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Porous ion emitters—A new type of thermal ion emitter

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ABSTRACT

A new type of porous refractory material has been developed as a thermal ionization emitter that is an improvement over both direct filament and resin bead loading. The porous ion emitter is sintered onto the center of a conventional thermal ionization filament and an aqueous solution containing the sample wicked into this emitter. Application of the porous ion emitter to uranium is demonstrated to provide a utilization efficiency ranging between 1% and 2% across a sample size range of 0.2–10 pg, better than that achieved from resin beads and much better than that achieved with direct loading onto a filament. The technique improves sensitivity and reduces the chance of losing a high value sample when manipulating a single resin bead containing an entire sample.

1. Introduction

The most sensitive and accurate method for analyzing a number of elements is mass spectrometry [1]. Thermal ionization mass spectrometry (TIMS) is widely applied in particular to actinides at low levels [2–5]. TIMS is used for environmental monitoring, and for nuclear non-proliferation monitoring. TIMS requires a very clean sample and instruments do not run in an automated mode for low-level analysis, as it is easy to evaporate the whole samples before data is collected. This makes TIMS expensive and time consuming, but it is still used for analyses requiring the ultimate in sensitivity and accuracy.

The TIMS resin bead technique has better sensitivity for actinides than direct loading of the solution onto a filament [1,3,5]. It is generally thought that there are two reasons for this. A resin bead initially concentrates the analyte to a very small area. A larger percentage of the ions are transmitted down the flight tube of the mass spectrometer due to the lens having better ion transmission from the ion optical center. The resin bead technique also aids in formation of actinide carbides [6]. This allows higher conversion of sample to ions since the actinide is released from the carbide at a higher temperature where a higher percentage will be ionized.

As demonstrated by Burger et al. [1] uranium is effectively analyzed by the resin bead technique. An ionization efficiency of 0.58% for cation resin beads is reported [1]. This was an increase over the direct filament loading technique, which produced an efficiency of <0.1% [1]. There has been some data reported for cavity sources, although this technique was not reproduced by Burger's work and is not easily adaptable to commercial TIMS instruments.

Various techniques are reported in the literature describing methods for increasing ionization efficiency. Carbon helps through the formation of carbides [7,8]. The addition of carbon can be in the form of benzene vapor to a heated filament [9]. Rhenium helps due to a higher work function than other refractory filament metals [10]. Thus it is used as the base filament and has been used to cover beads for improved efficiency of ion production [10]. V-shaped filaments help with an increased potential for interaction with the rhenium surface or focusing. Platinum helps in the use of electroplated samples as well as having a higher work function than rhenium [11]. Burn-in of samples helps by allowing time for the burn off of interferences and conversion to the carbide at lower temperatures prior to attaining temperatures where the sample is evaporated from the filament [6].

A new system, the porous ion emitter (PIE), has been developed to take advantage of the above listed sources for improved ionization efficiency. The PIE consists of a mixture of rhenium and platinum powders of equal amounts by mass that are heated to the melting point of platinum to form a porous Pt/Re alloy fused to the filament. A liquid polymer ion exchanger is added to the metal structure after it has been sintered, followed by loading of a liquid sample by syringe. The PIE can be implemented in any TIMS source without instrument modification and is no more difficult and in some ways easier to apply than resin beads. The PIE and its applications to uranium are detailed in the sections that follow.

2. Experimental

2.1. Porous ion emitter preparation

The PIE is a mixture of rhenium (Aesar 325 mesh) and platinum metal powders (Alfa Aesar 325 mesh) alloyed together and sintered to the filament. These are prepared by mixing equal weight

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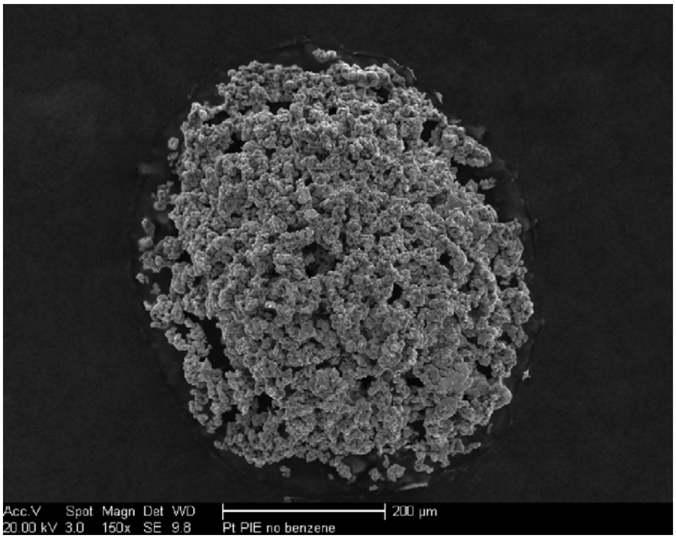

Fig. 1. PIE after sintering to remove hot glue.

portions of each pure metal (0.25 g each), melting hot glue (0.22 g, Craft variety, not well characterized) on a microscope slide on a hot plate, adding mixed metal and mixing with glue and drawn into a syringe (22 gauge needle). The greater the metal loading in the glue, the more effective the final PIE is at producing ions. The mixture is then expelled from the syringe into a small diameter rope of metal powder bound by the glue. The mixture is cooled to room temperature to solidify. The metal and glue rope can be stored until being cut under the microscope with a scalpel into 100 μm thick pieces that are set at the center of flat rhenium filaments. This is then heated to 150 °C in a convection oven for 1 min to fix the PIE to the filament. A number of these filaments are mounted in a vacuum, brought to 1700 °C over 15 min and held at this temperature for 20 min. This heat treatment accomplishes two things: (1) it volatilizes the hot glue and (2) just melts the platinum allowing formation of a platinum/rhenium alloy that binds the structure together and to the filament [12]. The remaining mixture of metals is a three-dimensional porous structure sintered to the center of the rhenium filament that cannot be removed (Fig. 1).

Two drops of a water soluble cation or anion exchange polymer are wicked into the PIE (polystyrene sulfonic acid for cations was used for the uranium analyses) and dried. These ion exchange polymers are polymerized but not cross-linked so they are water soluble and are diluted to have a concentration of 3% by mass.

2.2. Sample application and pre-treatment

Liquid samples are added from a 0.5 μL syringe. Usually 0.1–0.2 μL of a sample is added using a syringe pump and heat lamp. This is allowed to air dry and then placed in a vacuum chamber with a number of other filaments and evacuated. The filaments are slowly heated by applying current at a rate of increase of 15 °C per minute until reaching ∼1400 °C. The pressure in the chamber is increased to 5E-5 torr with benzene and the temperature is increased to 1600 °C over 3 min and held for 5 min after which the filaments are transferred to a VG54 mass spectrometer (circa 1990) for analysis. This is identical to the treatment of resin beads and helps convert the actinide to the carbide. Benzene vapor also decomposes to carbon and loads the rhenium filament with carbon as well as making a rhenium carbide surface with a slightly higher work function of 5.25 eV [13]. Sample inspection under a microscope demonstrated that no PIE was ever lost over the course of processing approximately 100 samples. This is in contrast to resin beads where microscopic examination demonstrated that during the benzene treatment approximately 20% of the beads detached from the filament on which they were mounted out of 100 processed. Another 5% were lost after mounting in the mass spectrometer and before completion of analysis based on loss of signal from a standard sample. We have not been able to explain why our losses of resin beads are this high other than inexperience. This loss rate does not invalidate the resin bead method when used by an experienced analyst, but it does illustrate the required skill level. TIMS analysis using PIES is far easier to master than resin bead analysis.

2.3. Sample analysis

Analysis can start when the pressure is less than 2E-8 torr. The samples are heated to 2.1 A over 5 min followed by 0.1 A incremental increase in current until the uranium signal reaches ∼100 counts per second. Filament temperatures were not measured and could be misleading. The PIE is likely at a lower temperature than the filament since the porous nature of the PIE will cause it to be a better black body radiator than the smooth filament. The PIE temperature could not be measured since there was no line of sight during analysis. Filament alignment and focusing conditions are optimized and the sample run to exhaustion with increased filament current and lens focusing periodically throughout the analysis. The analysis scheme is designed to provide a signal that can be readily integrated to give a total efficiency similar to the technique for total evaporation that is used to allow correction of fractionation [14].

3. Results and discussion

The best combination of materials was 50% each by mass of rhenium and platinum with a range of ±10%. PIE performance was reduced less than a factor of 2 at 25 and 75% platinum, so the ratio is not critical. Although additional testing of Re/Pt ratios is probably not needed, optimization of the size of the Pie and application to other elements is warranted.

Additional means of reducing uranium were also investigated like hydrogen reduction and additional carbon added as Aquadag^{TM}. It was thought that the utilization efficiency may be lowered if some of the uranium was not being totally reduced to the carbide by the benzene treatment. Neither introduction of hydrogen before or during the benzene treatment nor the addition of additional carbon in the form of Aquadag^{TM} after the benzene treatment improved ionization efficiency. Treating the samples at 2.5 A vs. 1.75 A during benzene treatment did show an improvement in efficiency as shown by the data in Fig. 2. This improvement is likely due to a more complete reduction of the uranium to the carbide.

The PIEs need to be sufficiently porous to allow the ion exchange polymer solution to wick into the structure and for subsequent wicking of the sample solution. Pore size is a function of the size of the rhenium powder. 325 mesh and 200 mesh rhenium powder were used in developing the PIE. The smaller rhenium powder produced a more compact PIE, but still allows the liquid polymer and sample to wick into the PIE. In general, the data shows the more compact PIE provides better sample utilization efficiency as the PIE made from the larger rhenium powder produced a range of 0.2–0.6% utilization efficiency. Since platinum melts and alloys with rhenium in the process to sinter the PIE, the size of platinum powder was not varied. The polymer solution does need to be diluted to approximately 3% by mass with water to reduce viscosity to where it wicks into the interior of the PIE. When not diluted, the polymer did not move into the interior of the PIE structure, but remained on the peripheral surface. This did not allow for adequate interaction

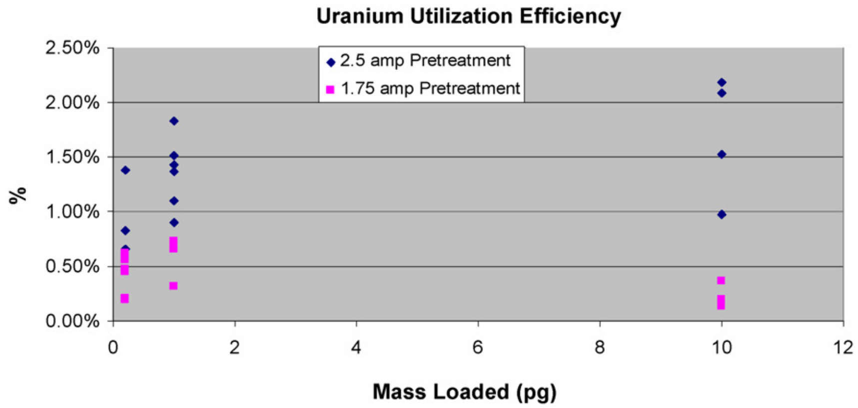

Fig. 2. Utilization efficiency for uranium analysis from PIEs after 1.75 and 2.5 A pre-treatment.

of the sample, polymer, and metals of the PIE system. The results were poor (<0.1% utilization efficiency).

The PIE brings rhenium/platinum metal alloy and carbon intimately together with the analyte. Different then a resin bead, there is platinum present and the exchange polymer is in more direct contact with the rhenium metal. The platinum has a higher work function than rhenium. The three-dimensional structure allows for more interactions of a neutral atom with additional hot metal surfaces as it diffuses out of the PIE structure increasing opportunities for ionization. The small footprint of the PIE allows for capture of the entire sample near the ion optical center of the lens as well as for creation of ions near this center. If there is any migration of the analyte, it would have to follow a tortuous path to travel away from the center. This enhances ion transmission. For a resin bead, the carbon matrix dissolves into the filament and has the potential for the analyte to migrate and thus to increase the ionization region. Additionally, the PIE allows for the manipulation of the sample in a liquid form until loaded on the PIE that has been previously fixed on the filament.

Uranium was measured at the mass loadings of 10, 1, and 0.2 pg. The total number of ions collected at the detector was divided by the atoms loaded on the filament to determine utilization efficiency. The data for these results is plotted in Fig. 2. The 10 pg samples that are the most comparable to the work Burger et al. [1] presented, resulted in an efficiency of 1.7% on average with the range of results being 1.0–2.2% ($n = 4$). The reported data does not show a trend to higher utilization efficiency at lower mass loadings. The data does show improved sample utilization efficiency over resin beads in the picogram range of mass loaded. It also shows improved utilization efficiency at a higher pre-treatment temperature.

Due to uranium being ubiquitous in the environment, it is difficult to work at low levels without contamination from reagents and the environment. Blank PIEs that included the reagents used and the exchange polymer were analyzed in the instrument and determined to have a blank contribution on the order of 0.01 pg. The average of the counts detected at the Daly detector for the blanks was subtracted from the total counts detected for a sample before calculating the utilization efficiency. This background correction was applied to all data points in Fig. 2.

The need for subtraction of uranium background from the PIE itself does pose a problem for low-level analysis of this isotope. However, forensic analysis of uranium is primarily concerned with uranium-233 and uranium-236 isotopes [15]. These are not present in nature, except at very low levels. Analyses of these isotopes will be in the presence of large 238 and/or 235 signals, so that abundance sensitivity would be more of a consideration than contamination at the 238 or 235 mass. The resin bead and PIE would be expected to have similar abundance sensitivity based on their initial small size at the start of analysis. The evaluation of abundance sensitivity for samples from a PIE presents an area for further work.

There are multiple potential reasons for the enhanced performance of the PIE over a resin bead. The PIE may be more effective at keeping ion emission closer to the center of the ion focusing lens during analysis, it might provide better conversion efficiency to the carbide, or it might be due to an increase in the number of interactions with the metal–carbide surface.

4. Conclusion

A porous thermal ion emitter constructed from rhenium/platinum alloy tightly bonded to a rhenium filament has been developed. This type of emitter has been demonstrated to have reliability and sensitivity superior to the established resin bead method for uranium. The overall efficiency was determined to range between 1% and 2.2% for uranium, an improvement over the resin bead method (0.58%) [1]. No samples were lost over the course of analyzing ∼100 samples. Potential exists for further improvement of the PIE system through varied metal compositions and for application to other actinides. The PIE does allow for loading of the sample in a liquid phase instead of the manipulation of the sample on a single resin bead susceptible to loss.

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