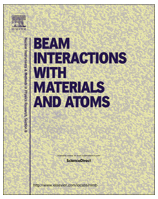
Nuclear Instruments and Methods in Physics Research B xxx (2015) xxx–xxx

Contents lists available at ScienceDirect

Nuclear Instruments and Methods in Physics Research B

journal homepage: www.elsevier.com/locate/nimb



Electrodeposition as an alternate method for preparation of environmental samples for iodide by AMS

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ARTICLE INFO

Article history:
Received 24 November 2014
Received in revised form 3 March 2015
Accepted 5 March 2015
Available online xxxx

Keywords:
Radioiodine
Accelerator mass spectrometry, AMS
Electrodeposition
^{129}I-AMS sample preparation
^{129}I

ABSTRACT

This paper presents an evaluation of an alternate method for preparing environmental samples for ^{129}I analysis by accelerator mass spectrometry (AMS) at Idaho National Laboratory. The optimal sample preparation method is characterized by ease of preparation, capability of processing very small quantities of iodide, and ease of loading into a cathode. Electrodeposition of iodide on a silver wire was evaluated using these criteria. This study indicates that the electrochemically-formed silver iodide deposits produce ion currents similar to those from precipitated silver iodide for the same sample mass.

Precipitated silver iodide samples are usually mixed with niobium or silver powder prior to loading in a cathode. Using electrodeposition, the silver is already mixed with the sample and can simply be picked up with tweezers, placed in the sample die, and pressed into a cathode. The major advantage of this method is that the silver wire/electrodeposited silver iodide is much easier to load into a cathode.

1. Introduction

In most ^{129}I-AMS laboratories, iodine is chemically separated and purified from environmental samples and precipitated as silver iodide. The silver iodide is mixed with niobium or silver metal powder as a binder and medium for electrical conductivity in an AMS source and loaded as a target for the sputter ion source, where it is converted into a beam of negatively charged ions for AMS analysis. Numerous procedures have been reported to produce iodide targets. In most cases, carrier is added during the purification step to increase the total quantity of silver iodide formed during the precipitation step [1,2]. The use of a large quantity of carrier allows the determination of the ^{129}I concentration in the sample directly without measuring the ^{127}I concentration. In many cases the ^{127}I concentration is of no interest. Our laboratory is interested in both the ^{129}I concentration and 129/127 ratio. Yiou et al. [3] reported the extraction and AMS measurement of carrier free $^{129/127}$I (as iodine) from sea water using silver powder [4]. Problems with these preparation schemes include the desire to routinely run carrier-free samples and to streamline the cathode loading process. Other concerns include ion source memory, and difficulties in determining minute quantities of ^{127}I. This work evaluated an alternate method of forming silver iodide that could process small quantities of iodide, which could then be easily loaded into an AMS cathode.

2. Experiments and results

2.1. Electrodeposition of iodide

Prior to electrodeposition, it is necessary to ensure that iodine (I_2) species in the sample are converted to iodide (I^-) to facilitate the deposition as AgI. Other iodine species will not deposit at the potential used in this study. The chemistry scheme evaluated is described in later sections of this paper (Sections 2.4 and 2.5).

A diagram of the experimental setup is shown in Fig. 1. The electrochemical cell was a typical three electrode setup which allows potential to be controlled at the working electrode. Fifteen centimeters of 51 μm diameter silver wire (99.95%), mass ~3 mg, [Surepure Chemetals, LLC, product # 2702] was formed into a coiled ball by wrapping around a 1.0 mm rod and used as the working electrode. A Bioanalytical Systems [BAS Inc.] low leakage Ag/AgCl reference electrode and platinum foil counter electrode were used. The counter electrode was platinum foil. A cell, volume 3 mL, was fabricated from poly-tetrafluoro-ethylene (PTFE). The solution was stirred using a PTFE coated magnetic stir bar. A photograph of the electrochemical cell during operation is shown in Fig. 2. A Bio-Logic VSP 5-channel potentiostat was used to control the electrodeposition of iodide.

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http://dx.doi.org/10.1016/j.nimb.2015.03.015
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Please cite this article in press as: M.L. Adamic et al., Electrodeposition as an alternate method for preparation of environmental samples for iodide by AMS, Nucl. Instr. Meth. B (2015), http://dx.doi.org/10.1016/j.nimb.2015.03.015

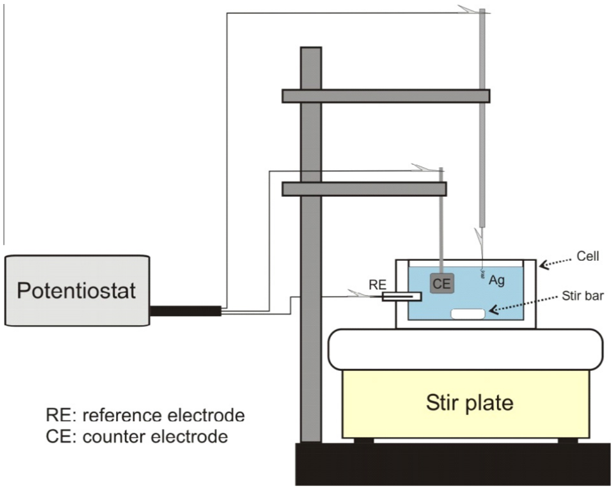

Fig. 1. Diagram of experimental setup.

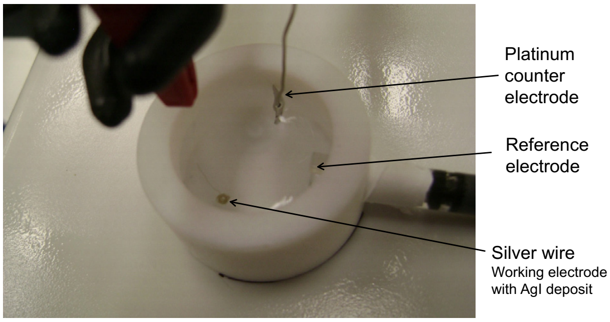

Fig. 2. Photograph of electrochemical cell.

Deposition was performed at constant potential on the coiled Ag wire. A potential of 0.0 V was determined to be optimum for silver iodide formation in dilute sodium hydroxide and tetramethyl ammonium hydroxide (TMAH) solutions as determined by bulk deposition/stripping experiments. These experiments involved performing the deposition at constant potential followed by stripping off the deposit. Stripping was performed by sweeping the potential negative in a blank NaOH solution following deposition. The removal of iodide was observed in a peak starting at −0.3 V. The integrated area of the peak can be related to the amount of iodine deposited using the Faraday constant. This allowed a method to quickly assess the amount deposited. The amount of iodide deposited was generally proportional to the deposition time. The deposition rate decreased as iodide concentration decreased due to mass transport. Typically, a deposition time of 2 h was used for samples with an expected total iodide of 1 μg and greater. Below 1 μg total iodide, a deposition time of 20 h was used.

2.2. SEM images of electrodeposited AgI

Scanning electron microscopy (SEM) micrographs of electrodeposited silver iodide are shown in Fig. 3. The electrodeposited silver iodide uniformly covers the silver wire. The higher-magnification image shows the individual silver iodide crystals. At thinner deposit levels, the coating is mechanically stable and is not removed when the sample is compressed into a cathode for AMS analysis.

2.3. Effect of quantity of iodide on the ratio measured by AMS

A series of known solutions ranging from 0.1 to 50 μg iodide were prepared using a material with a $^{129}\mathrm{I}/^{127}\mathrm{I}$ ratio of 1.855×10^{-10}. Samples were prepared in triplicate at the following levels: 0.1, 0.5, 1, 5, 10, 25 and 50 μg for analysis by the 0.5 MV TANDY AMS facility at the Laboratory of Ion Beam Physics at ETH Zurich, Switzerland. The measurements were performed using a modified MC-SNICS ion source, the accelerator was running at 300 kV terminal voltage and charge state 2+ at the high-energy (HE) spectrometer as describe was selected in as described in [7]. Helium stripping provides high transmission (>50%) through the accelerator and the HE spectrometer with the magnet-ESA-magnet setup reduces effectively interferences from other masses (mainly $^{127}\mathrm{I}$). Typical AMS iodide ion currents (measured in a Faraday cup after the first HE magnet) for various loads prepared from electrodeposited silver iodide are also summarized in Table 1. These ion currents are comparable to those obtained with loads from precipitated silver iodide for the same sample mass. A 1:100 dilution of AgI with silver powder produces a current similar to an electrodeposited 25 μg iodide sample (around 100 nA). The bouncing time for $^{127}\mathrm{I}$ measurement and the parameters of the current integrators are adjusted (longer than the standard $^{127}\mathrm{I}$ settings) to correctly measure these lower currents. Typical background currents from Ag dummy targets are around 1 nA. Small sample masses result in low currents and as the current decreases the measured ratio drops off due to instrument background of the current measurement. There appears to be a break at approximately 10 μg where there is enough total iodide present in the cathode to produce sufficient ion current that results in the correct $^{129}\mathrm{I}/^{127}\mathrm{I}$ ratio. The “actual” column in this table takes into account the efficiency of the electrodeposition. The efficiency of

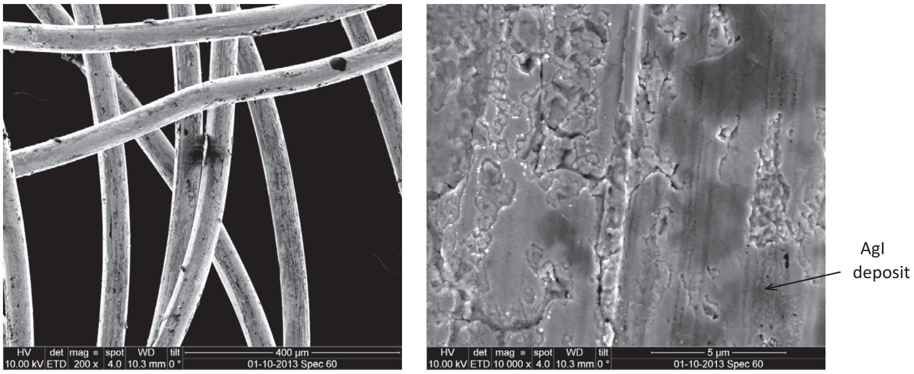

Fig. 3. Scanning electron microscopy photographs at 200× and 10,000× magnification of iodide electrodeposited on silver wire.