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

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F I N A L R E P O R T

The initial goal of sampling, analyzing and speciating geothermal waters from selected sites in Oregon and Washington, was expanded to include an element of basic research necessary to complete the project. Interference and matrix effects encountered in the analysis of complex geothermal samples became a major problem in the study. To overcome these problems, we launched a major effort to apply the Generalized Standard Addition Method to the two primary analytical tools used in our research under this contract; ICP-Atomic Emission Spectrometry (AES) and Anodic Stripping Voltammetry (ASV). The results were published in two research papers that are included with this report. The ICP-AES paper acknowledges DOE support but the ASV paper mistakenly does not. The affect on the research performed under this contract is seen in completely accurate concentration values for all analytes. These papers should be considered as the primary fruit of the contract period.

As the remainder of this report shows, analytical goals for the four hot springs studied were achieved but speciation attempts by ASV fell short of our goals. New research in speciation by electrochemical methods has been initiated by a former graduate student, Dr. Steve Brown, now on the chemistry faculty at Washington State University. Dr. Brown's investigations may yield new tools for speciation that will overcome the difficulties we encountered.

We have gained an appreciation of sampling and chemical analysis of "real-life" samples. Several problems were encountered during our early attempts to collect representative samples from remote geothermal sites. Also, the proper handling of the samples, once collected, proved to be a major problem. However, these problems were eventually solved and the proposed research has remained as planned from the beginning of the project.

After the sampling equipment described in the next section was constructed, we took the equipment into the field and began sampling studies which lasted from summer 1979 to late 1981. The primary goal for the analysis of our early samples was to determine the total concentrations of electrochemically active elements, and other selected elements to be found at each of four geothermal sites.

The following sections describe the in-field sampling equipment constructed for our studies, procedures developed or adapted for our study, and the results obtained on representative samples taken from geothermal sites.

Sampling

Sampling of geothermal waters followed the accepted practices recommended by the National Bureau of Standards and the Environmental Protection Agency for ultratrace analysis of natural waters. The preparation of sampling vessels and the purification of water and reagent chemicals were our most time-consuming tasks.

A portable filtration unit was constructed according to A. J. Hebert and G. G. Young (Anal. Chem., 49, 672 [1977]). The unit accepts standard millipore acetate filters (HAWP-142, 0.45 μm , 142 mm plain white filter sheet). The filter is placed over a leaf-channel filter support plate and a large Teflon O-ring. The 125-mm diameter by 2-mm deep recess in the upper Teflon disk ensures even distribution of incoming water. All samples are collected in Ultrex HNO_3 leached 500-ml Nalgene bottles and kept refrigerated until analyzed.

Garland Hot Springs - Washington

Table I gives the total elemental concentrations of the 19 elements, that can be analyzed by our ICP-AES instrument, in a representative Garland Hot Springs sample. The large amounts of Mg, Fe, Ca and Si are certainly not unexpected. The total arsenic concentration of 1.5 ppm and the low, but detectable, concentration of Cd, 12 ppb are quite interesting and worthy of further consideration. Of course, the elemental concentrations in Table I are total amounts of these elements, representing all of the oxidation states present as well as free and complexed ions.

Figure 1 is an anodic stripping voltammetric (ASV) analysis of the deionized, distilled water produced in our laboratory. All of the reagents used in our ASV procedure (acid/base and ionic strength buffers, etc.) are produced using this water. Standard addition calibration allowed us to determine that 0.57 nanograms (10^{-9} g) per milliliter (ng/ml) Pb, 0.10 ng/ml Cd and no detectable Cu are present in our laboratory blank.

Figure 2 shows a typical ASV analysis of a Garland Hot Springs samples. Again, using the method of standard additions, we found 0.67 ng/ml Pb, 0.18 ng/ml Cd and a barely recognizable trace amount of Cu that was too small for quantitation. These results are quite low and precluded a more detailed analysis.

Baker Hot Springs, Washington

Table I shows the results of ICP-AES analysis for a representation sample from Baker Hot Springs, Washington. Again, all values represent total elemental concentration and include all chemical states. All concentrations, except Si, are substantially lower than the concentrations obtained from the Garland Hot Spring samples. The low values obtained for As and Cd proved too difficult for chemical state analysis.

Figure 3 shows an ASV run for a representative Baker Hot Springs sample. Electrochemically active Pb and Cd are present at levels lower than our lab blanks! It should be remembered that ASV determines only electrochemically active species in free chemical states. Total concentration analysis results are given by ICP-AES.

The presence of the inverted peak at -300 mv presented some rather major difficulties as it is in the Cu position. A combination of qualitative analysis and cathodic stripping analysis explained the anomaly. Figure 4 show cathodic scan of the sample. The presence of the inverted peak is due to SO_2 which was confirmed by qualitative analysis. Since SO_2 is reduced to H_2SO_2 , a strong interference is present and Cu analysis is not possible.

Hunter Hot Springs - Oregon

Table I shows the concentration for 19 elements from a representative Hunter samples. This site contained the largest Cu and Fe concentrations that are encountered. These concentrations fluctuated wildly from sampling to sampling over a range of 30.0 ppb for Cu and 130.0 ppb for Fe. The other concentration remained stable. ASV analysis of these samples encountered the same difficulties mentioned above; low amounts of Pb and Cd and a sulfur interference for Cu. Additionally, we were unable to obtain reliable results for arsenic speciation even though the amounts were high.

McCredie Hot Springs - Oregon

Table I contains the ICP-AES results from two representative samples from McCredie Hot Springs. Sample #1 was taken from the main spring and Sample #2 was a small side spring running only during our November 1980 trip. The values for the two springs agree quite closely even though the temperature difference is significant. As with the Hunter samples, Cu and Fe fluctuated over similar ranges. We feel that these are natural fluctuations as we ran several checks on our sampling and analysis protocols in order to detect deterministic errors. ASV analysis attempts were unsuccessful for the reasons given above.

TABLE I

ICP-AES ANALYSIS (TOTAL ELEMENTS CONC.)

OF REPRESENTATIVE GEOTHERMAL WATERS

(parts per billion)

<u>ELEMENT</u>	<u>DETECTION LIMIT</u>	<u>GARLAND</u>	<u>BAKER</u>	<u>HUNTER</u>	<u>MCCREDIE #1</u>	<u>MCCREDIE #2</u>
Ni	5.6	---	---	---	---	---
Cu	0.4	4.0	---	9.0	3.5	2.6
Fe	2.8	12.1	6.0	147.1	8.4	10.1
Co	3.2	---	---	---	---	---
Cd	1.7	12.0	---	---	2.3	---
Zn	1.5	7.0	---	---	---	---
Mn	0.5	563.0	4.0	---	90.9	90.5
Ag	1.7	---	---	---	---	---
Cr	2.5	---	---	---	---	---
Mg	1.3	62500.	380.0	292.1	898.3	843.0
Pb	14.5	---	---	---	---	---
Ca	1.0	224000.	6700.	13740.	243700.	232300.
Be	1.8	4.0	---	---	---	---
As	23.3	1500.	12.0	118.9	152.7	124.3
Tl	23.3	860.0	19.0	---	---	---
Sb	115.8	---	---	---	---	---
P	81.8	---	---	---	---	---
Si	4.1	43800.	46500.	57460.	32340.	31740.
Se	24.6	---	---	?	?	?
Na	4.3	?	?	191700.	641500.	663500.
ph	---	---	---	6.7	6.0	6.1
Temp	---	---	---	76.0°C	74.0°C	55.0°C

FIGURE 1
Lab Blank

ID.....1.	DEP. POT....-1000. MV
RPM.....3500.	END POT.....0. MV
DEP. TIME...300. MSEC	SCAN RATE...1000. MV/SEC
SCAN TIME...1000. MSEC	REST POT....-1000. MV
GAIN.....2.

FIGURE 2
Garland Hot Springs

ID.....11.	DEP. POT.....-1000. MV
RPM.....3500.	END POT.....0. MV
DEP. TIME...300. MSEC	SCAN RATE...1000. MV/SEC
SCAN TIME...1000. MSEC	REST POT.....-1000. MV
GAIN.....2.

FIGURE 3
Baker Hot Springs

ID.....6.	DEP. POT.....-1000. MV
RPM.....3500.	END POT.....0. MV
DEP. TIME...300. MSEC	SCAN RATE...1000. MV/SEC
SCAN TIME...1000. MSEC	REST POT.....-1000. MV
GAIN.....2.

FIGURE 4
Baker Hot Springs
Cathodic Scan

ID.....8.	DEP. POT....0. MV
RPM.....3500.	END POT.....-1000. MV
DEP. TIME...20. MSEC	SCAN RATE...-100. MV/SEC
SCAN TIME...10000. MSEC	REST POT....0. MV
GAIN.....0.

Publications Resulting From Work Supported By This Contract

1. Pseudopolarigraphic Determination of Metal Complex Stability Constants in Dilute Solutions by Rapid Scan Anodic Stripping Voltammetry

ANALYTICAL CHEMISTRY 51, 2133, 1979.

2. Generalized Standard Addition Method for Multicomponent Instrument Characterization and Elimination of Interferences in Inductively Coupled Plasma Spectrometry

ANALYTICAL CHEMISTRY 53, 2207, 1981.

3. The Generalized Standard Addition Method: Intermettalic Interferences in Anodic Stripping Voltammetry

ANALYTICA CHIMICA ACTA 134, 119, 1982.