Optimization of Nd(III) pre-concentration on a rotating disk mercury film electrode in aqueous solution

By P. D. Schumacher*, S. M. Miley, J. O. Schenk and S. B. Clark

Department of Chemistry, Washington State University, Pullman, WA 99163, USA

(Received December 21, 2009; accepted in final form September 28, 2010)

*Mercury film electrode / Cyclic voltammetry /
Trivalent f-elements / Nuclear forensics / RDE / ICP-MS*

Summary. Current work indicates that trivalent lanthanides will consistently sorb to a rotating disk mercury film electrode in bulk aqueous solution thus allowing the user to pre-concentrate trivalent lanthanides for further separation. However, the mechanism of sorption to the mercury film is largely unknown, making it difficult if not impossible to predict *a priori* the conditions under which pre-concentration is optimized. In the present study, we explore some of the electrochemical factors affecting this pre-concentration process to optimize the technique for use in a wide variety of aqueous media. Trivalent neodymium (Nd(III)) is used as a model for the trivalent *f*-element cations. The factors investigated include pH of solution, rotation rate of the electrode, concentration of mercury, potential application waveforms, order of deposition, and time dependency.

1. Introduction

Trace, trivalent *f*-element detection is becoming an increasingly popular tool for environmental analysis, nuclear waste monitoring, and nuclear forensics [1–3]. Lanthanide and actinide isotopic signatures provide forensic information used by law enforcement, federal, and international agencies to determine the origin and transit route of nuclear materials [3]. Historically, trivalent *f*-elements were isolated *via* solvent extraction, a time consuming and reagent-intensive process [4]. Additionally, analytical scale separations of trivalent lanthanides from each other and from the trivalent actinides have been a challenging facet of *f*-element chemistry for many years due to the similar valence electron configuration of these elements, resulting in similar chemistry [5–7]. Advances in current radiochemical methods are needed as the current approaches are time-intensive and not conducive to analysis in a field environment. Electroanalytical chemistry offers a transformational opportunity to develop improved lanthanide and actinide radiochemical separations. Previous work has indicated that while trivalent *f*-elements would consistently electrodeposit onto a rotating mercury film electrode (MFE) in bulk aqueous solution, the system investigated was not optimized [8]. Further, the mechan-

ism by which the trivalent *f*-elements electrodeposit onto a MFE is not clearly understood [9]. Expanding upon previous research, experiments were designed using trivalent neodymium to investigate the optimal electrochemical parameters for trivalent lanthanide accumulation on a MFE, including pH of solution, rotation rate of the electrode, concentration of mercury, potential application waveform, order of deposition, and time dependency. Trivalent neodymium was chosen for this study as it is a suitable analog for trivalent actinides, namely Am(III). In addition, it does not exhibit a (III)/(II) redox reaction, which is observed with Eu(III) and can complicate interpretation of electrochemical data.

1.1 Reagents

The reagents [Hg(NO₃)₂ and LiCl] used in the study were reagent grade, purchased from Fisher Scientific, (Waltham Massachusetts USA, www.fishersci.com) and used as received. The Neodymium solutions were obtained from a stock solution in 2% HNO₃ purchased from Hi-Purity Standards (Charleston South Carolina USA, www.highpuritystandards.com).

1.2 Apparatus

Electroanalytical measurements were made on a (Model 100B) Bioanalytical Systems, (West Lafayette Indiana USA, www.basinc.com) potentiostat. The working electrode was a 3 mm glassy carbon rotating disk electrode (GCRDE), (Pine Instruments, Grove City, Pennsylvania USA, www.pineinst.com). The reference and auxiliary electrodes were Ag/AgCl and Pt wires respectively. The electrochemical setup was the same as described in our previous work [8]. For ICP-MS, measurements, aliquots were diluted in a 2% HNO₃ solution for subsequent analysis on a Hewlett Packard 4500 ICP-MS utilizing an internal indium standard and scanned in the positive mode using standard ICP-MS procedures. Analysis of electroanalytical and ICP-MS data was performed using GraphPad Prism version 5.02 for Windows, (GraphPad Software, San Diego California USA, www.graphpad.com).

1.3 Procedures

Procedures were similar to previous work and are diagramed in Fig. 1 [8]. Briefly, a GCRDE was inserted into a 5 mL

* Author for correspondence (E-mail: pschumacher@wsu.edu).

Fig. 1. Experimental design showing the general process followed for deposition and stripping. Volumes are given since they were held constant throughout and concentrations omitted since they changed throughout the course of the research.

Fig. 2. A typical CV showing Nd(III) deposition onto a MFE. Scan begins and ends at 0.0 V at a rate of 100 mV/s. The MFE was rotating at 2000 rpm, $[\text{Hg}^{2+}] = 10^{-3}$ M and $[\text{Nd(III)}] = 10^{-5}$ M. Deposition onto the MFE for Nd(III) occurs in the range -2.1 to -2.4 V. Potential is reported vs. Ag/AgCl.

cell containing 2.5 mL of Hg^{2+} solution in 0.1 M LiCl as the background electrolyte, and a deposition potential was applied *via* either cyclic voltammetry (CV), scanned from 0.0 to -2.65 V at 100 mV/s or potential step amperometry (PSA) where the potential was held at 0.0 V and then stepped to -2.65 V with the current recorded as a function of time. The electrode was rotated at various rates but rotation rates were consistent within a single experiment. When the scan completed, 2.5 mL of Nd(III) solution was added to the 5 mL cell, and the deposition potential was again applied.

After formation of the Nd(Hg) amalgam as seen in Fig. 2, the electrode was removed from the solution while still rotating. This step was added after discovering that a single concentric drop of liquid remained on the tip of the elec-

trode potentially biasing results. The sides of the electrode were wiped with a Kim-Wipe and the electrode was inserted into a separate 1.5 mL cell containing 250 μL 2% HNO_3 . A stripping potential was applied *via* CV scan starting at 0.0 to 2.65 V at 100 mV/s while rotating the electrode. After completion of the scan, a 90 μL aliquot was removed from the cell for ICP analysis. Each cell was then washed with 2% HNO_3 and rinsed with deionized water. All experiments were completed in triplicate. For all experiments, optimum was defined as the greatest amount of Nd(III) accumulated on the electrode as determined by ICP-MS.

2. Results and discussion

The first sets of experiments were designed to test for bias in the procedures. Following the procedures previously discussed, an experiment was run with only Hg^{2+} present in 0.1 M LiCl. Aliquots from these experiments were analyzed for Nd(III) by ICP-MS with no Nd(III) detected. These experiments validated our cleaning procedures for the glass cell as trivalent *f*-elements are known to adsorb onto glass and it was essential to remove all traces of analyte between experiments [10]. Next, an experiment was run with only Nd(III) present in 0.1 M LiCl. Analysis of the aliquots removed at the end of the stripping step by ICP-MS indicated a small amount of Nd(III) present ($4.48 \times 10^{-12} \pm 1.7 \times 10^{-12}$ moles). This was an unexpected result since our previous work showed that trivalent *f*-elements would not electrodeposit on a bare GCRDE. Upon analysis of each step in the procedure, it was discovered that a small drop of solution remained on the GCRDE upon removal from the deposition solution after wiping with a Kim-Wipe since the rotator was stopped while the electrode was still im-

mersed in the solution. To correct this bias, the electrode was slowly removed from the deposition solution while still rotating ensuring no drop remained on the end of the electrode. The Nd(III) experiments were repeated with this added step and analysis of the aliquots by ICP-MS indicated no Nd(III) present thus validating the procedures as non-biased with no carryover between experiments.

2.1 pH

Since trivalent *f*-elements are known to undergo hydrolysis at high pH it was necessary to understand how the pH changed during the course of the experiment and insure that conditions for hydrolysis did not occur [11]. To reduce possible interferences, 2% HNO₃ was used to adjust the pH instead of a buffer solution. A series of pH measurements were made on starting and ending solutions. Equal volumes

of Hg²⁺ (1.0×10^{-3} M) and Nd(III) (1.0×10^{-5} M) solutions mixed before an experiment resulted in a pH of 3.7 ± 0.1 . Measurements made on the same solution After electrodeposition, the measured solution pH was 3.8 ± 0.1 . This is an expected result since the experiments occur in the potential window for H₂O reduction, which removes hydronium ions and thereby leads to an increase in pH. Results of these measurements indicated that 2% HNO₃ was suitable for adjusting the pH and would inhibit hydrolysis of trivalent *f*-elements during the course of the experiments.

2.2 Mercury concentration

The effect of mercury concentration was investigated to determine if an optimal concentration exists for formation of the mercury film. In Fig. 3a, moles accumulated reflects the amount of Nd(III) accumulated on the surface of the elec-

Fig. 3. Results of Nd(III) accumulation as determined by ICP-MS. For all panels, the y-axis is moles of Nd(III) accumulation on the end of the working electrode and each datum point represents triplicate runs. Error bars are 1σ SD. In panel A, accumulation of Nd(III) is dependent on Hg²⁺ concentration. In panel B, the linear regression does not significantly deviate from zero indicating no effect. In panel C, PSA and CV samples were ran at 500 RPM (circles), 2000 RPM (squares) and 4000 RPM (triangles) for 10, 20, and 30 s. CV was run with one, two, and three deposition scans. There is no discernable difference between potential application waveforms. In panel D, Hg first is for sequential electrodeposition and shows an order of magnitude greater accumulation compared to *in situ* electrodeposition. In panel E, accumulation is linear for 180 s and increase by an order of magnitude after which no further accumulation is evident.

trode as determined by ICP-MS. For each mercury concentration, PSA was used. Results show that 1×10^{-3} M Hg^{2+} accumulated an order of magnitude more Nd(III) than other mercury concentrations. This observation agrees with previous work by Yoshida and Kihara [12]. They found that electrolytically deposited mercury was strongly dependent on the concentration of Hg^{2+} in solution and could not be significantly affected by potential, electrode surface area or electrolysis time [12]. At optimal mercury concentration, varying the concentration of Nd(III) leads to a sorption isotherm [8].

2.3 Rotation rate

The influence of rotation rate on Nd(III) accumulation was also studied. Samples were analyzed at varying rotation rates between 500 to 4000 RPMs. The concentration of Nd(III) used was 2.0×10^{-5} M and Hg^{2+} concentration was 2.0×10^{-3} M based on previous optimization parameters. In Fig. 3b, the x -axis is the square root of rotation rate expressed as rotations per second, which comes from the Levich equation.

$$i_L = (0.620)nFAD^{2/3} \omega^{1/2} \nu^{-1/6} C \quad (1)$$

This equation models the diffusion and solution flow conditions around the GCRDE. The linear regression line does not significantly deviate from zero, indicating no effect for rotation rate. Based upon the work of Leddy and Bard, one can conclude that at steady state, the flux through, across and to the film are all equal, thus a stationary electrode could be used for the experiments [13]. Since the electrode and rotator are optimized for 2000 rpm, this was the chosen rotation rate for the majority of experiments.

2.4 Potential application waveforms

The next parameter analyzed was the type of waveform applied to determine if different waveforms affected Nd(III) accumulation. Different waveforms will lead to different charge densities on the surface of the electrode potentially causing irreversible faradic processes [14]. Also, if charge transfer kinetics define the efficiency of Nd(III) accumulation, CV is expected to show a lower accumulation of Nd(III). CV and PSA application waveforms were used to determine if one technique was optimal. In Fig. 3c for each set of experiments, the total electrolysis time was roughly equivalent for each waveform, thus allowing a direct comparison to be performed and valid. Each technique yielded similar results, indicating that both work effectively. In addition, charge transfer kinetics do not define the efficiency of Nd(III) accumulation.

2.5 Order of deposition

Samples were analyzed to determine the accumulation difference between sequential electrodeposition and *in situ* electrodeposition. In sequential electrodeposition, the mercury film is formed in the absence of an analyte and the analyte then added to the solution when a second deposition potential was applied. For *in situ* deposition, both the mercury and analyte are present in solution and a deposition potential applied. CV and PSA waveforms were analyzed and Fig. 3d

shows that with both waveforms, an order of magnitude of accumulation is gained by depositing the mercury film prior to the addition of the analyte. This was an interesting outcome as previous work with trace transition metals indicated that *in situ* deposition increased sensitivity and lower limits of detection (LOD) [15, 16]. Since the mechanism by which trivalent f -elements electrolytically form a mercury amalgam is not understood, the reason for greater accumulation at pre-formed mercury films is not clear [9]. However, based on the results, one possible hypothesis that deserves further investigation is that Nd(III) reduction is an inner-sphere electrode reaction requiring mercury as the substrate for electron transfer.

2.6 Time dependence

After analyzing pH, rotation rate, optimal mercury concentration, electrochemical waveform, and order of deposition to determine optimal parameters, the LOD was determined. In previous work, the LOD was determined to be 10^{-7} M. After applying the optimal parameters, the LOD was determined to again be 10^{-7} M (data not shown). To investigate the effect of deposition time on Nd(III) accumulation, PSA was applied and triplicate aliquots were analyzed in 30 s intervals starting at 30 s thru 300 s with $[\text{Nd(III)}] = 10^{-7}$ M. In Fig. 3e, each point represents three separate experiments at that specific time. Results indicate that an order of magnitude in accumulation is observed for a factor of 6 increase in time. The accumulation

Follows a linear trend, with a correlation coefficient of 0.97, through 180 seconds after which no further accumulation is observed. Additionally, within the 95% confidence interval, the line originates at the origin. The reason for why Nd(III) accumulation levels off after 180 seconds and does not reach the same accumulation amount seen in previous experiments is unclear and deserves further investigation. As previous work demonstrated, a monolayer of Nd is expected to sorb to the MFE and once saturated, no further accumulation is expected [8]. Each of the optimization experiments accumulate, within error, approximately 1.5 to 2.0×10^{-10} moles, which agrees with previous work [8]. Pre-concentrating at much lower levels did not accumulate an equivalent amount indicating that other factors are present. What is evident is that accumulation via electrodeposition exhibits a large, linear dynamic range making it suitable as a pre-concentration technique.

3. Conclusions

The optimal electrochemical parameters for trivalent lanthanide accumulation on a rotating MFE, including pH of solution, rotation rate of the electrode, concentration of mercury, electroanalytical technique, order of deposition, and time dependency were investigated. The experimental design was tested and the procedures are such that no carry-over of trivalent f -elements occurs making them suitable for quantitative work. The pH of the solution is not an issue as long as it remains below the onset of hydrolysis for trivalent f -elements. While a rotating disk electrode was used in this investigation, results indicate that a stationary electrode in quiescent solution should work. Optimal accumulation

of trivalent *f*-elements is dependent upon the concentration of Hg^{2+} in solution and shows greater accumulation with sequential deposition. The potential application waveform has no discernable effect since charge transfer kinetics does not define the efficiency of electrodeposition. Finally, the technique is suitable for pre-concentration of trivalent *f*-elements as electrodeposition displays a large, linear dynamic range and long electrolysis time.

Acknowledgment. The authors would like to thank Dr. Charles Knaack and Dr. Paul Olin of the Washington State University GeoAnalytical Lab for their assistance with the ICP-MS experiments. The authors would also like to thank the US Army for its funding of P.D. Schumacher and the Academic Research Initiative of the Joint Domestic Nuclear Detection Office, Department of Homeland Security (contract number 2009DN077ARI033) and the National Science Foundation (contract number ECCS-0833548) for funding this study.

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