A new pulsed glow discharge source with enhanced ion extraction for small non-conductive samples and atmospheric sampling

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An ionization source designed to efficiently utilize sub-milligram quantities of electrically non-conducting compounds (i.e. oxides) for prolonged periods of mass spectrometric analysis is described. The source is coupled to a quadrupole ion trap mass spectrometer in this report, but could readily be modified for alternative types of mass spectrometers. The coaxial design glow discharge ion source is unique in that it incorporates a focusing lens behind the discharge surface to steer ions towards the ion sampling plate and thereby improve sensitivity. Non-conducting oxide samples are infused in indium and set in one end of an electrically conductive rod, to which the voltage is applied. Transmission efficiency is sufficient to allow the measurement of isotopes of tungsten from a tungsten rod using glow discharge pulse widths as narrow as 2 μs, which is on the order of single-atom laver sputtering. The sputtering and ionization processes occurring in the discharge produces mainly atomic metal ions, regardless of the chemical form of the metals in the samples. This latter aspect is particularly useful for intended applications involving actinide samples, and allows a minimal amount of sample handling. In a second application, a metal capillary is used in place of the rod to create an atmospheric sampling glow discharge. In this mode, the ion-focusing lens was also found to enhance ion signals arising from volatile vapors entering the discharge from the capillary.

1. Introduction
Recent work in our laboratory has focused on the gas-phase ion chemistry of lanthanide and actinide ions in quadrupole ion traps (QIT).1–3 Until recently we have used a conventional direct insertion probe described by Duckworth et al., utilizing a pulsed dc power supply.4 While this type of sample probe has proved adequate for metal pin samples, it is less well suited for non-conducting samples. For bulk non-conductive samples an rf discharge can be struck with the sample, provided the sample can be machined to suit the source configuration.5 For small non-conductive samples, they must be pressed/fused onto or contained within a conducting matrix, such as copper powder or indium metal.5–7 While we have found these approaches satisfactory for lanthanide oxide samples,3 the fragility of pressed pins and the ease with which oxides can fall off an indium or gold surface is not acceptable for radioactive actinide compounds. For the latter, the sample must be more robust and not bear the risk of losing material. We have therefore developed an alternative sample preparation method, and mounting procedure, that enables very small quantities of sample to be used with optimal efficiency.

Taylor et al.8 showed that the application of a positive potential to the sampling plate significantly increased the extraction efficiency of positive ions from a steady state plasma. This counter-intuitive enhancement was shown to arise, primarily, from an increase in the plasma potential and electron temperature with increasing positive potential on the sampling plate. Taylor et al. also proposed that the increase in electron temperature with increasing positive potential on the sampling plate could also significantly increase the number of metastable atoms for Penning Ionization. Because the majority of the sampled ions are thought to form very close to the sampling plate orifice,9,10 it was speculated that the increase in metastable atoms was also contributing to the enhanced ion signals. To our knowledge, the effects of auxiliary electrodes on ion transmission have not been determined for pulsed glow discharges. Our experiments and ion trajectory simulations suggest that when sampling ions from a pulsed glow discharge a negative potential on the sampling plate and a positive potential to an additional auxiliary electrode behind the discharge sample is most beneficial.

The goal of the current project is to obtain a sufficient abundance of actinide metal ions from an easily prepared source to perform gas-phase ion chemistry in the quadrupole ion trap. The nature of the source also lends itself to quick and easy modifications to make it an atmospheric sampling glow discharge, similar to one described before.11 As has been pointed out recently,12–14 new gas sampling inlets for pulsed glow discharge sources could have significant benefits for gas chromatographic (GC) detection sources, providing structural and molecular information. The gas-sampling design presented here could easily be configured to accept the analytes eluting from a GC column.

2. Sample preparation
One form of the samples used in these studies employs a stainless steel rod (~1.5 mm od) with a 1 mm diameter hole drilled 6 mm in from one end. An indium metal wire containing uranium dioxide was prepared and then pressed into the hole in the stainless steel rod. (Caution. Uranium oxide is radioactive and toxic and should be handled with appropriate care. All experiments reported here were performed in a radiological facility at Oak Ridge National Laboratory.) Indium–uranium dioxide wires were formed by mixing indium metal powder with finely powdered depleted uranium dioxide and rolling the mixture between two titanium plates to form a uniform, straight wire of ~1 mm diameter. Typically, several (1–7) weight percent oxide was used. This wire was then inserted and forced down into the hole in the stainless steel rod. This resulted in expansion of the indium to “lock” it in place. The end of the indium that extended slightly beyond the stainless steel was cut off flush with the stainless steel. The final product
This stainless rod with the indium insert was then employed as the sample for the mass spectrometer studies. After completion of the work, examination of the sputtered end showed that the oxide-containing indium insert had suffered significant erosion, whereas the stainless rod had remained virtually unchanged. Ion signals arising from the stainless steel tube could be obtained in the QIT under appropriate conditions, but the signals arising from indium were considerably more prevalent, presumably due to the increased sputtering rate for indium.17

3. Experimental

A schematic of the new source design is shown in Fig. 1. The QIT and previous glow discharge (GD) design is discussed in detail elsewhere.18 A quarter-inch Swagelock fitting with an electrically isolating Vespel ferrule (Supeltex M-2, Supelco, St Louis, MO, USA) is welded on to the front plate of the ion source. The ferrule is pre-drilled for 1/16″ tubing and there is no electrical conductivity between the Swagelock fitting and the inserted rod. A cylindrical lens with an internal diameter of 3.5 mm, termed the ion focusing lens (IFL), surrounds the 1/16″ metal rod. The rod serves both as the electrical feedthrough and the sample or sample holder. The voltage is applied externally via an insulated crocodile clip or push-on connector. (Caution. This design exposes a small section of the cathode rod. High voltages can be lethal and care should be taken to prevent contact with exposed electrodes.) The cathode–sampling plate distance can be adjusted by loosening the Swagelock fitting and sliding the tubing in or out. In this study, the cathode surface was usually optimized as being flush with the ion focusing lens at ~4 mm from the sampling plate. The rod could be removed and replaced by loosening the Swagelock fitting and sliding it out. By replacing the rod with a stainless steel capillary having an internal diameter ~0.125 mm, the source is converted to an atmospheric sampling glow discharge similar to the one described before.19 Under these conditions, a larger fraction of the source pressure is due to the incoming air, and the remainder is made up with argon or helium and depends on the capillary id.

An insulating alumina tube separates and centers the metal rod within the ion focusing lens and prevents arcing between the two. The sampling plate is electrically isolated, and biased negatively for extracting analyte ions. The source chamber is cylindrical in shape, and has an internal diameter and length of ~3 cm. The source region is evacuated to a base pressure of 3 × 10⁻⁹ Torr and operated at ~0.8 Torr Ar in the pulsed mode. For atmospheric sampling, helium proves useful in reducing the amount of sputtered ion signal and has metastable levels above the ionization potential (IP) of most incoming gases, enabling it to ionize higher-IP gases than argon. In-line getters (SAES Pure Gas Inc., San Luis Obispo, CA, USA) purify the argon and helium prior to use. The argon is purified because contaminants in the discharge gases of pulsed glow discharge are known to quench metastable argon atoms and inhibit ionization efficiencies.19–21 especially in the afterpeak of pulsed glow discharges.22–24 Purified helium in the trapping region prevents uranium ions from undergoing undesirable ion–molecule reactions. Typical operating conditions are given in Table 1.

A quadruple output power supply (QUAD 710, ORTEC, Grayson, GA, USA) supplied the lens voltages to lenses 1–4 in Fig. 1. High voltage supplies (EG&G 556, ORTEC) with tolerances for higher current were necessary for the ion focusing lens and ion extraction plate lenses because they are exposed to the glow discharge plasma. During operation in steady-state GD mode, currents of several hundred microamps were measured between the grounded chamber and the ion extraction plate and ion focusing lenses. A high voltage pulse generator (PVX-4140, Directed Energy Inc., Fort Collins, CO, USA) applied a square wave generated by a pulse generator (BNC 8010, Berkley Nulceonics Corp., San Rafael, CA, USA) to the output of a high voltage power supply (210-03R, Bertan, Valhalla, NY, USA). The trigger for the pulse generator is taken from a circuit board within the electronics tower of the mass spectrometer. The ion source and lens system are fitted to a standard Teledyne Discovery 2 QIT mass spectrometer (formerly Mountainview, CA, USA).

4. Results and discussion

To test the source design, a tungsten rod served as the glow discharge feedthrough and sample. After a short pre-sputtering of 5 min at ~800 V in steady-state dc mode, the sample was analyzed using the pulsed glow discharge set-up. Under these conditions, it is not necessary to gate the lens elements because ions are only transmitted to the trap during, and within 2 ms after, the voltage application to the sample.22 Fig. 2 shows a mass spectrum obtained using a 20 μs glow discharge pulse width. Oxley et al.25 demonstrated that pulse widths this short provide only enough sputtering for a few atomic layers of the sample surface. While we do not present a direct comparison of this new source with the previous source, this level of sensitivity is estimated to be at least a 10-fold improvement over our previous design. This estimation is based on the difference in the glow discharge pulse widths necessary to achieve comparable ion signals on the two designs. Because the new and old designs both incorporate the same ion optics between the sampling plate and the trap, the source design is solely responsible for the increased sensitivity.

It is well known that in pulsed glow discharges a significant number of the sputtered analyte ions are formed after the pulsed voltage has been removed.22,23,26,27 In this afterpeak

| 1/16″ rod (sample) | ~0.8 to ~1.6 kV |
| IFL (ion focusing lens) | +100 V |
| ISP (ion sampling plate) | −100 V |
| SP diameter | 0.2 mm |
| IFL-SP spacing | 4 mm |
| L1 | −360 V |
| L2 | −100 V |
| L3 | −900 V |
| L4 | −400 V |
| End cap electrode (during ion injection) | 0 V |
| GD source pressure | 0.8 Torr Ar or He |
| Trap pressure | 0.3 mTorr He |
regime the majority of the plasma gas ions recombine, and metastable states of the discharge noble gas ionize residual sputtered atoms. At this time, the plasma potential decreases significantly and the electrical potentials applied to auxiliary electrodes can have different effects on the ions compared with the steady state plasma. The lack of plasma potential is important for the modeling to be at all representative of the afterpeak conditions. Simulations of the geometry and voltage effects of the discharge were performed using SIMION software. These calculations assume a collisionless environment, no plasma potential or space charge effects, and do not account for gas flow dynamics. Accepting that the modeling is relatively crude, given the necessary assumptions, we feel that these calculations are still informative and reveal insight into the possible cause of the observed enhancements.

Fig. 3 shows the behavior of five uranium ions formed during the afterpeak at slightly different positions. Simulations involve different configurations and potentials. Fig. 3(a) shows a conventional geometry cathode pin and sampling plate, with a negative potential of 100 V applied to the sampling plate. Ions formed under these conditions are attracted to the sampling plate, but are defocused and accelerated away from the sampling orifice, which is located in line with the center of the cathode sample. Only ions formed directly between the cathode and the sampling orifice are extracted under these conditions. Fig. 3(b) shows the effects of a grounded electrode (ion focusing lens) surrounding the cathode. The ions are no longer steered away from the sampling orifice, but orthogonal to the sampling plate surface. Although this grounded lens appears somewhat more favorable than having no lens at all, the benefits appear to be small. However, by applying a positive potential of 100 V to the focusing lens, Fig. 3(c), the ions are now focused towards the ion-sampling plate orifice. Presumably, a larger volume of the afterpeak ions is transmitted to the sampling plate and is sampled by the QIT mass spectrometer under these conditions. Fig. 3(d) shows that by further increasing the focusing lens voltage to +500 V, several ions are accelerated back to the cathode surface and away from the sampling plate. These simulations reflect the experimental results, in which a grounded or highly positive ion focusing lens generated smaller ion signals than voltages of approximately +100 V.

These simulations suggest that ions formed in the afterpeak of a pulsed glow discharge are not only attracted to the sampling plate, but under the appropriate conditions may undergo some degree of focusing on the sampling orifice. Although collisional effects have not been taken into account, these initial simulations suggest that the ion focusing lens could be aiding the extraction of ions from a larger volume of the afterpeak than would be extracted under normal operating conditions. This larger effective sampling volume is assumed to account for the observed signal enhancements.

Fig. 4 shows a mass spectrum obtained from the uranium oxide sample discussed in Section 2. The sample was pre-sputtered at −800 V for 5 min before analysis. Longer pulse widths of 5–20 ms were necessary in this case because the
uranium is a minor constituent of the sample. Mass selective instability\textsuperscript{11} and filtered noise fields\textsuperscript{30–33} (FNF) were also used to prevent major ions, such as $\text{Ar}^+$, $\text{Ar}_2^+$, and $\text{In}^+$, from being trapped during ionization and to enhance the sensitivity for uranium ions. A subsequent isolation event was then used to eject unwanted uranium oxide ions and other minor isotopes appearing in the region. The result, shown in Fig. 4, is that a sufficiently large abundance of bare uranium ions is obtained from the sample for conducting ion–molecule reaction studies.

The same sample was used for several hours a day for several weeks, and did not need replacing or cleaning. It is often necessary to pre-sputter the sample if it is unused for prolonged periods—presumably due to a build up of pump oil residues or oxides on the sample surface. We plan to use the same preparation method for plutonium oxide to continue our studies of gas-phase ion chemistry across the actinide series.

Helium is used instead of argon because it greatly reduces the ionization potential (IP) of helium, and its higher ionization potential serves as tunable plasmas, could benefit from this phenomenon. By replacing the $1/16^\prime$ metal rod with a narrow bore metal capillary, air from the laboratory is sampled directly into the discharge region. The metal capillary acts as the cathode.

By replacing the $1/16^\prime$ metal rod with a narrow bore metal capillary, air from the laboratory is sampled directly into the discharge region. The metal capillary acts as the cathode. Often, atmospheric sampling glow discharges operate with no discharge region. The metal capillary acts as the cathode. The higher ionization potential (IP) of helium, and its higher ionization potential serves as tunable plasmas, could benefit from this phenomenon. By replacing the $1/16^\prime$ metal rod with a narrow bore metal capillary, air from the laboratory is sampled directly into the discharge region. The metal capillary acts as the cathode.

Fig. 5 Mass spectra obtained from the glow discharge source in the atmospheric sampling mode with 50 ms ionization time in He: (a) cotton applicator dipped in perfluorobutylamine supported ~5 mm in front of the sampling plate orifice; and (b) Freon 12 ($\text{CF}_3\text{Cl}_2$) sprayed for $<1$ s, orthogonally 60 cm in front of the capillary (capillary used was 316 stainless steel, 8 cm long with 0.125 mm id).

References