for 20 sec., after which a 10 sec quiescent period was provided. With 2 seconds remaining, the potential was again switched to the rest potential, and another scan, exactly like the first, was used to monitor the background. Current measurements were subtracted, point by point, and the result was plotted on the Tektronix 4012 screen, and stored on disk. The deposition potential was redefined, and another run was automatically performed, exactly like the first, but at a different deposition potential. This process was continued, until a specified number of runs was performed. The resultant file of ASV runs could be used to generate a pseudopolarogram for each peak present in the voltammogram. A pseudopolarogram run, like that described above, was performed for each solution. The electrode film was maintained between solutions to insure that uniform conditions applied within a series of runs; it was washed with distilled water between analyses of different solutions to prevent carryover of ligand.

Data Reduction. The ASV peak heights were measured with an interactive graphics routine. The plating potentials and peak heights were plotted for each solution, resulting in a series of pseudopolarograms for each metal.

Because, for ASV the peak current is directly proportional to charge stripped, the pseudopolarograms were examined for reversibility by plotting the deposition potential E_d versus $\log [i_L - i/i]$,

where the limiting current, i_L , was estimated from the top of the step-shaped wave, and i was the peak current monitored for the metal of interest on the ASV run where the deposition potential E_d was used. A straight line, with slope of approximately $59.1/n$ mv resulted for a reversible system; non-linear relationships, or slopes drastically different from the $59.1/n$ value expected were treated as irreversible systems.

For reversible systems, the least squares best estimate was used to calculate $E_{1/2}^*$ from $\log [(i_L - i)/i] = 0$. The error in this value is estimated at 1% relative. For irreversible systems, estimates were made of $E_{1/2}^{*irr}$ by extrapolating the foot of the wave upward, estimating the limiting current, and evaluating the potential for a current value equal to one-half the limiting current. The error in this value is somewhat larger, about 3-5% relative.

Values for $E_{1/2}^*$ (or $E_{1/2}^{*irr}$) were then plotted versus the log of ligand concentration, and the slopes of the resultant linear relationships were evaluated via linear regression analysis.

Intercepts were also calculated. The errors in $E_{1/2}^*$ were used to obtain an estimate of the errors in the ligand number, p , and the stability constant, $\log \beta$, calculated from the slope and intercept, respectively. The more exact method of DeFord and Hume (30) as modified by Varga and others (32-33) was not used here, as the scope of such a study (which would require at least 10-20 pseudopolarograms) was beyond this work, whose intent is to demonstrate the feasibility of the technique. Instead, the simpler method of Lingane (2, 3) was used. Future experimentation, involving sufficient runs to use the DeFord and Hume procedure, is planned.

RESULTS AND DISCUSSION

Cadmium and Lead Complexation by Chloride

A series of KCl solutions of fixed 0.10M ionic strength and pH = 5.00 were examined with the pseudopolarographic technique. A staircase scan with $\tau = 10.0$ msec was used in the ASV runs, with 150 sec plating times used for deposition. Twenty ASV experiments, differing in plating potential by 40 mv, were run. The rest potential was -1200 mv (S.C.E.) and the plating potentials ranged from -1000 mv to -200 mv (S.C.E.). Both the Pb and Cd pseudopolarograms were observed to behave reversibly, with slopes from -30 to -33 mv (theoretical -29.8 mv). Table I lists the $E_{1/2}^*$ values obtained for cadmium as a function of chloride concentration. From the table, a least-squares fit gives a ligand number p of 1.1 ± 0.1 and an equilibrium constant of $\log \beta = 3.2 \pm 0.2$.

For lead, shifts were much smaller, as shown in Table II. From the table, a least squares fit gives a ligand number of 0.7 ± 0.2 and a stability constant of $\log \beta = 1.4 \pm 0.3$. Values for the lead-chloride system are much less precise because of the small shifts, combined with the error in locating $E_{1/2}^*$. More ASV runs would better define the curve, and better located $E_{1/2}^*$ values here, resulting in less error.

Results here agree reasonably well with previous literature values, as shown in Table III.

Cadmium and Lead Complexation by Carbonate

A series of Na_2CO_3 solutions at pH = 7.87 were prepared with fixed ionic strength (0.1M) by addition of KNO_3 . Metal concentration was nominally 2 ng/ml for both Cd and Pb. An experiment, identical to the one used for the chloride studies,

was performed. Neither the Cd, nor the Pb polarogram was totally reversible, slopes being greater than -38mv.

Table IV lists the shifts in the half-wave potential for lead. Using these values, a ligand number of 0.9 ± 0.1 and a stability constant of $\log \beta = 6.1 \pm 0.1$ may be calculated.

It should be noted that a plot of $E_{1/2}^*$ versus $\log [\text{HCO}_3^-]$ also gives a linear relation, with a slope indicating a ligand number of 0.9 as well. Stumm (34) has shown, however, that all reported bicarbonate complexes may be better interpreted as carbonate complexes. Thus, the data reported here are regarded as indicative of carbonate, rather than bicarbonate species.

Results for lead agree quite well with published values, as shown in Table V.

Results for cadmium are listed in Table VI. The observed shifts are quite small, within even the error attributed to the assignment of $E_{1/2}^*$ values. At this pH, cadmium is apparently not significantly complexed by carbonate. Similar results were obtained by differential pulse polarography and ASV of more concentrated Cd-CO_3^{2-} systems (35). CdCO_3 was observed at higher pH values, however (34).

Cadmium and Lead Complexation by Glycine

A series of solutions of glycine, adjusted to pH = 4.68, was made up, again with a total ionic strength of 0.1M. Pseudopolarographic analysis was performed as described previously, using the same conditions as before. Table VII shows the shifts in $E_{1/2}^*$ for Pb and Cd as a function of the glycine concentration. Again, shifts are within the error of the experiment, and no complexation has resulted for either the Pb or the Cd. The interaction of glycine with Pb and Cd has been studied by ASV and DPP analysis of more concentrated solutions, where no

complexation of Cd or Pb was observed (35), although glycine complexes of Cd have been claimed (36), but this work is in question (37).

Structure of Arsenic (III) in Aqueous Solution

Arsenic has received a considerable amount of attention in the past, primarily due to the analytical difficulties associated with its relative insolubility in mercury (38, 39). A variety of electrochemical techniques have been applied in efforts to improve the detection limit values for arsenic analyses (40-46). No concerted effort has been applied to studies of As speciation in dilute solution using electrochemical methods, however. Recent advances in the field, brought about by the use of gold wire (43) or gold film (47) electrodes combined with ASV, suggested that an attempt was feasible.

A solution of As (III) in 0.1M KNO_3 was prepared. The pH was adjusted to a series of values with dilute HClO_4 and dilute NaOH. The nominal As concentration was 1.0 ng/ml. The effects of pH on the $E_{1/2}^*$ value for the As stripping peak on an Au film electrode were briefly investigated by obtaining pseudopolarograms for As at several pH values.

The pseudopolarograms were obtained using 300 sec plating time, followed by background subtracted staircase ASV, with a step height of 3.66mv and a delay time of 16.7 msec. Total scan time was 5 sec. It was observed here that linear scan ASV gave much poorer peaks as well as less effective removal of background, while for other pseudopolarograms, little difference (other than sensitivity) was observed. The same film was used for all runs. Plating potentials varied between -200 ms and +300 mv versus the S.C.E., with a rest potential of -200 mv (S.C.E.). Solution volumes were 75 ml.

A typical pseudopolarogram obtained at pH = 2.85 and 1.0 ng/ml As (III) is shown in Figure 1. The sequence of ASV runs generating this pseudopolarogram is depicted in Figure 2, where the decay in peak height shows along the y axis. The peak potential for the As peak remains constant. A logarithmic analysis of the pseudopolarograms give slopes near those expected for a reversible system (theoretical -19.8 mv); the values observed were -20, -18, -19 and -18 mv for the four pseudopolarograms.

The peak heights for As on Au films drastically decrease with decreasing pOH, as shown in Figure 3. The runs performed in basic solution gave broad, distorted peaks indicating that the As is converted into a highly irreversible form in basic solution. An analysis of runs in acidic solution with data given in Table VIII, gives a ligand number of 3.0 ± 0.1 and an intercept of -548.3 mv. The intercept cannot be converted, as was done before, to a log β value as (1) no $E_{1/2}^*$, free value could be obtained for As (III), and (2) values of D_{As} are certainly not comparable to $D_{As(OH)_3}$, due to the large collection of water molecules expected for the "free" As (III) ion (48). Thus, no convenient route to a stability constant for the complex predicted, $As(OH)_3$, exists. Support for such a complex is found in the Raman spectra of dilute solutions of As_4O_6 ; in acid solutions, the only detectable species is $As(OH)_3$. $As(OH)_2O^-$, $As(OH)O_2^{2-}$ and AsO_3^{3-} also appear in basic solutions (49). Such a result is consistent with the ligand number of 3 in acidic solution, and with the degradation of the As peak in basic solution, as the amount of $As(OH)_3$ decreases.

Estimation of Lead Species in Geothermal Water

A sample of air-exposed geothermal water obtained from the Lawrence Livermore Laboratory, (Department of Energy) project in

the Imperial Valley, California, was filtered under air through a 0.45 μ filter. The pH was 1.99. The pH was adjusted to 5.00, and the filtrate was diluted by a factor of 40 to obtain an approximate ionic strength, mostly as NaCl, of 0.1M. Nominal concentration of minor elements were Pb (7 μ g/ml), Cu (25 ng/ml), Fe (6 μ g/ml) and Sn (1 μ g/ml). A pseudopolarographic scan at low sensitivity was performed, and is plotted for Pb in Figure 4. The half-wave potential, of -501 mv, is consistent with the shift observed above for PbCl^+ in 0.1M KCl at pH = 5.00. It is reasonable to assume that the Pb exists primarily as PbCl^+ in this solution. An attempt was made to examine data for cadmium, but the much larger Pb wave obscured the Cd wave. In view of the high Pb concentration, simple ligands present, and convenient ionic strength, this solution must be regarded as only a model system, and many more ligands and systems must be studied to ascertain direct speciation like that approximated above, but it certainly seems feasible. Work is underway to demonstrate this feasibility in natural systems with metal concentrations in the low ppb range. Thus direct assessment of chemical models (e.g., 50) seems feasible. This is particularly useful in view of the drastically different effects of different complexes in natural systems, especially as regards bioavailability and toxicology (51-53).

CONCLUSIONS

Pseudopolarography has been shown to provide a rapid, sensitive means of performing measurements in very dilute solution (ng/ml or less). Because the theoretical treatment is so closely related to classical polarography, the considerable literature on the polarographic analysis of solutions may be applied to the problem of analysis of pseudopolarographic waves.

Results identical to those obtained by other, less sensitive, means were obtained for the Cd-Cl, Pb-Cl and Pb-CO₃ systems. Cd-CO₃, Cd-glycine and Pb-glycine were found not to interact in the pH ranges studied.

The speciation of As(III) in acid solution was examined using the new technique. The complex As(OH)₃ was identified as the dominant electrochemically-active species, consistent with Raman results.

The speciation of Pb in a geothermal water was examined by pseudopolarography. A shift consistent with a PbCl⁺ complex was observed.

The new technique of pseudopolarography, performed with rapid-scan ASV instrumentation, appears to be a major advance in the area of chemical speciation.

CREDITS

This work was partially supported by the Office of Naval Research. S.D.B. gratefully acknowledges the support, during the 1977-78 year, of an A.C.S. Analytical Division Fellowship, sponsored by the Perkin Elmer Corp. The authors are pleased to acknowledge the assistance of Robert M. Corn. The authors also acknowledge Dr. J. Harrar, Lawrence Livermore Laboratory, for providing the geothermal water sample and the Department of Energy for support associated with the speciation of geothermal waters.

REFERENCES

1. J. Hevrovsky and D. Ilkovič, Coll. Czech. Chem. Comm., 7, 198 (1935).
2. J. M. Kolthoff and J. J. Lingane, Chem. Rev. 24, 1 (1939).
3. J. J. Lingane, Chem. Rev., 29, 1 (1941).
4. M. J. Stiff, Water Research, 5, 171 (1971).
5. H. Gardiner, Water Research, 8, 23 (1974).
6. G. C. Barker, Anal. Chim. Acta, 18, 118 (1958).
7. G. C. Barker and A. W. Gardner, Z. Anal. Chem., 173, 79 (1960).
8. G. C. Barker and J. L. Jenkins, Analyst, 77, 685 (1952).
9. P. E. Sturrock and R. J. Carter, CRC Crit. Rev. Anal. Chem., 5, 201 (1975).
10. B. Breyer and H. H. Bauer, "Alternating Current Polarography and Tensammetry", Interscience, New York, N.Y., 1963.
11. D. E. Smith, in "Electroanalytical Chemistry", A. J. Bard, ed., Vol. 1, p. 1, Dekker, New York, N.Y., 1966.
12. D. E. Smith, CRC Crit. Rev. Anal. Chem., 2, 247 (1971).
13. R. Clem, Anal. Chem., 50, 102 (1978).
14. M. Whitfield, in "Chemical Oceanography", 2nd edn., Vol. 4, p. 1, Academic Press, London, 1975.
15. W. R. Matson, Dissertation, Mass. Inst. Technology, Cambridge, Mass., 1968.
16. T. M. Florence and G. E. Batley, Talanta, 22, 201 (1975).
17. T. M. Florence and G. E. Batley, Talanta, 23, 179 (1976).
18. G. E. Batley and T. M. Florence, Anal. Lett., 9, 397 (1976)
19. W. Davidson and M. Whitfield, J. Electronanal. Chem., 75, 763 (1977).

20. Z. Galus, "Fundamentals of Electrochemical Analysis", Wiley, London, 1976.
21. P. Dalahay, "New Instrumental Methods in Electrochemistry", Interscience, New York, N.Y., 1964.
22. S. Bubic and M. Branica, Thalassia Jugo., 9, 47 (1973).
23. H. Nürnberg, P. Valenta, L. Mart, B. Raspor and L. Sipos, Z. Anal. Chem., 282, 357 (1976).
24. W. T. DeVries and E. Van Dalen, J. Electroanal. Chem., 8, 366 (1964).
25. W. T. DeVries, J. Electroanal. Chem., 9, 448 (1965).
26. W. T. DeVries and E. Van Dalen, J. Electroanal. Chem., 14, 315 (1967).
27. S. D. Brown and B. R. Kowalski, Anal. Chim. Acta (in press).
28. G. Mamamtov, P. Papoff and P. Delahay, J.A.C.S., 79, 4034 (1957).
29. A. Zirino and S. Kounaves, Anal. Chem., 49, 56 (1977).
30. D. D. DeFord and D. N. Hume, J.A.C.S., 73, 5321 (1951).
31. W. Davidson, J. Electroanal. Chem., 87, 395 (1978).
32. L. P. Varga, Anal. Chem., 41, 323 (1969).
33. L. N. Klatt and R. L. Rouseff, Anal. Chem., 42, 1234 (1970).
34. H. Bilinski, R. Huston and W. Stumm, Anal. Chim. Acta., 84, 157 (1976).
35. R. Ernst, H. E. Allen and K. H. Mancy, Water Research, 9, 969 (1975).
36. J. H. Smith, A. M. Cruikshank, J. T. Donoghue and J. F. Pysz, Jr., Inorg. Chem., 1, 148 (1962)
37. K. Momoki, H. Sato and H. Ogawa, Anal. Chem., 39, 1072 (1967).
38. F. Vydra, K. Stulik, E. Julakova', "Electrochemical Stripping Analysis", Halstead Press, London, 1976.

20. Z. Galus, "Fundamentals of Electrochemical Analysis", Wiley, London, 1976.
21. P. Dalahay, "New Instrumental Methods in Electrochemistry", Interscience, New York, N.Y., 1964.
22. S. Bubic and M. Branica, Thalassia Jugo., 9, 47 (1973).
23. H. Nürnberg, P. Valenta, L. Mart, B. Raspor and L. Sipos, Z. Anal. Chem., 282, 357 (1976).
24. W. T. DeVries and E. Van Dalen, J. Electroanal. Chem., 8, 366 (1964).
25. W. T. DeVries, J. Electroanal. Chem., 9, 448 (1965).
26. W. T. DeVries and E. Van Dalen, J. Electroanal. Chem., 14, 315 (1967).
27. S. D. Brown and B. R. Kowalski, Anal. Chim. Acta (in press).
28. G. Mamantov, P. Papoff and P. Delahay, J.A.C.S., 79, 4034 (1957).
29. A. Zirino and S. Kounaves, Anal. Chem., 49, 56 (1977).
30. D. D. DeFord and D. N. Hume, J.A.C.S., 73, 5321 (1951).
31. W. Davison, J. Electroanal. Chem., 87, 395 (1978).
32. L. P. Varga, Anal. Chem., 41, 323 (1969).
33. L. N. Klatt and R. L. Rouseff, Anal. Chem., 42, 1234 (1970).
34. H. Bilinski, R. Huston and W. Stumm, Anal. Chim. Acta., 84, 157 (1976).
35. R. Ernst, H. E. Allen and K. H. Mancy, Water Research, 9, 969 (1975).
36. J. H. Smith, A. M. Cruikshank, J. T. Donoghue and J. F. Pysz, Jr., Inorg. Chem., 1, 148 (1962)
37. K. Momoki, H. Sato and H. Ogawa, Anal. Chem., 39, 1072 (1967).
38. F. Vydra, K. Stulik, E. Julakova', "Electrochemical Stripping Analysis", Halstead Press, London, 1976.

TABLE 1

SHIFT OF $E_{1/2}^*$ WITH CHLORIDE CONCENTRATION
FOR CADMIUM^a

$E_{1/2}^*$	$[Cl^-]$	$\log [Cl^-]$
-745±5	0.0050	-2.3
-758±5	0.010	-2.0
-775±5	0.050	-1.3
-789±5	0.10	-1.0
-725±5	0	--

^a I = 0.10, pH = 5.00

TABLE II

SHIFT OF $E_{1/2}^*$ WITH CHLORIDE CONCENTRATION
FOR LEAD^a

$E_{1/2}^*$	$[Cl^-]$	$\log [Cl^-]$
-480±5	0.005	-2.3
-485±5	0.01	-2.0
-495±5	0.05	-1.3
-499±5	0.1	-1.0
-475±5	0	--

^a I = 0.10, pH = 5.00

TABLE III

COMPARISON OF RESULTS FOR
CADMIUM AND LEAD CHLORIDE SPECIES

<u>Metal</u>	<u>P</u>	<u>I</u>	<u>log β</u>	<u>Reference</u>
Cd	1	1.0	1.7 - 2.2	54
Cd	1	0.1	3.2	This work
Pb	1	0.1	1.0 - 1.6	54
Pb	1	0.1	1.4	This work

TABLE IV

SHIFT OF $E_{1/2}^*$ WITH CARBONATE CONCENTRATION
FOR LEAD^a

$E_{1/2}^*$	$[\text{HCO}_3^-]$	$\log [\text{CO}_3^{2-}]$	$[\text{CO}_3^{2-}]$
-623±5	5.2×10^{-3}	-1.02	0.095
-595±5	2.6×10^{-3}	-1.3	0.047
-551±5	5.2×10^{-4}	-2.0	0.0095
-545±5	2.6×10^{-4}	-2.3	0.0047
-501±5	0	--	

^a I = 0.1, pH = 7.87

TABLE V

COMPARISON OF RESULTS FOR
LEAD CARBONATE SPECIES

<u>Method</u>	<u>I</u>	<u>Pb</u> ^a	<u>pH</u>	<u>log β</u>	<u>Reference</u>
ASV	0.1	200	7.3 - 10.3	6.4	34
DPP	0.1	200-50	5.0 - 9.1	6.1	34
Polarog.	1.7	20000	10.9	8.2 ^b	55
DPASV	0.1	500	-	6.3	56
Cyclic voltammetry	0.7	10	7.2	6.21	57
Pseudopolog.	0.1	2	7.87	6.1	This work

^a in ng/ml^b value is log β_2

TABLE VI

SHIFT OF $E_{1/2}^*$ WITH CARBONATE CONCENTRATION
FOR CADMIUM^a

$E_{1/2}^*$	$[CO_3^{2-}]$
-728±5	5.2×10^{-3}
-722±5	2.5×10^{-3}
-725±5	5.2×10^{-4}
-725±5	2.6×10^{-4}
-720±5	0

^a I = 0.1, pH = 7.87

TABLE VII

SHIFT OF $E_{1/2}^*$ WITH GLYCINE CONCENTRATION
FOR CADMIUM AND LEAD^a

$E_{1/2}^*$ (Cd)	$E_{1/2}^*$ (Pb)	[Glycine]
-720±5	-537±5	.005
-715±5	-539±5	.01
-715±5	-539±5	.05
-715±5	-545±5	.1
-715±5	-537±5	0

^a I □ 0.1, pH □ 4.68

TABLE VIII

SHIFT OF $E_{1/2}^*$ WITH HYDROXIDE CONCENTRATION
FOR ARSENIC^a

$E_{1/2}^*$	<u>pH</u>	<u>pOH</u>
-42±3	6.65	8.35
-33±2	4.26	9.74
86±1	3.56	10.44
108±1	2.85	11.15

^a I = 0.1M (KNO₃)

CAPTIONS FOR FIGURES

Figure 1: Pseudopolarogram for arsenic on gold.

Figure 2: Sequence of runs used to generate pseudopolarogram.

Figure 3: Dependence of arsenic peak on pOH.

Figure 4: Pseudopolarogram of lead species in geothermal water.

Figure 1

Figure 2

Figure 3

Figure 4

PUBLICATION
BY ERDA
AUTHORIZED ☐NOTICE OF RESEARCH PROJECT
SCIENCE INFORMATION EXCHANGE
SMITHSONIAN INSTITUTION

SIE NO.

ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION

ERDA CONTRACT NO.

SUPPORTING DIV. OR OFFICE: _____

NAME & ADDRESS OF CONTRACTOR OR INSTITUTION: (State the division, department, or professional school, medical, graduate or other, with which this project should be identified.)

Department of Chemistry
University of Washington
Seattle, WA 98195

TITLE OF PROJECT:

Trace Metal Characterization and Speciation in Geothermal Effluent by
Multiple Scanning Anodic Stripping Voltammetry and Atomic Absorption Analysis

NAMES, DEPARTMENT, AND OFFICIAL TITLES OF PRINCIPAL INVESTIGATORS AND OTHER PROFESSIONAL SCIENTIFIC PERSONNEL: (not including graduate students) engaged on the project, and fraction of man-year devoted to the project by each person.

Bruce R. Kowalski
Associate Professor
Department of ChemistryNO. OF GRADUATE STUDENTS ON PROJECT: 2 NO. OF GRADUATE STUDENT MAN-YEARS: 1

SUMMARY OF PROPOSED WORK: (200-300 words, omit Confidential Data). Summaries are exchanged with government and private agencies supporting research, are supplied to investigators upon request, and may be published in documents. Make summaries substantive, giving initially and for each annual revision the following: OBJECTIVE; SCIENTIFIC BACKGROUND FOR STUDY; PROPOSED PROCEDURE; TEST OBJECTS AND AGENTS.

Geothermal power production has recently become important as a possible long-term energy source, particularly in the western U.S. Recent studies have shown geothermal power plants to have a significant environmental impact on the ground water of the area. The heavy metals arsenic and mercury are special problems, as both are concentrated by flora and fauna exposed to the effluent waters. Because the toxicity of these and other metallic pollutants present in geothermal effluent depends on the chemical form, or speciation, of the particular metal, any serious study of the environmental impact of a geothermal development should include studies of trace metal speciation, in addition to trace metal concentration. This proposal details a method for determining metal speciation in dilute waters. The method is based on ion-exchange and backed by atomic absorption spectrometry and multiple scanning anodic stripping voltammetry. Special laboratory studies will be performed on mercury, arsenic and selenium speciation in synthetic geothermal water. The method will be applied to three known geothermal areas in Washington and Oregon, with emphasis on the speciation of mercury, arsenic and selenium in these waters.

RESULTS TO DATE: During the first year of funding the computer controlled electro-chemical instrumentation was built and tested. Using this instrumentation, we developed a new experimental procedure to determine the chemical form (speciation) of metal ions in very dilute solutions (ng/ml). This method was tested on model systems including Pb, Cd, and As with Cl^- , CO_3^{2-} and glycine ligands. Finally, the speciation of lead in a geothermal water was examined and the PbCl^+ complex

(continued next
page)

	PROGRAM CATEGORY NO.
BUDGET	
PRIMARY	
SECONDARY	

Signature of Principal Investigator

DATE: May 25, 1979

INVESTIGATOR -- DO NOT USE THIS SPACE

Results to date (continued):

was observed and quantitated. The experimental design for sampling and analysis of geothermal waters in the Pacific Northwest is nearly complete. Sampling will begin this summer.