

## Trace metal analysis of geothermal waters

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The determination of trace amounts of arsenic, mercury, and gold in geothermal water samples by differential pulse anodic stripping voltammetry (DPASV) was investigated. Optimum parameters affecting voltammetric behavior, such as deposition potential, supporting electrolyte, and nature of working electrode were first determined. A thin film gold electrode (TFGE) was used for the analysis of As(III) in 6 M HCl, and Hg(II) in 0.1 M HNO<sub>3</sub>. The analysis of Au(III) was carried out in 0.2 M HCl using a glassy carbon electrode (GCE). The deposition potentials employed for each metal were -0.150 V, 0.000 V, and -0.500 V for As, Hg, and Au, respectively.

The stripping peaks observed at -0.05 V, +0.50 V and +0.70 V (vs. SCE) for As(III), Hg(II) and Au(III), respectively, were utilized for their quantitative determination. The detection limit for each metal were 0.2 ppb for As(III), 0.02 ppb for Hg(II) and 0.04 ppb for Au(III). Different sample pretreatment procedures were devised for each metal. The concentration ranges obtained by DPASV were 6.6 - 10.1 ppm As(III), 0.02 - 0.07 ppm Hg(II) and 0.2 - 8.4 ppb Au(III) in some geothermal water samples analyzed.

**Key Words:** geothermal waters, arsenic, mercury, gold, anodic stripping voltammetry

TRACE METALS ARE FREELY DISTRIBUTED IN THE ENVIRONMENT through air and water and biomagnified through the various food chains. Quantitative determination of these metals is therefore useful in determining their toxicological effects on plants and animals. Analytical results could also form a sound basis for the necessary environmental protection measures to keep pollution at safe levels.

The Philippines uses geothermal energy which is harnessed through wells that discharge large quantities of geothermal water. Chemical studies [1-4] have been carried out on this natural water system and its chemical composition had been determined using spectrophotometric methods [4].

The geothermal water system contains trace metals including As, Hg, and Au. Arsenic and mercury are both toxic and must be monitored in this natural water system, while gold is used in hydro-geochemical prospecting. The safe limit for mercury and arsenic level in Philippine drinking waters has been set at 0.002 and 0.05 ppm, respectively, based on the 1990 Department of Environmental and Natural Resources (DENR) Administrative Order Number 34.

This research work employs differential pulse anodic stripping voltammetry (DPASV) to determine trace amounts of arsenic, mercury, and gold in geothermal waters found locally. This technique requires inexpensive and simple instrumentation and is considered extremely sensitive, making it very useful in environmental investigations involving trace analysis. However, there has been

no reported local study on the application of this technique to trace metal analysis of geothermal water system. The most commonly used technique for trace metal analysis is flame atomic absorption spectroscopy, which is less sensitive than DPASV. Neutron activation analysis and X-ray fluorescence can also be employed but these techniques necessitate the use of radioactive materials and expensive detectors.

### Experimental

#### Reagents and Chemicals

All solutions were prepared from reagent-grade chemicals and ultrapure water which was triple distilled and passed through Barnstead Nanopure II Water Filter System.

#### Voltammetric Analysis

DPASV was carried out using a Polarographic Analyzer (AMEL 466) with a saturated calomel reference electrode (SCE), a platinum wire auxiliary electrode and a bare or thin-film glassy carbon working electrode. Bare glassy carbon electrode (GCE) was fabricated in the laboratory using a glassy carbon (GC) rod of 3 mm diameter sealed with Araldite resin into a clean glass tubing [5]. The thin film gold electrode (TFGE) was prepared by pre-plating bare GCE with a gold film using  $2 \times 10^{-4}$  M Au(III) solution, and a deposition potential of -0.500 V.

A deposition time of 2.0 minutes was used for Hg analysis, while 5.0 minutes was used for As analysis [5]. All potential values given in this study are referred to the

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SCE. Test solutions analyzed voltammetrically were first deaerated by bubbling nitrogen gas through the solution. Each voltammetric run consists of a deposition step, followed by the electrochemical dissolution (stripping step) of the deposited species back into the solution. The stripping step is accomplished by applying a potential scan in the reverse direction, and the magnitude (peak height) of the resulting stripping current can be related directly to the concentration of the electroactive (analyte) species being determined.

### Sample Preparation

**Preliminary sample treatment.** The geothermal water samples analyzed were supplied by the Philippine National Oil Company (PNOC). The samples were taken from Tongonan, Leyte and from Bacon - Manito (Bacman) geothermal projects (see Table 1). They were acidified to pH 2 at the sampling sites using 1:1 (v/v)  $\text{HNO}_3$  solution. The samples were filtered using a 0.45  $\mu\text{m}$  millipore membrane filter, and placed in clean, acid-washed polyethylene plastic bottles and stored in a cool, dry place prior to DPASV analyses.

**Arsenic.** The first step involved acid digestion [7], to near dryness, of a 2-5 mL aliquot of the filtered geothermal water sample to which was added 3.0 mL of an acid mixture containing (v/v) 24  $\text{HNO}_3$  : 24  $\text{HClO}_4$  : 1  $\text{H}_2\text{SO}_4$ . To the residue was added 1.0 mL concentrated HCl and the resulting mixture was transferred to a reduction-distillation tube. This was followed by the addition of 1.0 mL of

the reducing agent, acidic 10% CuCl solution. Nitrogen gas was bubbled through the reconstituted mixture for 12 minutes while heating. The reduced metal ion, As(III), in the form of  $\text{AsCl}_3$  (HCl) vapor was absorbed into 5.0-mL ultrapure water in the receiver test tube. This solution of  $\text{AsCl}_3$  was acidified by adding 11.0 mL concentrated HCl and subsequently diluted to 25.0 mL; making the final solution 6 M in HCl. This was then analyzed voltammetrically.

**Mercury.** Mild digestion [8] was carried out after adding to a 5.0-mL aliquot of the filtered geothermal water sample, 0.50 mL of Lefort mixture containing (v/v) 1 HCl : 3  $\text{HNO}_3$  : 0.75 mL 10%  $\text{KMnO}_4$  (aq) solution, and 25 mL 30%  $\text{H}_2\text{O}_2$ . To ensure complete breakdown of any organically-bound Hg which may still be present, the mixture was also UV-irradiated using a 15-watt UV lamp for 2 hours [8]. The excess permanganate was destroyed with a 12% aqueous solution of hydroxylamine hydrochloride ( $\text{NH}_2\text{OH}\cdot\text{HCl}$ ) added dropwise until the color disappeared. The resulting solution was diluted with 0.1 M  $\text{HNO}_3$  to 25 mL and analyzed voltammetrically.

**Gold.** A 25-mL aliquot of filtered geothermal water sample was treated with 1.0 mL of 7 M HCl, saturated with  $\text{Cl}_2$  gas [9]. This was mixed using a mechanical shaker (Burrell, Model 75) for 10 minutes and then left to stand for another 5 minutes. Benzidine test was used to detect unreacted or excess  $\text{Cl}_2$ . The addition of 0.10-mL portions of 7 M HCl, saturated with  $\text{Cl}_2$  was continued until the presence of excess  $\text{Cl}_2$  was detected. This condition indicated complete conversion of Au ions into its tetrachloro

Table 1. Geothermal Walter Samples Analyzed.

Sample Number	Code	Location/Description	Depth, m
1	LGP <sup>a</sup> W108 #399 WBR <sup>b</sup>	Well 108	1820.7
2	LGP RI-MAH # 151	Mahanagdong, Reinjection water	f
3	LGP W202 # 249 WBR	Well 202	1896.9
4	BMGP <sup>c</sup> PAL 15D#75 WBX <sup>d</sup>	Palayan-Bayan	2330.3
5	BMGP CN-1 #29 MS <sup>e</sup>	Cawayan	2553.3
6	BMGP OP-3D #49 WBX	Osiao-Pangas	2443.4
7	T-213/R(SAM) 154	Tongonan, Sambaloran, Reinjection water	f
8	T-206/212-305	Tongonan, mixture	f
9	T-206/101-320	Tongonan, mixture	f

<sup>a</sup> Leyte Geothermal Project

<sup>b</sup> Sample taken from Weber Separator

<sup>c</sup> Bacon-Manito (BACMAN) Geothermal Project, Sorsogon/Albay boundary

<sup>d</sup> Sample taken from Werbox

<sup>e</sup> Sample taken from Mini-Silencer

<sup>f</sup> Water came from different sources (wells)

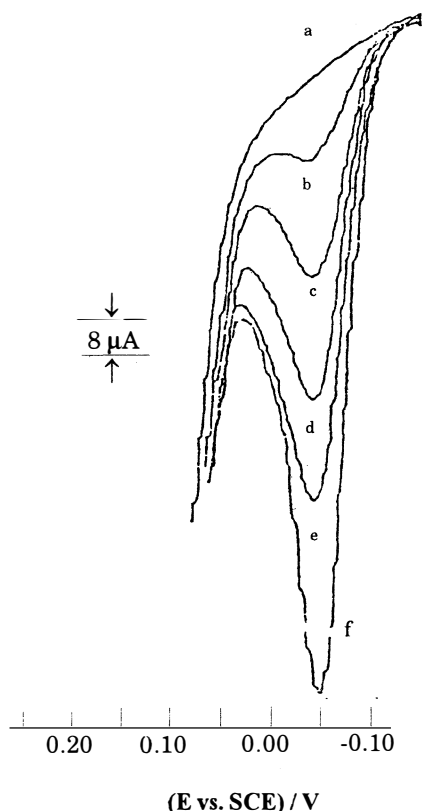
complex form  $\text{AuCl}_4^-$  [9]. The unreacted  $\text{Cl}_2$  was then displaced by bubbling  $\text{N}_2(\text{g})$  until completely removed (benzidine test) prior to its voltammetric analysis.

## Results and Discussion

### Optimization of Voltammetric Parameters

The effect of some parameters, such as supporting electrolyte and working electrode on the resulting voltammograms, on sensitivity and reproducibility were evaluated for each of the trace metal studied. This was accomplished by observing the behavior of the stripping peak which is dependent on two important voltammetric parameters namely: the peak potential ( $E_p$ ) and the peak current ( $i_p$ ).  $E_p$  is the qualitative parameter, which is characteristic of a particular electroactive species, while  $i_p$  is used as the quantitative parameter, and directly related to the analyte concentration. Based on the results obtained, the stripping peak was observed to be dependent on the type of supporting electrolyte and the kind of working electrode used.

The best supporting electrolyte for As(III) voltammetric analysis was found to be 6 M HCl. Using



**Figure 1:** DPASV voltammograms of standard As(III) solution in 6 M HCl medium at a TFGE. Scan rate, 5 mV/s; 2 minutes deposition at -0.150 V. (a) 0, (b) 30, (c) 50, (d) 70, (e) 90, and (f) 120 ppb As(III.)

this supporting electrolyte, broad As(III) stripping peaks were obtained with both Pt disc and gold wire (GWE) working electrodes; while there was no peak observed when GCE was used. With a TFGE working electrode a well-defined As(III) stripping peak was obtained. The gold film working electrode was found to be unstable at higher HCl concentrations. The GCE substrate was also damaged at HCl concentrations higher than 7 M. The DPASV voltammograms of standard As(III) solutions obtained using TFGE in 6 M HCl are shown in Figure 1.

As(V), however, did not yield any stripping signal in any of the working electrodes used. This observation agrees with the literature data that As(V) is electroinactive [7].

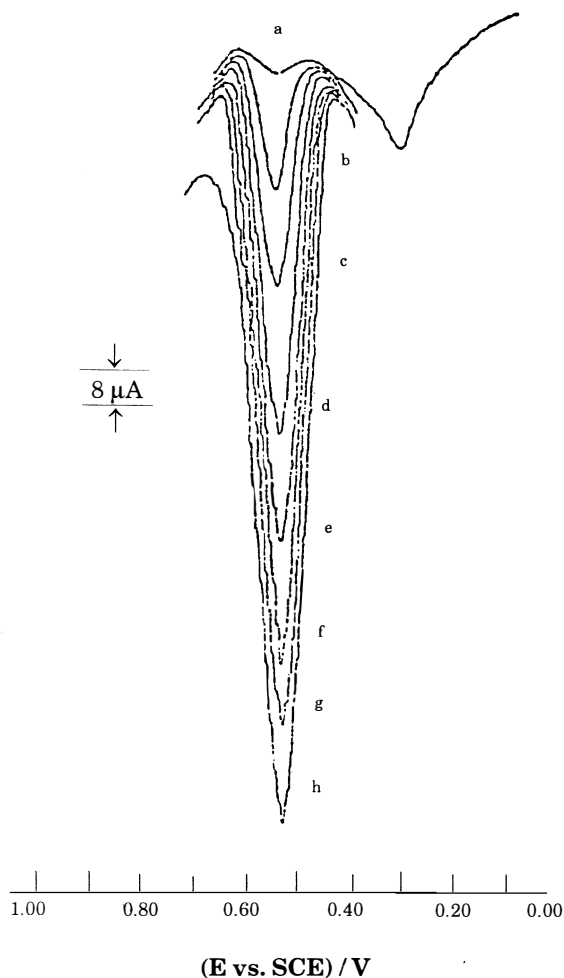
In 0.10 M  $\text{HNO}_3$ , the bare GCE gave a well-defined Hg(II) stripping peak (+0.20 V); while two peaks, one broad (+0.30 V) and the other well-defined (+0.50 V), were observed using TFGE. The well-defined peak observed in TFGE was more enhanced than the one obtained using GCE. Thus TFGE was preferred over bare GCE. The appearance of two Hg peaks can be explained from the nature of Hg deposition on the electrode which consists of two stages [6]: First, is the monolayer deposition of Hg(0) which gave rise to the stripping peak at +0.30 V and then, the bulk Hg(II) deposition which gave rise to the stripping signal at +0.50 V. The well-defined peak which was observed at +0.50 V was used for quantitation of Hg(II) since its peak height increased linearly with increased Hg(II) concentration. Both GWE and Pt discs gave no peak within the potential range scanned (0.00 to +0.600 V). Using TFGE, two broad small peaks were obtained when 0.10 M aqueous solutions of HCl,  $\text{H}_2\text{SO}_4$  or KCl were used as supporting electrolyte. There was no peak observed when 0.10 M  $\text{NH}_4\text{OH}$  was the supporting electrolyte. This result is expected since most metal ions form stable ammonia complexes, and in a basic environment, they readily form insoluble hydroxides. An aqueous solution of  $\text{HNO}_3$  (0.10 M) was thus considered as the most suitable supporting electrolyte for Hg(II) voltammetric analysis. Figure 2 illustrates the typical voltammograms for Hg(II) in 0.10 M  $\text{HNO}_3$  at a TFGE.

For Au(III), no peak was observed with 0.10 M solutions of  $\text{HNO}_3$ ,  $\text{H}_2\text{SO}_4$ , HOAc, NaOAc and  $\text{NH}_4\text{OH}$ . A fairly well-defined peak was obtained in both 0.10 M KCl and 0.10 M HCl, while 0.10 M KBr aqueous solution was found unsuitable due to the high background signal. Only the chloride medium was found suitable for Au(III) analysis since the oxidation of  $\text{Cl}^-$  occurs at potentials more positive than that of Au(III) at a GCE working electrode. The best supporting electrolyte for Au(III) analysis was determined to be 0.20 M HCl. DPASV voltammograms of standard Au(III) at a GCE in 0.20 M HCl are shown in Figure 3.

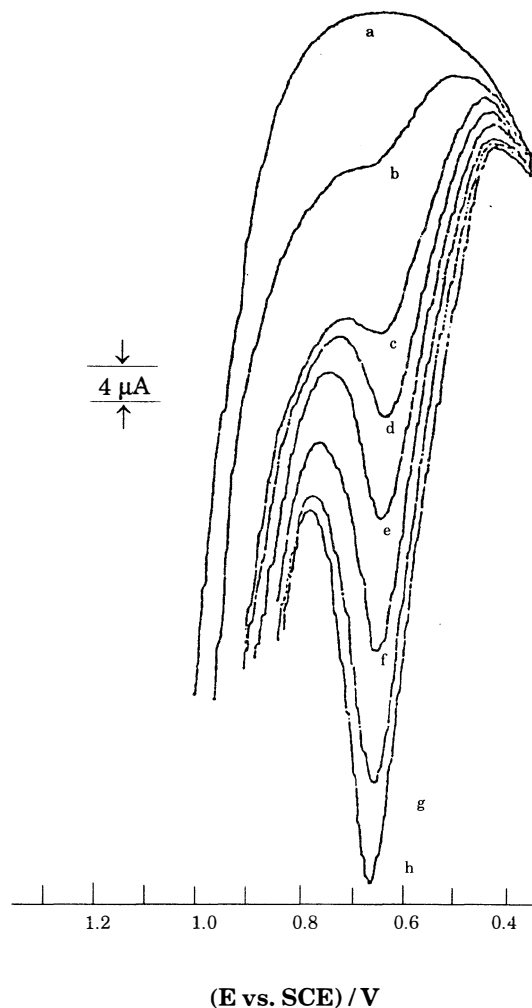
Table 2 gives a summary of the optimum parameters used in the DPASV analyses of the three trace metals.

### Concentration Dependence

The dependence of the stripping peak current on concentration was determined for each of the three trace metals. The calibration plots for the different trace metals are



**Figure 2:** DPASV voltammograms of standard Hg(II) solution in 0.1 M HNO<sub>3</sub> at a TFGE. Scan rate, 10 mV/s; 2 minutes deposition at 0.00 V. (a) 0, (b) 5, (c) 10, (d) 15, (e) 20, (f) 25, (g) 30, and (h) 35 ppb Hg(II).



**Figure 3:** DPASV voltammograms of standard Au(III) solution in 0.20 M HCl at a GCE. Scan rate, 10 mV/s; 10 minutes deposition at -0.500 V. (a) 0, (b) 5, (c) 10, (d) 14, (e) 19, (f) 24, (g) 29, and (h) 34 ppb Au (III).

**Table 2.** Summary of optimum parameters used in the anodic stripping voltammetric analyses of arsenic, mercury, and gold.

	As(III)	Hg(II)	Au(III)
Supporting electrolyte	6 M HCl	0.10 M HNO <sub>3</sub>	0.20 M HCl
Working electrode	TFGE <sup>a</sup>	TFGE <sup>b</sup>	GCE <sup>c</sup>
Deposition potential, V	-0.150	0.000	-0.500
Deposition time, min	2.0	2.0	10.0
Scan rate, mV/s	5.0	10.0	10.0
Scan range, V	-0.150 to +0.400	0.000 to +0.650	+0.200 to +1.000

<sup>a</sup> Thin film gold electrode. GCE pre-plated with 0.0002 M Au(III) in 0.50 M HCl plating solution, using a deposition potential and deposition time of -0.500 V and 5.0 min., respectively.

<sup>b</sup> Same as (a) but using a deposition time of 2.0 min.

<sup>c</sup> Bare glassy carbon electrode.

**Table 3.** Arsenic(III) content in Geothermal Water Samples.

Sample Number	[As(III)], ppm	RSD*(%)
1	9.4	1.0
2	8.7	6.5
3	9.2	3.8
4	6.6	25.0
5	10.1	3.2

presented in Figure 4. A linear responses were obtained in the ppb levels. For Hg(II), a linear calibration plot of peak current observed at +0.50 V against Hg(II) concentration was obtained within the concentration range 0 - 50 ppb Hg. The Au(III) stripping signal observed at +0.80 V was linearly dependent on the Au(III) concentration up to 50 ppb. Higher Au(III) concentration caused positive displacement of  $E_p$  and significant peak broadening. The stripping signal observed at -0.05 V was linearly dependent on the As(III) concentration for the range 0 - 1.2 ppm

#### Limit of Detection

The limit of detection is generally defined as the concentration that would give an analytical signal significantly different from the blank. This was determined for each metal by measuring the DPASV signals for each supporting electrolyte (blank) in the same working electrode used in the analysis at the most sensitive setting of the instrument. Twenty blank determinations were carried out. Using two times the standard deviation of these signals measured (uA) and the analytical sensitivity (slope of the calibration plot), the limit of detection was found to be 0.20 ppb for As(III), 0.02 ppb for Hg(II), and 0.04 ppb for Au(III).

#### Analysis of Geothermal Water

**Arsenic.** Aside from DPASV, other voltammetric methods for As(III) determination were investigated. Among these were differential pulse cathodic stripping voltammetry (DPCSV) on a thin-film Hg electrode with Cu(II) co-deposition [10] and Se(IV) co-deposition [11]. Cu(II) can form a stable Cu-As complex which is stripped during the cathodic (reduction) scan. The cathodic stripping peak occurs at about -0.45 V in 1.0 M HCl. Se(IV) can also form a complex with As(III) which can also be cathodically stripped at about -0.50 V in 0.10 M  $H_2SO_4$ . The use of Cu-coated GCE in 1.0 M  $HClO_4$  in DPASV analysis was also tried. All these methods had relatively poor detection capabilities and hardly reproducible results.

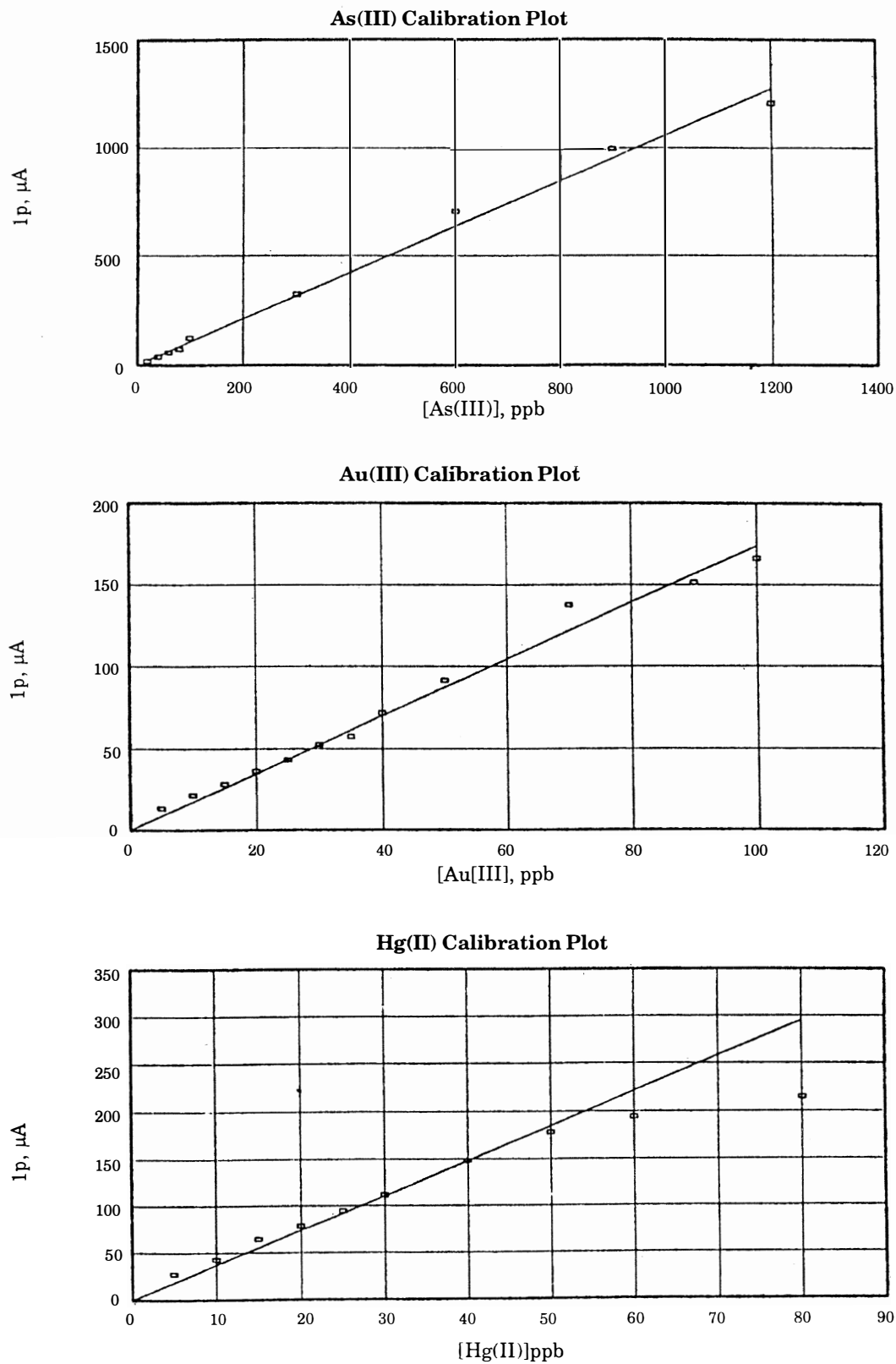
The DPASV method used in As(III) analysis was a modified method of Davis [7]. Instead of using tubular pyrolytic graphite electrode, a glassy carbon electrode coated with gold (TFGE) was utilized. The water samples were filtered prior to analysis thus, only the dissolved metal species were determined in this DPASV study. In

the sample preparation, acid digestion was done to destroy naturally-occurring organic compounds in geothermal water, which could interfere in the analysis of As(III). It also oxidized all the arsenic species into its nonvolatile form, As(V). The addition of cuprous chloride in the reduction-distillation step converted the As(V) to As(III). Bubbling the mixture with  $N_2$  (g) displaced the  $AsCl_3(HCl)$  vapors which was then absorbed in ultrapure water. The resulting solution was made 6 M in HCl, and analyzed by DPASV.

When this reduction-distillation step was omitted, no As(III) voltammetric signal was obtained. An As(V) solution which was acid-digested and reduced-distilled gave DPASV signals identical with those obtained from a separate solution of As(III) with the same concentration. The reduction-distillation step freed As(III) from its matrix and eliminated any matrix interference in the determination this metal ion. With the matrix interference eliminated, the calibration plot technique was used for the quantitation of As(III) in the samples. Results of the analysis of five geothermal water samples are summarized in Table 3. The concentration of As(III) in the geothermal water samples analyzed ranged from 6.6 to 10.0 ppm with an average relative standard deviation of 7.9%.

**Mercury.** A modified method of Sipos [8] was employed for Hg(II) analysis of the geothermal water samples. Gold film, pre-plated on GCE or TFGE, was utilized instead of a gold disc working electrode. Sample digestion was carried out to oxidize possible mercury - organo complexes in the sample. The sample was UV irradiated for 2 hours to ensure complete decomposition of organic matter and to release organically-bound Hg. Aliquots of ultrapure water were also digested in the same manner as the water samples to serve as blank. Hg(II) was detected in the digested blank and this must have come from the reagents used in the digestion step. The Hg(II) content of the sample was corrected for the blank. Quantitation of Hg(II) in geothermal water samples was done by standard addition method in order to minimize matrix interference effects. Ions like Cd(II), Pb(II), Zn(II), and Ca(II), although present in geothermal waters, do not interfere in the analysis since their stripping peak potentials are far removed from those of the trace metals being determined. Results of Hg(II) analysis are summarized in Table 4. The Hg concentration ranged from 0.02 - 0.07 ppm with an average relative standard deviation of 7.8%.

**Gold.** Treatment of the geothermal water sample with 7 M HCl, saturated with  $Cl_2$  (g) was carried out to convert Au(III) into its tetrachloro complex, which is the desired form of Au for voltammetry. The excess  $Cl_2$  (g) was removed by bubbling  $N_2$  (g) into the solution. The voltammetric procedure employed was a modified method of Jakubec and Sir [9]. The supporting electrolyte used was 0.20 M HCl (aq) instead of a non-aqueous medium consisting of 0.50 M  $HClO_4$  in absolute ethanol. Voltammetric runs in the non-aqueous medium hardly gave reproducible results and required frequent renewal of the GCE surface due to decreased sensitivity after successive runs. Like mercury, standard addition technique was also employed in the quantitation of Au(III). Water samples were not diluted in the preparation of test solutions for the



**Figure 4.** Calibration plots for DPASV analyses of As(III), Au(III), and Hg(II).

**Table 4.** Mercury(II) content in Geothermal Water Samples

Sample Number	[Hg(II)], ppm	RSD*(%)
1	0.070	4.6
2	0.055	13.7
3	0.031	4.0
4	0.024	4.6
5	0.063	2.6
6	0.051	17.5

**Table 5.** Gold(III) content in Geothermal Water Samples.

Sample Number	[Au(III)], ppb	RSD*(%)
7	0.24	4.8
8	8.40	6.3
9	1.80	13.0

voltammetric analysis of Au(III), and the results obtained are given in Table 5. The Au(III) concentration ranged from 0.2 - 8.4 ppb with an average relative deviation of 8.0%.

The concentration ranges of the trace metals obtained in the geothermal water samples were within the values reported in the literature [2, 3].

#### **Correlation of Results Obtained Using DPASV and Spectrophotometry**

The geothermal water samples were also analyzed by another technique. As(III) was determined spectrophotometrically using silver diethyldithiocarbamate (SDDC) as complexing agent, while Hg(II) and Au(III) were analyzed by suitable AAS methods. Results using spectrophotometry and DPASV are summarized in Table 6. Analysis of As(III) by AAS was not carried out due to the unavailability of the As lamp during the time of analysis. The Spectrophotometric-SDDC method is a colorimetric method involving formation of a colored complex between As(III) and SDDC. The As(III) values obtained using this method were higher than the values obtained by DPASV. Many ions present in the geothermal water system such as Cr(III), Cu(II), Hg(II) and Ni(II) could interfere. The As(III) values obtained by DPASV were more reliable since the use of the reduction-distillation step in the sample preparation eliminated any matrix interference. The DPASV values are in agreement with literature values for geothermal water system [2, 3]. The Hg(II) values obtained by DPASV analysis were observed to be higher than those obtained by AAS but these were considered more reliable than those obtained by AAS since the AAS values were

**Table 6.** Summary of results obtained using DPASV and Spectrophotometry

Sample Number	[As(III)], ppm	
	SPEC-SDDC <sup>a</sup>	DPASV <sup>b</sup>
1	15	9.4
2	23	8.7
3	21	9.2
LOD <sup>c</sup>	0.01	0.0002

Sample Number	[Hg(II)], ppm	
	AAS <sup>d</sup>	DPASV
1	0.012	0.070
2	0.005	0.055
3	0.005	0.031
4	0.006	0.024
5	0.007	0.063
6	0.006	0.051
LOD	0.0002	0.00002

Sample Number	[Au(III)], ppb	
	AAS <sup>e</sup>	DPASV
7	< 200	0.24
8	< 200	8.40
9	< 200	1.80
LOD	< 200	0.04

<sup>a</sup> Spectrophotometric silver diethyldithiocarbamate method

<sup>b</sup> Differential pulse anodic stripping voltammetric method

<sup>c</sup> Limit of detection

<sup>d</sup> Cold vapor atomic absorption spectroscopy

<sup>e</sup> Atomic absorption spectroscopy, direct aspiration

very near the AAS limit of detection. Au(III) was determined by the direct AAS aspiration technique and results were below the detection limit for the method.

#### **Conclusion**

This research work has demonstrated the capability of electrochemistry in trace analyses. In addition to the usual spectrophotometric techniques employed for trace analysis, DPASV was found to be a suitable analytical tool in trace analyses of arsenic, mercury, and gold in geothermal water samples.

The working electrodes used in this study utilized the laboratory-built bare GCE, and were modified by pre-plating with gold solution just prior to the actual analysis, as in the case of Hg and As determination. The TFGE was found to be a suitable and simple working electrode as compared with the previously reported gold-film coated

pyrolytic graphite for Au analysis, and twin gold working electrode for Hg analysis. To further enhance sensitivity of the method, DPASV was employed.

By appropriate sample treatment and control of analytical parameters, interferences from other metal ions have been minimized or eliminated. The reduction-distillation step in the analysis of arsenic eliminated any possible matrix interference.

This electrochemical study has provided some baseline information on the levels of three trace metals in some geothermal water samples found locally, but further research work is needed to determine electrochemically the other important trace metals contained in this natural water system.

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