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**TRACE MULTIELEMENT ANALYSIS OF REACTOR
MODERATOR WATER: SIMULTANEOUS DETERMINATION
OF COPPER, GOLD, SILVER, AND MERCURY USING
DIFFERENTIAL PULSE STRIPPING VOLTAMMETRY (U)**

by

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ABSTRACT

A rapid, inexpensive trace multi-element analysis of reactor moderator heavy water is described. Samples were analyzed for copper, silver, gold, and mercury at the low ppb level using Differential Pulse Stripping Voltametry (DPSV). These ions are kept below 25 ppb to avoid possible vessel corrosion. A high concentration of aluminum and iron in the samples prevented analysis by ICP spectroscopy. The DPSV method also avoided volatilizing highly tritiated samples.

Differential Pulse Stripping Voltametry is a commonly used electroanalytical technique for determining trace levels of metals in aqueous solutions. However, application of this method for routine analytical support in a plant laboratory environment was limited due to the method's sensitivity to interferences^{1,2}. This paper describes a DPSV method which is rugged enough to be used for routine analytical support and addresses method interferences.

INTRODUCTION

The three production reactors at the Savannah River Site (SRS) use aluminum clad target and fuel rods as part of the assembly for the production of tritium, a radioactive isotope of hydrogen^{3,4}. Copper, gold, silver, and mercury if present would cause pin-hole corrosion of the aluminum metal, in the presence of chloride ions⁵. If this were to occur, the moderator water in the reactor vessel would come in contact with the uranium metal in the fuel rods and cause an exothermic reaction⁶. A method was required to confirm that these metals had not been introduced into the reactors. The method needed to accurately analyze for these metals at the part per billion level and be rugged enough that it could be performed by technicians on a routine basis in the plant laboratory. The method developed was differential pulse stripping voltametry on a platinum electrode.

Differential Pulse Stripping Voltametry is an electrochemical technique used to qualitatively and quantitatively identify trace metal ions in multi-element mixtures⁷. The experimental procedure is a two step process: deposition and stripping. The deposition step involves the electrolytic deposition of a chemical species onto an inert electrode surface at a constant potential. These species are then stripped off the surface of the electrode by the application of a differential pulse potential waveform to the electrode which causes dissolution of the deposit. The differential pulse mode corrects for background and charging current and thus yields lower detection limits. The data produced is a series of vertical current peaks along a horizontal potential axis. The location of these peaks along

the potential axis corresponds to the identity of the ion which was deposited. The height of the peak is directly proportional to the concentration of the analyte in solution.

Stripping voltammetry is suitable for the determination of metal ions which are readily reduced to the metallic states and reoxidized. As many as four to six metal ions can be simultaneously determined.

EXPERIMENTAL

All electrochemical experiments were done using a BAS100A Electrochemical Analyzer (BioAnalytical Systems, Inc., West Lafayette, IN). The BAS100A was interfaced with a Houston Instruments Digital Plotter (model DMO-2) and an IBM PC/2 personal computer for data storage and manipulation.

The analysis cell consisted of a 20 ml glass voltammetry cell with a cell top containing a platinum wire auxiliary electrode (BioAnalytical Systems, Inc., West Lafayette, IN), a silver/silver chloride micro-voltametric reference electrode (BioAnalytical Systems, Inc., West Lafayette, IN), and an ultra-micro-voltametric platinum working electrode (BioAnalytical Systems, Inc., West Lafayette, IN). The working electrode was cleaned before each stripping run by cycling the working electrode potential between +1500 mV and -1500 mV at a sweep rate of 50,000 mV/sec in 0.1 M KNO₃ for 5 seconds.

Reagents

All reagents and solutions were prepared from distilled, deionized D₂O which had been boiled and passed through an ion exchange resin for purification. Unless otherwise noted, all stock reagents were used as received from the manufacturer.

Aqueous stock solutions of 2 M KNO₃ were prepared fresh daily from reagent grade materials. 10 ppm standard solutions of copper, gold, silver, and mercury were prepared by dilution of 1000 ppm standard solutions from Spex Industries. These standard solutions were prepared fresh immediately prior to each day's use.

Procedure

The electrochemical procedure was carried out in a fume hood rated at 200 linear feet per minute with constant monitoring for tritium. A 10 ml aliquot of the sample was mixed with 0.5 ml of 2 M KNO₃, yielding an approximate electrolyte concentration of 0.1 M. The solution was deoxygenated by sparging with helium for 2 minutes immediately prior to the experimental run. The working electrode potential was held at -700 mV for 200 seconds, and after a quiet period of 30 seconds, swept in the positive direction to 900 mV at 4 mV/sec using a differential pulse waveform. The pulse width was 25 msec, the pulse period was 250 msec, and the pulse height was 100 mV. The solution was stirred throughout the deposition period to maximize the amount of plating on the electrode surface. A background voltamogram was recorded using 10.0 ml D₂O plus 0.5 ml 2 M KNO₃. This voltamogram was stored digitally in the BAS100A analyzer and subtracted from the sample scan. Thus the resulting current was due only to electroactive species in the sample.

Daily bioassays were performed on the analysts and no uptake of tritium was ever detected.

DISCUSSION

In 0.1 M KNO_3 solution, the peaks for gold, copper, mercury, and silver appeared at approximately -420, -64, +5, and +320 mV versus a Ag/AgCl reference electrode. No matrix interferences were seen between the metal ions in solution. Amalgamation between gold and mercury in solution was not a problem in dilute solutions, although it did contribute to increased RSD values at concentrations above 2 ppm. In dilute aqueous solutions, the current signals from non-acidified solutions degraded over time. This was attributed to the instability of metal ions in non-acidified solutions and to the metal ions plating out on the sides of the sample bottle⁹.

Figure 1 shows the differential pulse stripping voltamogram for a typical moderator water sample. As a comparison, Figure 2 shows that sample spiked with 25 ppb Cu, Au, Ag and 5 ppb Hg. The background current due to KNO_3 has been digitally subtracted from both voltamograms.

Procedural Modifications for Routine Plant Support

There were four problems associated with implementing this method for routine sample analysis to be performed by a lab technician: 1) sample contamination, 2) preparation of an accurate standard curve, 3) reproducible results, and 4) data analysis.

Sample Contamination

Because of the low (ppb level) detection limits of this method, all reagents, standards, and solvents must be ultra-pure. Scrupulous care had to be taken in washing glassware, electrodes, and all materials which came in contact with the sample. All glassware was soaked in 6 M nitric acid, rinsed with 18 M Ω deionized water, and oven dried before use. Teflon or PTFE bottles are recommended for sample collection. Glass was not practical for collection of radioactive samples and polyethylene both adsorbs metal ions from solution and leaches contaminant species into solution¹⁰.

Preparation of a Standard Curve

Calibration curves were prepared by spiking the 10 ml sample with 25 μl aliquots of 5 ppm standards of copper, gold, silver, and mercury, making the sample an additional 12.5 ppb in concentration. A DPSV was then run and the current peak height and location was recorded for each element. A plot of peak current versus element concentration was linear with an x-axis intercept equal to the element concentration. The calibration curves for each of the four elements are shown in Figure 3.

The Standards were prepared fresh for each use by dilution of 1000 ppm stock standards with deionized D_2O .

Results

The electrochemical cleaning step was crucial to getting reproducible results. This condition of the electrode surface must be in the same condition for each experimental run. The electrodes were soaked in 3 M nitric acid over night to clean off any oxide layer which may have formed during the course of the days experiments. Sample preparation was minimal, consisting of the addition of an electrolyte solution (0.5 ml of 2 M KNO_3) to the sample. A sample could be prepared, run, and analyzed in 15 minutes.

The samples were also found to contain a significant amount (ppm level) of aluminum, iron, and one other species which is probably chromium. These metals did not interfere with detection of the metal ions in question.

Data Analysis

The height above the zero-current axis was measured and converted into current. This current was assumed to be due to sample signal, regardless of whether there was a stripping peak present. This removed the subjective judgement from the technician and simplified data analysis.

Accuracy and Precision of Elemental Measurements

Tables 1 and 2 contain the data from replicate measurements of the National Institute of Standards Technology (NIST) standards and from a representative sample. The accuracy and precision of the measurements were sufficient for routine analyses.

The quality of the measurements depends on preparing an accurate standard curve. The validity of this curve should be verified before each analysis by running a NIST elemental standard.

Method Limitations

At low ppb detection limits, the method is very sensitive to interferences or contamination. Any species which can be oxidized or reduced on a platinum electrode may mask or distort the current response from the metal ions of interest. Therefore, this method is limited to clean dilute samples or samples with a representative blank which can be used to subtract out the current response attributable to the interfering species.

This is a screening method in that some elements can not be positively identified since they strip out at the same potential value. In this event, the working electrode or supporting electrolyte can be changed, since it is less likely that two different elements will plate and strip at the same potential value in different electrolyte systems or on different electrodes. Developmental work currently in progress in this laboratory will enable positive identification of unknown elemental species in solution.

CONCLUSION

Samples of tritiated moderator water were analyzed for copper, gold, silver, and mercury and found to be within operating specifications. The samples were analyzed rapidly, accurately, and with low detection limits. Most importantly from a practical standpoint, these analyses were performed by technicians on a routine basis in a plant support laboratory with good accuracy and reproducibility.

REFERENCES

1. Wang, J., American Laboratory, 15, 7, pp 14-23 (1983).
2. Ellis, W.D., J. Chem. Ed., A, 31 (1973).
3. Weirick, L.J., "Electroplating and Corrosion Protection, Surface Metallurgy or Uranium and Uranium Alloys," Vol 3, Am. Soc. for Metals (1981).

4. Mettox, D.M., *Electrochem. Technol.*, 2, p 295 (1964).
5. Bohn, J., Uhlis, H.H., *J. Electrochem. Soc.*, 116, p 906 (1969).
6. Katz, Seaberg, Marss, "Chemistry of the Actinide Elements, Volume 2," Chapman and Hall, New York (1986).
7. Wang, J., "Stripping Analysis," VCH Publishers Inc. (1985).
8. Almon, A.C., "Basic Data for the Analysis of Trace Metal Ions using Differential Pulse Stripping Voltametry," WSRC-RP-89-865, Westinghouse Savannah River Company, Aiken, South Carolina 29808, (October, 1989).
9. Smith, B.W., Parsons, M.L., *J. Chem. ED.*, 50, 10, pp 679-681 (1973).
10. Kissinger, P.J., Preddy, C.R., Shoup, R.E., Heineman, W.R., "Laboratory Techniques in Electroanalytical Chemistry," Marcel Decker, New York (1984).

Table 1: Replicate Results - Standard Sample

	<u>Metal Ion Concentration (ppb)</u>			<u>Mercury</u>
	<u>Copper</u>	<u>Gold</u>	<u>Silver</u>	
Calibration Standard	25.0	25.0	25.0	5.0
Run #1	24.4	25.0	24.9	3.2
Run #2	26.1	27.1	25.3	5.2
Run #3	25.8	25.9	25.1	4.9
Mean	25.4	26.0	25.1	4.4
Standard Deviation	0.9073	1.0530	0.2000	1.0790

Table 2: Replicate Results - Sample #33878

	<u>Metal Ion Concentration (ppb)</u>			<u>Mercury</u>
	<u>Copper</u>	<u>Gold</u>	<u>Silver</u>	
Run #1	10.1	15.0	10.4	4.1
Run #2	12.2	16.5	11.6	3.5
Run #3	11.0	14.4	12.1	5.1
Mean	11.1	15.3	11.4	4.2
Standard Deviation	1.05	1.08	0.87	0.81

200pA

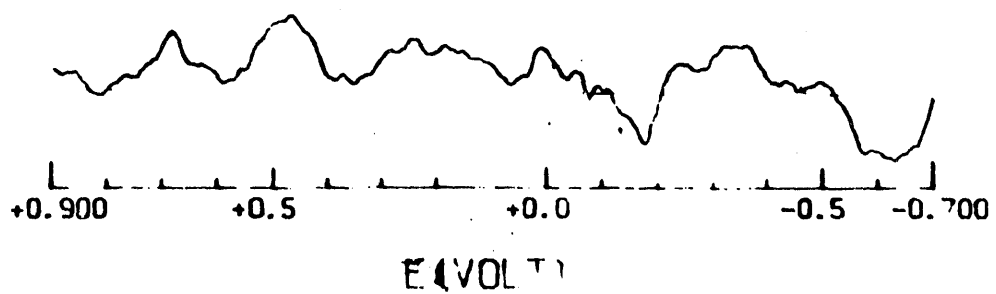


Figure 1: DPSV of Typical Moderator Water Sample, (10 mL sample plus 0.5 mL 2 M KNO₃)

200pA

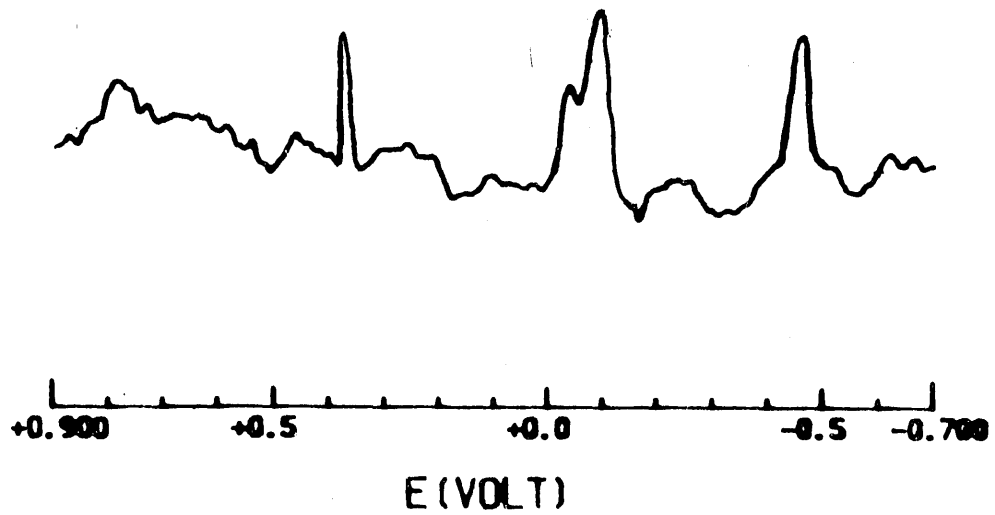
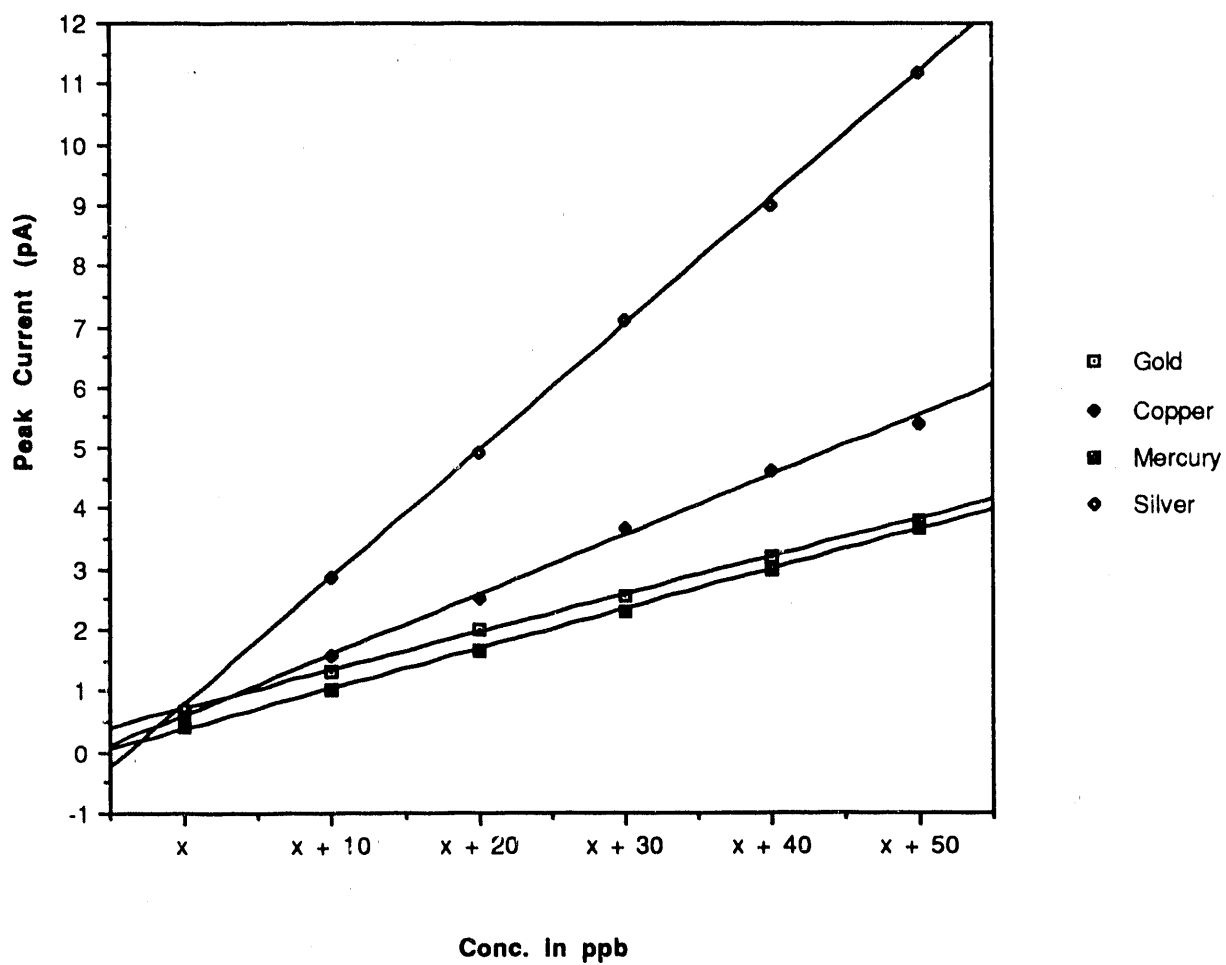


Figure 2: DPSV of Typical Moderator Water Sample, (10 mL sample plus 0.5 mL 2 M KNO₃) Spiked to 25 ppb Cu, Au, Ag and 5 ppb Hg.

Figure 3: Standard Addition Method Calibration Curve for Cu, Au, Ag, and Hg in 0.1 M KNO₃ (x is the initial element concentration in the sample).



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