ELSEVIER

International Journal of Mass Spectrometry 178 (1998) 51–63

International Journal of Mass Spectrometry

Adsorptive stripping voltammetry as a sample pretreatment method for trace uranium determinations by inductively coupled plasma mass spectrometry

Jack R. Pretty, Gary J. Van Berkel, Douglas C. Duckworth*

Chemical and Analytical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831-6375, USA

Received 20 September 1997; accepted 26 March 1998

Abstract

Adsorptive stripping voltammetry was investigated as a route for improving trace level quantification of uranium via on-line matrix elimination and analyte preconcentration. On the basis of prior literature reports, propyl gallate was selected as a chelating agent for adsorptive accumulation of uranium (VI) at a mercury thin-film electrode (MTFE). Off-line electrochemical studies indicated that the uranium-propyl gallate (U-PG) complex accumulated (−0.15 V) at a MTFE when the uranium containing sample was mixed (1:1 v/v) with 5×10^{-5} M PG in 0.05 M sodium acetate buffer (pH 4.5), and could be stripped into 0.05 M sodium acetate or 0.1 M ammonium nitrate, an inductively coupled plasma mass spectrometry (ICP-MS) compatable matrix, by a potential scan to −1.4 V. A thin-layer, flow-by electrochemical cell was placed on-line with ICP-MS and the same basic stripping procedure performed, but ^{238}U was not detected when the stripping potential was applied. Combining a potential step to −1.2 V with injection of 1% HNO_3 did, however, effectively release the uranium to the ICP-MS. Matrix elimination was successful, and 24-fold signal enhancement was achieved with a 10 min accumulation, consuming just 0.8 mL of a 0.5 μg/L uranium solution. Quantitative performance was tested on NASS-4 Open Ocean Seawater (2.68 ± 0.12 μg/L uranium) by using calibration plot and standard addition methods. Nonlinearities, as functions of both analyte concentration and deposition time, were observed and are consistent with saturation of the MTFE, suggesting that the technique is most applicable to ultratrace uranium analysis or appropriately diluted samples. (Int J Mass Spectrom 178 (1998) 51–63)

Keywords: Inductively coupled plasma mass spectrometry; Adsorptive stripping voltammetry; Propyl gallate; Uranium; Matrix elimination; Preconcentration

1. Introduction

With quantitative multielement and isotopic capabilities, and ng/L detection limits, inductively coupled plasma mass spectrometry (ICP-MS) is currently unrivaled in trace element analysis [1–4]. Matrix effects, however, are frequently problematic [5]. High concentrations of dissolved solids can result in polyatomic interferences, signal suppression, and signal instability. To address matrix effects, a variety of separation techniques have been employed on line, including hydride generation, ion exchange and chelation techniques, and solvent extractions [5, 6]. In addition to matrix elimination, varying degrees of analyte specificity and signal

* Corresponding author. E-mail: duckworthdc@ornl.gov

Presented at the Third Alfred O. Nier Symposium on Inorganic Mass Spectrometry, Durango, CO, May 5–9, 1997.

Dedicated to the memory of Al Nier.

1387-3806/98/$19.00
PII S1387-3806(98)14043-9

enhancement via preconcentration (~10–40×) are obtained with these approaches.

As an alternative, we have been investigating the use of an electrochemical cell for specific analyte preconcentration and cleanup with ICP-MS [7,8]. This route has been applied in several areas of atomic spectrometry, including ICP-AES [9] and ICP-MS [10–12]. These applications have been reviewed recently [13]. The earliest works of this type focused largely on matrix elimination by using cells with a flow-through electrode design (e.g. reticulated vitreous carbon). Although such cells provided fairly high analyte deposition efficiencies and effective matrix elimination, their relatively high void volumes limited signal enhancement [14].

Prior work in this laboratory demonstrated that a thin-layer, flow-by cell design possessed high analyte deposition efficiency and matrix elimination capabilities, providing signal enhancements greater than 100-fold with less than 10 mL of sample and 15 min or less of analysis time. This was initially demonstrated by using a standard Meinhard glass concentric nebulizer (650 μL/min) [7]. The excellent performance of this design resulted from the high working electrode area/cell volume ratio (providing high deposition efficiency) and low cell volume (1–4 μL, depending on the cell spacing gasket), resulting in a high concentration of analyte in the stripping peak and minimal peak dispersion (high signal enhancement). Even better performance was observed with high efficiency, low flow rate nebulizers. For example, a direct injection nebulizer, operating at 55 μL/min, afforded more than 100-fold increase in signal intensity by using less than 250 μL of sample [15]. Efficient matrix elimination was also demonstrated. A critical evaluation of deposition efficiency and signal enhancement has recently been reported for this cell as a function of a number of variable parameters (e.g. analyte concentration, electrode spacing, sample flow rates, and deposition times) by using a microconcentric nebulizer [8].

To date, the only electrochemical preconcentration technique successfully used on line with ICP-MS has been anodic stripping voltammetry (ASV) [16]. For elements that are unresponsive in ASV, such as uranium, adsorptive stripping voltammetry (AdSV) is often effective [17]. In AdSV the analyte is complexed with an organic chelating ligand, which, at a suitable applied potential, exhibits an affinity (e.g. electrostatic, hydrophobic) towards the working electrode (usually Hg), and deposits (accumulates) thereon. Detection of the accumulated analyte is normally performed by reducing the metal ion by using a negative (cathodic) potential scan and measuring the peak current. This reduction may or may not release the metal from the surface of the electrode. Stripping the analyte back into solution by some means (preferably by altering the electrode potential), is not required in batch systems, but is necessary for use in an on-line system with downstream detection by ICP-MS.

In earlier work [7], we investigated the on-line AdSV-ICP-MS analysis of uranium by using cupferron as the chelating ligand, following the AdSV protocol of Wang et al. [18]. The limited success achieved with this approach (tenfold signal enhancement from a 5.2 mL sample in 8 min) was thought to result from the flow rate used (650 μL/min), which damaged the MTFE and probably eroded the metal-ligand complex from the MTFE due to high linear velocity of the solvent stream through the cell. Additionally, reductive potential steps did not efficiently release the metal (or metal-ligand complex) from the cell. Chemical stripping (an injection of 1% HNO_3) was necessary to release the uranium to the ICP-MS.

In the present work, the AdSV-ICP-MS approach is reevaluated by using an improved electrochemical flow system [8] and an AdSV protocol based on complexation of uranium with propyl gallate (U-PG complex). Batch mode (off-line) electrochemical studies were performed to determine the conditions necessary for accumulation of U (VI) with subsequent stripping into an ICP-MS-compatible solution. Initial results for the quantification capabilities of the on-line AdSV-ICP-MS system are also reported.

2. Experimental

2.1. Instrumentation

2.1.1. Electrochemistry

Batch mode electrochemical experiments were performed by using a CHI660 electrochemical work-

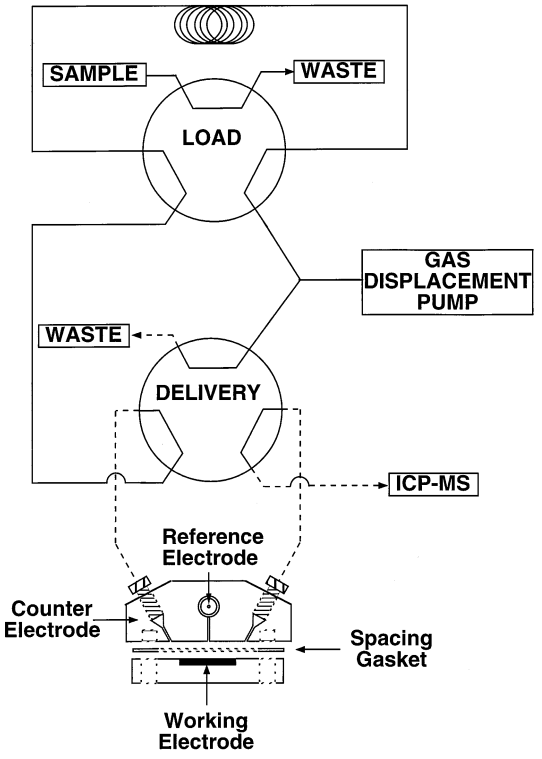

Fig. 1. Flow system for on-line AdSV-ICP-MS consisting of dual six-port valves (both valves shown in load mode), gas-displacement pump, and electrochemical flow cell. Solid lines represent 254 μm Teflon tubing. Dotted lines represent Teflon encapsulated fused silica tubing: 10 cm long, 75 μM-i.d. tubing to cell and 18 cm long, 60 M-i.d. tubing for outlets.

station (CH Instruments, Cordova, TN). The working electrode was a mercury thin film electrode MTFE formed by deposition of Hg onto a 3.0-mm-diameter glassy carbon working electrode disk (Bioanalytical Systems, Inc., West Lafayette, IN). A Ag/AgCl reference electrode (Model RE-5, Bioanalytical Systems) and a Pt wire counter electrode completed the cell.

For on-line studies with ICP-MS, a commercial thin-layer flow cell (LC-44, Bioanalytical Systems) was used (Fig. 1). The MTFE was prepared on line, plating Hg onto the glassy carbon electrode (6.0-mm diameter). A 51 μm thick Teflon gasket separated the working and stainless-steel counter electrodes defining a cell volume of approximately 3.5 μL. A Ag/AgCl reference electrode (Model RE-4, Bioanalytical Systems) was used.

Table 1
Operating conditions for ICP-MS

Radio frequency power	
Forward	1.3 kW
Reflected	<10 W
Gas flows (pressures)	
Coolant	13 L/min
Auxiliary	0.55 L/min
Nebulizer	0.975 L/min (4.6 bar)
Operating pressure	
Expansion	2.2 mbar
Intermediate	$<10^{-4}$ mbar
Analyzer	6.0×10^{-7} mbar
Sample flow rate	80 μL/min
Spray chamber	Scott-type double pass, water cooled
Sampling cone	nickel, 1.0 mm orifice
Sampling distance	10 mm from load coil
Single ion data acquisition	
m/z	238
Sweeps	1
Dwell time	327.68 ms
Channels	4095 (max)
Run time	22.4 min (max)

2.1.2. Inductively coupled plasma mass spectrometry

A VG PlasmaQuad II Plus (VG Elemental, Winsford, Cheshire, UK) was used in AdSV-ICP-MS experiments. The single ion data collection mode ($m/z = 238$) was used throughout the work. ICP-MS operating conditions are given in Table 1. A microconcentric nebulizer (Model M2, TransGenomic CETAC Inc, Omaha, NE), operating at 80 μL/min was used with a Scott-Type, double pass spray chamber.

For on-line work, a microprocessor controlled flow injection system (Microneb 2000, TransGenomic CETAC) consisting of two six-port, all-PEEK valves and gas-displacement pump (GDP) was employed (Fig. 1). The load valve was used to inject mercury plating solution, samples, and the 1% HNO_3 that was used in analyte stripping (see below). A peristaltic pump (Minipuls 2, Gilson, France) was used to load the 1.0 mL sample loop. The flow of 0.1 M ammonium nitrate from the GDP was split equally between

the two valves. Injected sample was directed through the load valve to the delivery valve, through the electrochemical cell, and to the ICP-MS or to waste. Teflon-encapsulated fused silica tubing (dashed lines in Fig. 1) was used to connect the electrochemical cell to the delivery valve (60 μm i.d.) and to connect this valve to ICP-MS and to waste (75 μm i.d.). Teflon tubing of 254 μm i.d. (solid lines in Fig. 1) was used for the other connections. Standard HPLC fittings made of PEEK were used for tubing connections.

2.2. Reagents

All solutions were prepared with deionized water (Milli-Q, Millipore Corp., Bedford, MA). For off-line electrochemical experiments, a 0.05 M sodium acetate (J.T. Baker Chemical Co., Phillipsburg, NJ) buffer was prepared at pH 4.5 with appropriate addition of acetic acid (J.T. Baker). 5.0×10^{-5} M propyl gallate (Aldrich Chemical Co., No. P5,330-6, Milwaukee, WI) was prepared by using the acetate buffer solution (PG/buffer). 0.1 M ammonium nitrate was prepared from 99.999% pure reagent (No. 25,606-4, Aldrich). For preparation of the MTFE, a 10 000 mg/L stock solution of mercury (High Purity Standards, Inc., Charleston, SC) was diluted with 1% nitric acid, prepared from dilution of Ultrex II grade HNO_3 (J.T. Baker) to a final concentration of 0.05 mM Hg. Sample standards were prepared by appropriate dilution of a 10 000 mg/L uranium stock solution (High Purity Standards, Inc.) with the acetate buffer solution.

Solutions for on-line ICP-MS work were as above with the exception of the solution used for plating the MTFE. This was 1.0 mM mercury (II) nitrate (Alfa Products, Morton Thiokol, Danvers, MA) in 0.5 M ammonium nitrate. Standards were prepared from a stock solution of 100 μg/L U (VI) in PG/buffer, serially diluted with PG/buffer as required. NASS-4 Open Ocean Seawater Reference Material for Trace Metals (National Research Council Canada) was mixed off-line (1:1 v/v) with the PG/buffer solution prior to analysis.

2.3. Electrochemical procedure

2.3.1. Batch mode adsorptive stripping voltammetry

Off-line AdSV followed the procedure detailed by Wang et al. [19]. Glassy carbon working electrodes were polished daily on a Microcloth pad moistened with Gamma Micropolish Alumina 3 (Buehler Inc., Lake Bluff, IL) and rinsed with Milli-Q water prior to use. Solutions were purged with argon and maintained under argon during use. To prepare the MTFE from the 0.05 M Hg solution, the potential on the glassy carbon electrode was held at 0.0 V for 10 s, then stepped to -0.8 V for 15 min while stirring the solution. The potential was then stepped back to 0.0 V for 1 min to strip impurities from the film.

Following preparation of the MTFE, it was transferred to 10 mL of U (VI) standard in PG/buffer. The U-PG complex was accumulated on the MTFE at -0.15 V with constant stirring. Following accumulation, stirring was halted and cyclic voltammetry (200 mV/s) or differential pulse stripping voltammetry (Initial $E = 0.0$ V, Final $E = -7.0$ V, Incr. $E = 0.004$ V, pulse amplitude = 0.05 V, pulse width = 0.06 s, sample width = 0.02 s, pulse period = 0.2 s) was performed with the MTFE in either 0.05 sodium acetate buffer or 0.1 M ammonium nitrate as described below. Potential limits for the scans were selected according to the requirements of the experiment. A potential cleaning step (60 s at -1.4 V) was performed between each analysis to clean the MTFE.

2.3.2. AdSV-ICP-MS

The glassy carbon working electrode was polished and rinsed in Milli-Q water prior to cell assembly. All sample, plating, and pump reservoir solutions were purged with argon before use. The GDP was loaded with 0.1 M ammonium nitrate. To prepare the MTFE, two 1.0 mL volumes of the mercury plating solution were injected at 200 μL/min holding the potential at 0.0 V for 1.0 min then stepping to -0.8 V for 9.0 min. The potential was then stepped back to 0.0 V.

Samples of uranium in PG/buffer were prepared off line for convenience, though successful on-line mixing for AdSV-ICP-MS has been demonstrated previously [7]. Solution flow rate for AdSV analysis

was 80 μL/min. All samples were accumulated at −0.15 V and stripped at −1.2 V unless otherwise stated. A cleaning step (−1.4 V for 30 s) was performed between each analysis. For most experiments, it was desirable to monitor the $^{238}U^{+}$ signals during deposition and stripping. For such cases, flow from the cell was directed to the ICP-MS during the accumulation step as well as the stripping step. When it was necessary to isolate the detector from high matrix levels (e.g., seawater samples), flow from the cell was diverted to waste during the accumulation step. Following accumulation the cell was flushed with 0.1 M ammonium nitrate for 90 s and then flow was redirected to ICP-MS for the stripping step. Other procedural details are explained in context below.

3. Results and discussion

3.1. Batch electrochemical studies

Off-line electrochemical tests were performed to evaluate the efficacy of the propyl gallate complexing ligand for uranium accumulation and stripping on-line with ICP-MS. It was particularly important to map the fate of the uranium upon stripping. The ability to selectively preconcentrate the U-PG complex in sodium acetate buffer has been demonstrated in the literature [19]. However, it was not demonstrated that the complex could be transferred to a sodium-free medium, and rapidly and quantitatively stripped back into solution through electrochemical means. This is necessary if the AdSV method is to be used on-line with ICP-MS.

In earlier studies, ASV methodology was successfully used on line with ICP-MS. Dilute HNO_3 was the electrolyte of choice, but when more moderate pH was required for the electrochemistry, 0.1 M ammonium nitrate (pH ~ 4.5) served as a suitable alternative. This matrix can be successfully used with ICP-MS as it produces few spectral interferences and is sufficiently volatile that deposits do not form at the sampling cone. The sodium acetate buffer was needed for U-PG complex deposition as indicated in the literature (partly because of variations in sample pH). However, it was necessary to prove that ammonium nitrate would not compromise the integrity of the U-PG adsorbed complex on the MTFE, and that it would be possible to strip into this unbuffered medium.

Off-line studies were made prior to adopting the AdSV protocol on-line with ICP-MS. In work by Wang et al. [19], repetitive cyclic potential sweeps between −0.1 and −0.55 V demonstrated the accumulation of the U-PG complex and successive reduction and oxidation of the complex on the surface. At these operating conditions, the complex was not removed from the electrode. In fact, each positive-going scan resulted in the accumulation of more U-PG complex until saturation was reached (2.87×10^{-11} mol cm^{-2}). A 60 s cleaning step at −1.4 V completely removed the complex prior to subsequent analyses. This report served as a guide in our subsequent off-line experiments.

Following a 150 s accumulation of 5.0 μg/L U (VI) from the PG/buffer solution, the MTFE electrode was transferred to either fresh 0.05 M sodium acetate buffer or 0.1 M ammonium nitrate (neither containing uranium or PG) and the potential scanned from 0.0 to −0.70 V (Fig. 2). Current peaks were observed corresponding to the reduction potentials for PG (−0.12 V) and the U-PG complex (−0.36 V). The identity of these peaks were confirmed via standard addition experiments (not shown). Similar peak stripping potentials were observed in sodium acetate [Fig. 2(a)] and ammonium nitrate [Fig. 2(b)] (small shifts were expected due to changes in electrolyte characteristics and background levels), with peak current magnitudes approximately equal in both media. These results demonstrated that the U-PG complex was not lost from the electrode in switching from the acetate buffer to 0.1 M ammonium nitrate, and that the electrochemical response of the complex was essentially unchanged in the latter medium.

It was then necessary to determine if the U-PG complex could be stripped from the electrode by potential scan and whether this would also proceed in 0.1 M ammonium nitrate. We accumulated the U-PG complex for 1.0 min in the PG/buffer system, then transferred the electrode into either fresh 0.05 M

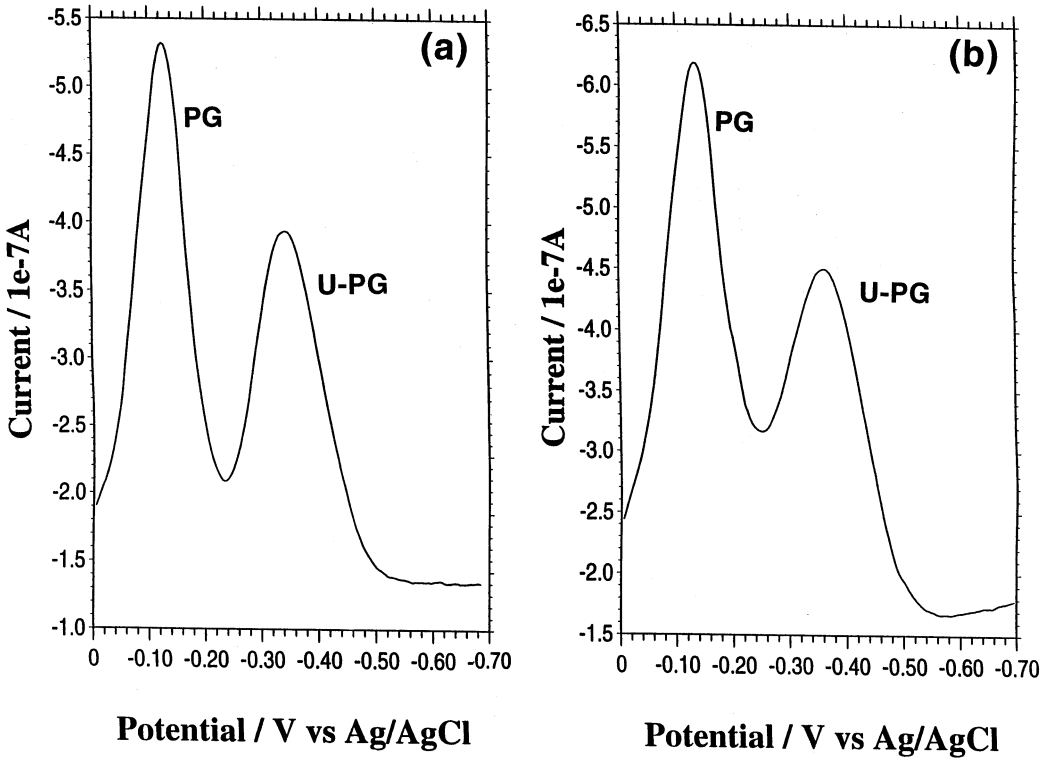

Fig. 2. Differential pulse stripping voltammograms of of 5.0 μg/L U (VI) in the presence of 5×10^{-5} M propyl gallate following a 150 s accumulation and stripping into (a) 0.05 M sodium acetate buffer blank and (b) 0.1 M ammonium nitrate blank.

sodium acetate buffer or 0.1 M ammonium nitrate for successive cyclic voltammetric scans between 0.0 and −1.4 V. If −1.4 V was sufficient to drive unreacted PG and U-PG complex from the electrode, then the reduction peak current previously observed for U-PG complex would be present on the initial cathodic scan, but subsequent scans would not show reductive peaks for the complex. The cyclic voltammetry data in Fig. 3 seems to confirm this behavior. The initial cathodic scan (segment 1) shows a peak for reduction of the complex, but subsequent anodic and cathodic scans (segments 2–4) did not exhibit the oxidative or reductive peaks that would indicate the presence of the U-PG complex at the MTFE. The scans were qualitatively similar regardless of whether acetate buffer [Fig. 3(a)] or 0.1 M ammonium nitrate [Fig. 3(b)] was used. Thus, it appeared that on-line medium exchange would be feasible, and uranium could be deposited from samples made up in buffer/PG then stripped into ammonium nitrate for detection via ICP-MS.

3.2. Mass spectrometric studies

The first test of AdSV on line with ICP-MS, by using propyl gallate as the chelating ligand, is shown in Fig. 4. Intensity of the ^{238}U ion signal versus time was monitored. Here, the effluent from the electrochemical cell was directed to the ICP-MS so that analyte deposition characteristics could be observed.

Fig. 3. Two successive cyclic voltammetric scans (potential range 0.0 to −1.4 V) for U-PG complex deposited on MTFE [sample 40 μg/L U (VI)] then transferred to (a) 0.05 M sodium acetate buffer or (b) 0.1 M ammonium nitrate. Labels indicate segment number and scan direction. Reduction peak of U-PG complex visible at approximately −0.4 V in segment 1 of each voltammogram.

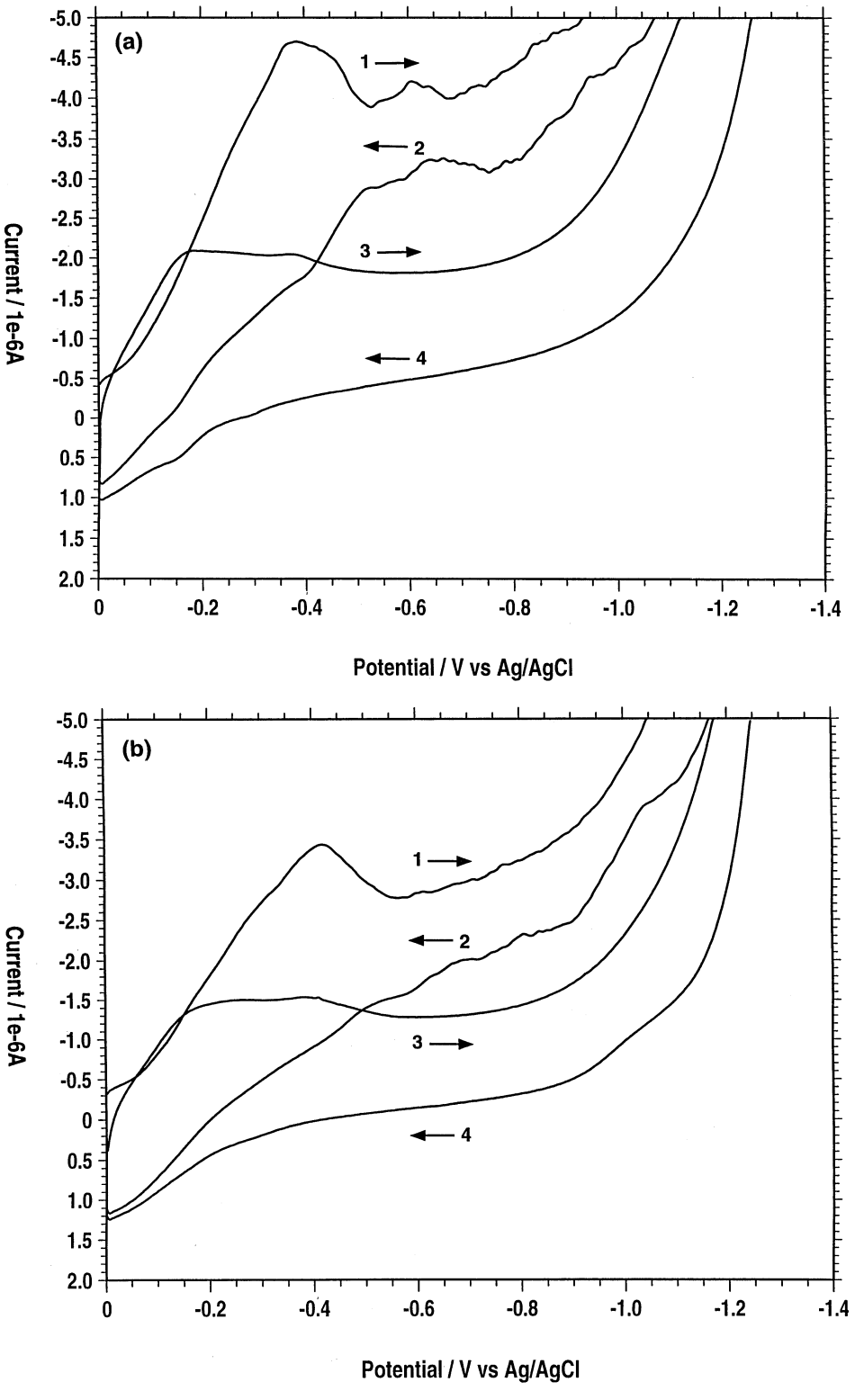

Fig. 3 *(caption on facing page)*

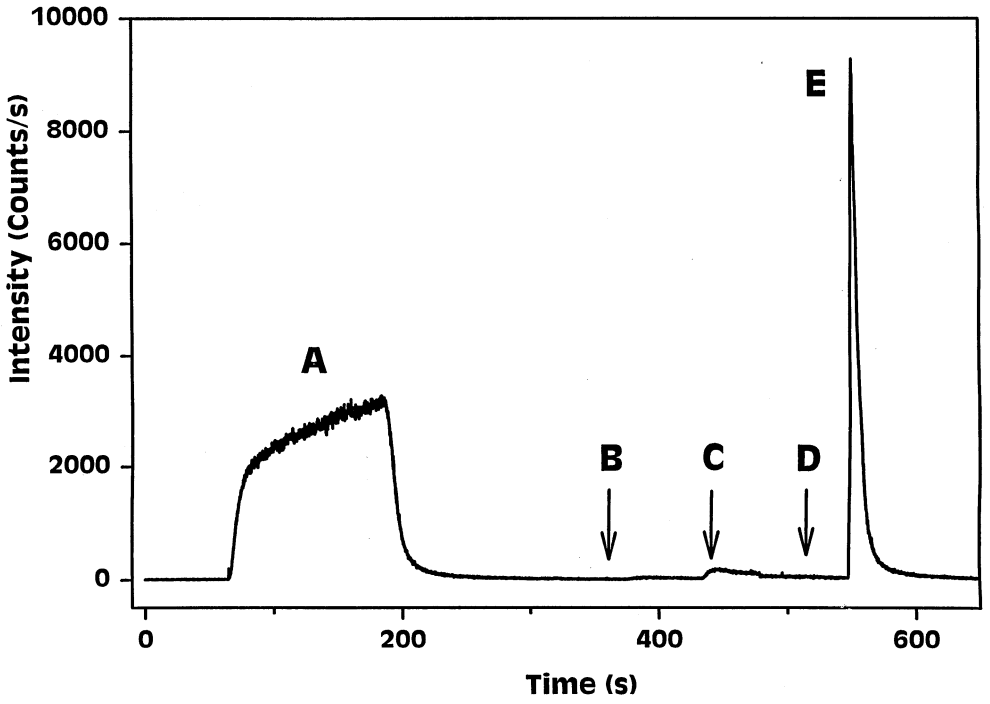

Fig. 4. Mass spectrometer response for m/z 238 ($^{238}U^{+}$) recorded during an AdSV-ICP-MS experiment. (A) Injection of U-PG complex with accumulation potential at −0.15 V [5 μg/L U (VI)], (B) potential step to −1.4 V, (C) potential step to −1.0 V, (D) potential step to 0.0 V, and (E) stripping peak signal produced on injection of 1% HNO_3.

The sample of 5.0 μg/L U (VI) in PG/buffer was injected for 2 min (A in Fig. 4) during which the MTFE was held at −0.15 V. The gradual rise in signal intensity during accumulation appears to be due to progressive saturation of the MTFE surface at this analyte concentration. This effect is exacerbated by the low electrode surface area (0.28 cm^2) and relatively high uranium concentration. As more of the surface is occupied, the deposition efficiency decreases (see below). Immediately following the accumulation period, the load valve was switched and the flow of sample was replaced by 0.1 M ammonium nitrate. During this period, the signal returned to baseline as the uranium sample was flushed from the electrochemical cell.

At point B in Fig. 4, the working electrode potential was stepped to −1.4 V, the cleaning potential used by Wang et al. [19] and in our batch experiments above. Only a very slight rise in signal was observed, suggesting that neither uranium nor the U-PG complex was released from the MTFE, or that after release they accumulated elsewhere in the system. To test the latter hypothesis, the working electrode was stepped in the positive direction to −1.0 V and a slightly larger signal was observed (C in Fig. 4). About 1.0 min later the potential was stepped to 0.0 V (D in Fig. 4), and signal once again dropped to baseline. When the MTFE is held at a negative potential, the counter electrode is at a positive potential relative to the MTFE. It is plausible, therefore, that a portion of the complex stripped from the MTFE is adhering to the counter electrode before it can be swept out of the cell (this would not occur in our batch system since the electrodes are not counterposed). A new in-house cell design that places the counter electrode upstream from the working electrode may eliminate redeposition of the U-PG complex.

In earlier work with AdSV-ICP-MS that used a cupferron ligand, it proved necessary to inject dilute nitric acid into the cell to release uranium into the

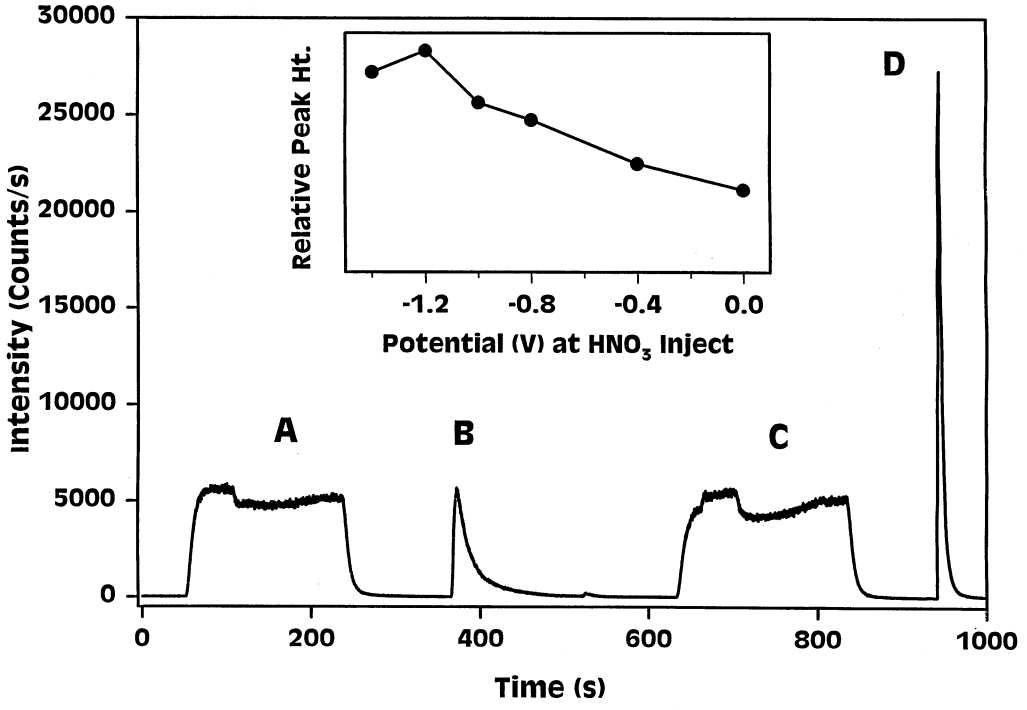

Fig. 5. Mass spectrometer response for m/z 238 ($^{238}U^{+}$) recorded during an AdSV-ICP-MS experiment in which stripping potential during chemical strip is varied. (A) Injection of U-PG complex with potential step from −1.2 V to accumulation potential of −0.15 V approximately 30 s after injection [2 min accumulation, 5 μg/L U (VI)], (B) stripping peak produced on injection of 1% HNO_3 at −0.15 V, (C) injection of U-PG complex with potential step from −1.2 V to accumulation potential of −0.15 V approximately 30 s after injection [2 min accumulation, 5 μg/L U (VI)], and (D) stripping peak produced on injection of 1% HNO_3 30 s after potential step to −1.2 V. Inset: plot of relative stripping peak response vs. potential applied at time of acid injection.

flow stream for detection [7]. The same phenomenon was observed here for the PG ligand system. Approximately 30 s after the potential had been stepped to 0.0 V (D in Fig. 4) an injection of 1% HNO_3 was made. A transient peak signal was observed (E in Fig. 4). The peak maximum was significantly higher than the steady-state signal intensity for the sample. Presumably, the change to acidic pH dissociates the U-PG complex so that the analyte is no longer retained anywhere within the cell. While stripping through electrode potential control is easier to implement, chemical stripping is an acceptable alternative. The concentrated uranium is stripped into dilute nitric acid that, like ammonium nitrate, is suitable for use with ICP-MS.

An option that had not been investigated in our prior AdSV-ICP-MS work was the combination of chemical and electrochemical stripping. Results of such a study are shown in Fig. 5. Again, cell effluent is directed to the ICP-MS at all stages of the experiment to allow analyte accumulation to be monitored. Sample was injected while the potential was held at −1.2 V; when a steady-state signal was obtained, the accumulation potential (−0.15 V) was applied for 120 s (A in Fig. 5). Initially, uranium accumulation decreased the steady-state signal by approximately 10%. As accumulation continued, progressive saturation of the electrode occurred as indicated by the gradual rise in signal. The sample valve was closed and the cell was flushed with 0.1 M ammonium nitrate. When the signal returned to baseline, 1% HNO_3 was injected with the potential still at −0.15 V (B in Fig. 5). Stripping appeared to be inefficient as the peak was rather broad and the peak height was just

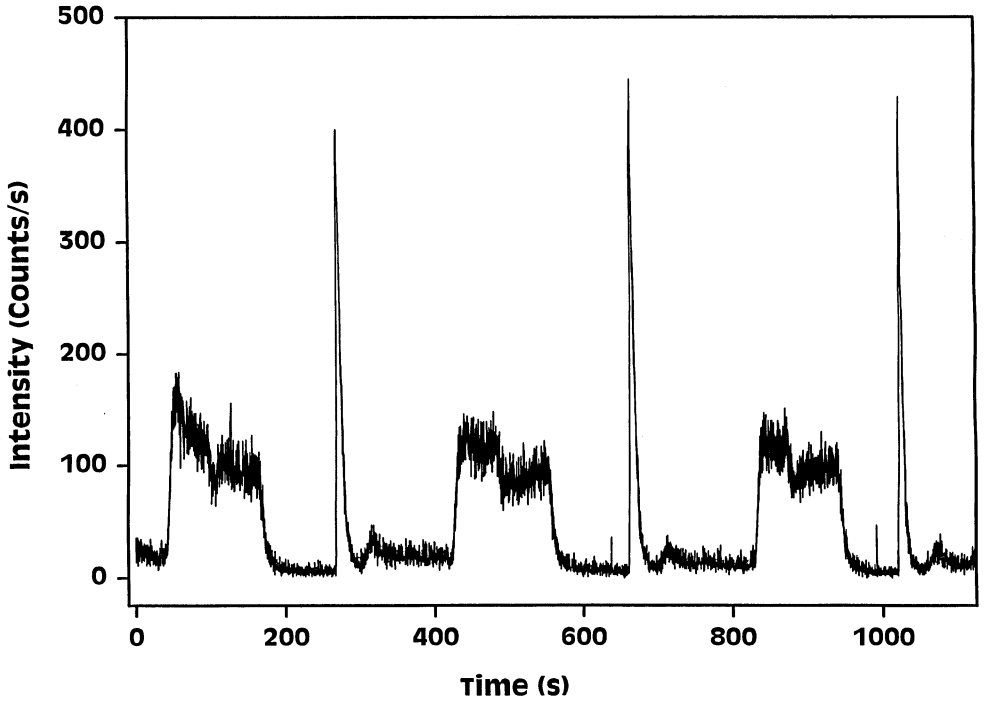

Fig. 6. Stripping peak reproducibility for three replicate runs of 100 ng/L U (VI). U-PG complex accumulated on-line for 60 s at −0.15 V, stripped by injection of 1% HNO_3 at −1.2 V.

equal to that of the continuous nebulization signal. The experiment was repeated (C in Fig. 5), but this time the potential was stepped 30 s prior to the injection of acid to −1.2 V. The resulting stripping peak was more intense and less broad, indicating more rapid and efficient stripping (D in Fig. 5).

In further trials, the potential applied to the electrode just prior to injection of acid was varied. The inset in Fig. 5 shows the relative stripping peak height as a function of this potential. Response was maximized at a stripping potential of −1.2 V, beyond which stripping efficiency decreased. These results show that simultaneous chemical (pH shift) and electrochemical stripping (cathodic step) processes provide efficient stripping of the U-PG complex with this electrode configuration. Thus, injection of 1% HNO_3 after a potential step to −1.2 V was used for stripping in all subsequent experiments. It was also discovered that after stripping, it was necessary to briefly step the electrode potential to −1.4 V, or analytical performance rapidly degraded. In subsequent work the potential was stepped to −1.4 V for 30 s, then returned to −1.0 V before each analytical run.

Adequate precision is important for successful implementation of AdSV-ICP-MS. Repeatablility is demonstrated in Fig. 6 for three analyses of 100 ng/L U (VI) in PG/buffer. The sample was injected with the potential held at −1.2 V and, once a steady-state signal was achieved, the accumulation potential (−0.15 V) was applied. After 60 s the sample valve was closed, the cell was flushed for 90 s with 0.1 M ammonium nitrate, and the analyte was stripped. The relative standard deviation (RSD) is 5.4% for the stripping peak heights ($n = 3$). Precision is probably affected by the fact that sodium acetate buffer is being delivered to the ICP-MS just prior to and during the accumulation periods. This resulted in some signal instabilities, which is most obvious in the first steady-state signal profile in Fig. 6. Even under these compromised conditions, acceptable repeatability was demonstrated.

AdSV-ICP-MS response as a function of accumu-

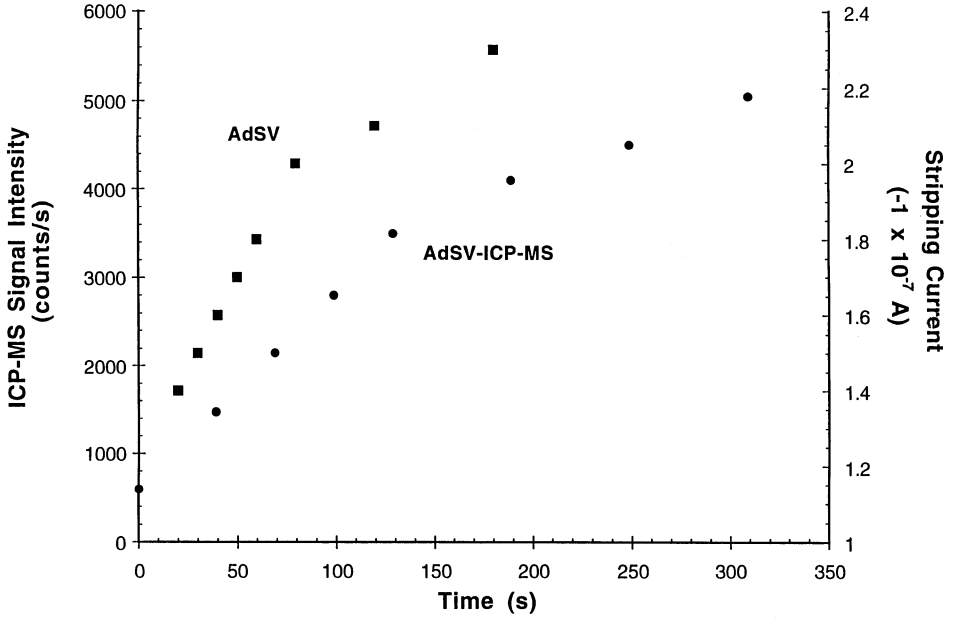

Fig. 7. Stripping peak response vs. accumulation time for 0.5 μg/L U (VI), measured off-line as peak current (AdSV, filled square) and measured on-line as intensity of ion signal at m/z 238 (AdSV-ICP-MS, filled circle). Data point at 0 s indicates intensity of ion signal for steady-state nebulization of 0.5 μg/L U (VI).

lation time at constant uranium concentration was investigated. Figure 7 shows the stripping peak response response of 0.5 μg/L uranium measured both off line and on line. In both cases we observed what appeared to be two distinct linear regions in the response curves. This phenomenon was not expected and the mechanism is not clearly understood. Similar response curves were observed in both modes when accumulation time was fixed and uranium concentration increased. Evidently the accumulation rate is higher for a clean Hg surface than for a surface already partly loaded with U-PG complex, leading to the behavior exhibited in the plot. These limits in dynamic range are consistent with the AdSV mechanism and are essentially a function of electrode surface area. Electrodes with higher surface area, such as reticulated vitreous carbon [10], should afford a greater linear dynamic range than the MTFE used in this work.

Typical signal enhancement capability provided by this method can be estimated from the data in Fig. 7. The point at 0 s accumulation time represents the signal intensity of the continuously nebulized sample (0.5 μg/L), flowing through the electrochemical cell to the ICP-MS. Because no matrix elimination is employed, the signal is certainly suppressed from the sodium in the acetate buffer. Nevertheless, this intensity does provide an estimate for measuring enhancement as a function of accumulation time. At 2.0 min, the point at which rollover occurs, an enhancement of 5.8 was observed. Enhancement continued at longer times, although the accumulation rate decreased due to the saturation effect. The decrease in the accumulation rate would not effect isotope dilution analyses: in such analyses, concerns about MTFE saturation are mostly eliminated, and enhancements can be exploited. Signal enhancement can also be influenced by the quality of the MTFE [7]. In other experiments not shown here, 10 min accumulation of 0.5 μg/L U (VI) resulted in signal enhancements of greater than 24-fold.

Despite the limited dynamic range, quantitative analyses of NRCC NASS-4 Open Ocean Seawater (certified level 2.68 ± 0.12 μg/L U) was attempted via calibration plot and standard addition methodologies. Calibration standards (100 ng/L to 9.1 μg/L)

Table 2
Results of AdSV-ICP-MS analyses of uranium in NASS-4 open ocean seawater. Measured and certified concentration reported in μg/L ± 95% CL (n = number of replicate determinations)

	Calibration curve results	Standard addition results
Correlation coeff. (R)	0.999 76	0.999 30
Measured concentration	3.94 ± 0.64 (n = 4)	3.6 ± 1.5 (n = 3)
Certified concentration	2.68 ± 0.12	2.68 ± 0.12
Deviation from certified value	+47%	+36%

were prepared by serial dilution (see Sec. 2). The seawater was mixed off line 1:1 v/v with PG/buffer and spiked with 100 μg/L U (VI) in PG/buffer as required [1.0 and 2.0 μg/L U (VI)]. Flow from the cell was diverted to waste during the accumulation step, to isolate the ICP-MS from the high NaCl level (3.1% in undiluted seawater) until subsequent washout with 0.1 M ammonium nitrate eliminated matrix from the cell. All work was performed by using a 60 s accumulation time.

The results of these analyses are shown in Table 2. Peak height RSD ranged from 5.0% to 15.8% (n = 3 to 6) for the calibration standards, and from 2.4% to 13.3% for the seawater samples (n = 3 or 4). The poor regression correlation coefficients result from roll-over at the higher concentrations, suggesting that greater dilution was required. The high experimentally determined uranium values obtained by both calibration plot and standard addition methods are consistent with such an electrode saturation effect. Examination of individual mean peak heights suggested some degree of drift in ICP-MS sensitivity; correction via internal standard could not be employed in the single ion monitoring mode. Isotope dilution should negate saturation effects on calibration plots and allow the use of longer preconcentration times or higher analyte concentrations. With time-resolved acquisition software, isotope dilution analysis could certainly be incorporated into AdSV-ICP-MS, suggesting one great advantage of this hybrid approach over AdSV alone.

4. Conclusions

The adsorptive stripping route is clearly more complex than the more common anodic stripping approach. One major limitation is the saturation of the MTFE at high concentrations or extended accumulation periods. Operational boundaries must be clearly understood in regard to deposition time and analyte concentrations. With these in mind, acceptable quantitative results should be possible. Isotope dilution may provide a better route for quantification via AdSV-ICP-MS because saturation effects would be of no consequence. These effects are due to the limited surface area available on the thin-layer electrode, thus a porous flow-through electrode that maximizes surface area may be of benefit. A new cell design that may reduce or eliminate the apparent redeposition of the U-PG complex is being investigated and may allow stripping via purely electrochemical means.

An additional concern that must be addressed in future work is the effect of coexisting elements that may compete for ligand binding, thereby decreasing the uranium response. However, a prior survey of the AdSV response of 13 elements indicated that only Ti (IV) and Mo(VI) were competive with U [19].

The simplicity of this on-line approach is promising, providing efficient matrix elimination while effecting analyte preconcentrations approaching those of other off-line column separations. However, in addition, the efficiency of an on-line approach, sample size requirements are greatly reduced, making it appealing for the analysis of small samples.

Acknowledgements

This research was sponsored by the Laboratory Directed Research and Development Program of Oak Ridge National Laboratory (ORNL), United States Department of Energy, under Contract DE-AC05-96OR22464 with ORNL, managed by Lockheed Martin Energy Research Corporation. The authors gratefully acknowledge the assistance of Shelby Morton (ORNL) and helpful communications with Professor Joseph Wang (New Mexico State University).

References

[1] Inductively Coupled Plasmas in Atomic Spectrometry, 2nd ed., A. Montaser, D.W. Golightly, (Eds.), VCH, New York, 1992.
[2] J.W. Olesik, Anal. Chem. 63 (1991) 12A.
[3] G. Horlik, Spectroscopy 7 (1992) 22.
[4] R.R. Ross, J.R. Noyce, M.M. Lardy, Radioactivity Radiochem. 4 (1993) 24.
[5] E.H. Evans, J.J. Giglio, J. Anal. At. Spectrom. 8 (1993) 1.
[6] E.R. Denoyer, A. Stroh, Am. Lab. Feb (1992) 74.
[7] F. Zhou, G.J. Van Berkel, S.J. Morton, D.C. Duckworth, W.K. Adeniyi, J.M. Keller, Applications of Inductively Coupled Plasma-Mass Spectrometry to Radionuclide Determinations, ASTM STP 1291, R.W. Morrow, J.S. Crain (Eds.), American Society for Testing and Materials, West Conshohocken, 1995, pp. 82–98.
[8] J.R. Pretty, D.C. Duckworth, G.J. Van Berkel, Anal. Chem. 69 (1997) 3544.
[9] D.A. Ogaram, R.D. Snook, Analyst 109 (1984) 1597.
[10] J.R. Pretty, E.H. Evans, E.A. Blubaugh, W.L. Shen, J.A. Caruso, T.M. Davidson, J. Anal. At. Spectrom. 5 (1990) 437.
[11] J.R. Pretty, E.A. Blubaugh, J.A. Caruso, Anal. Chem. 65 (1993) 3396.
[12] T-J. Hwang, S-J. Jiang, J. Anal. At. Spectrom. 11 (1996) 353.
[13] F. Zhou, Electroanalysis 8 (1996) 855.
[14] J.R. Pretty, J.A. Caruso, J. Anal. At. Spectrom. 8 (1993) 545.
[15] G.J. Van Berkel, F. Zhou, D.C. Duckworth, S.J. Morton, Proceedings of the 43rd ASMS Conference on Mass Spectrometry and Allied Topics, Atlanta, GA, 1995, p. 43.
[16] J. Wang, Stripping Analysis, VCH, Deerfield Beach, 1985.
[17] J. Wang, Voltammetry Following Nonelectrolytic Preconcentration, Electrochemical Chemistry, Vol. 16, A.J. Bard (Ed.), Marcel Dekker, New York, 1989, pp. 1–88.
[18] J. Wang, R. Setiadji, Anal. Chim. Acta 264 (1992) 205.
[19] J. Wang, J. Wang, J. Lu, K. Olsen, Anal. Chim. Acta. 292 (1994) 91.