## **Electronic Supplementary Information**

for

Coupling of an atmospheric pressure microplasma ionization source with an Orbitrap Fusion Lumos Tribrid mass analyzer for ultra-high resolution

isotopic analysis of uranium

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## Experimental

## New ion source components

In terms of the LS-APGD ion source, a major development was the design of an enclosed ion source housing and integrated control box. Figure 1 in the main manuscript is an expanded drawing of the source housing, with the essential operation components. The design and machining were performed by the Clemson University, Department of Physics machine shop. The assembly is designed to mount to any Orbitrap based instrument, and mounts directly to the faceplate of the ThermoScientfic Orbitrap Fusion Lumos in the place of the standard Thermo electrospray ionization (ESI) source, including the necessary mounting mechanisms and interlocks (The same design is also easily implemented on ThermoScientific ion trap and triple guadrupole instruments). The body is machined from 6061 aluminum, polished on the inner surfaces and sandblasted on the outside. Based on physical restrictions, the counter electrode is brought in perpendicular to the solution electrode. The gap between the two electrodes is controlled with a micrometer stage (Thor Labs, Newton, NJ, USA), with a resolution of 0.01 mm, with the distance between the solution electrode and the entrance to the ion transfer capillary fixed using a simple set screw and measured with a caliper with a resolution of 0.1mm. Fused silica windows mounted to the top and rear faces of the cover allow observation of the plasma. The high voltage (MHV), helium sheath gas, and liquid delivery connections are also mounted on the back face of the main platform. The source housing is not



Figure 1. Photograph of LS-APGD microplasma in operation under typical discharge conditions.

Fig.

atmosphere sealed in any special way, and is kept at ambient pressures throughout the operation of the LS-APGD. Figure 1 above is a photograph of the microplasma in operation in the unlit laboratory, looking down through the top view port.

The control/utility box was designed and assembled by GAA Custom Engineering, LLC (Benton City, WA), based on prior experimental designs and the input of the author team. The self-contained unit is comprised of a 10 x 5 x 9" polycarbonate shell (Metcase, Bridgeville, PA) to which the syringe pump (Chemyx OEM 30020, Stafford, TX) is mounted to the top, and the high voltage power supply (Ultravolt 1C24-P60-I5, Ronkonkoma, NY ) and sheath gas mass flow controller (Alicat BC-C1000-He-232-NPT, Tucson, AZ) are mounted within. The individual mass and liquid flow components had been tested in the previous implementations of the source, and now incorporated in their OEM forms. The components are powered from a common house AC line, that is converted to the necessary d.c. formats for each. The respective outputs (gas, liquid, and HV) are bundled as an umbilical cord to connect to the inputs on the source housing. A 7" diagonal (800x480 pixel) display with resistive touchscreen is mounted on the front of the control box, providing input to vary each of the operational parameters, with the screen and components under control of a Raspberry Pi 3 - Model B (New York, NY) system.

The ThermoScientific (San Jose, CA) Orbitrap Fusion Lumos Tribrid instrument was operated without any modifications, other than the replacement of the standard Thermo ESI source housing with that of the LS-APGD ion source housing. As this system employs an ion funnel assembly to focus ions emanating from the ion transfer capillary into the mass analyzer region, the role of its rf voltage on the ion throughput was evaluated. Additionally, the roles of in-source collisional induced dissociation (CID) energy on ion throughput and spectral composition were also evaluated. A significant difference between this study and our prior studies that used Thermo Exactive instruments, is the lower target gas pressure used in the higher-energy collisional dissociation (HCD) cell for the Lumos instrument. Previous efforts have shown HCD to be an effective means of eliminating water-related cluster species emanating from the microplasma source.<sup>19</sup> Lower CID efficiencies were noted on the Lumos platform, perhaps due the low pressures (0.005 Torr N<sub>2</sub>) required to operate the Orbitrap at a resolution of 1M. For this reason and except where otherwise noted, no HCD was used during these experiments. Other data acquisition parameters that were investigated included the number of microscans, number of scans, and the preset mass resolution. The overall Lumos operation was controlled using the provided TUNE software; data processing was completed using the QualBrowser software.

The respective discharge parameters and electrolytic solution makeup were held constant throughout the studies, with specific values derived from previous works (liquid flow = 30  $\mu$ L min<sup>-1</sup>, sheath gas flow = 0.5 L min<sup>-1</sup>, and discharge current = 30 mA). Research grade helium (Linde, St. Priest, France) was employed as the sheath gas in the LS-APGD source operation. The electrolytic solution for the basic characterization in the elemental analysis mode was 2% HNO<sub>3</sub> (Fisher Optima, Pittsburgh, PA). The aqueous, primary test mixture was composed of Rb, Ag, Ba, Pb, and U, all at a concentration of 0.5  $\mu$ g mL<sup>-1</sup>, prepared from primary solutions from High Purity Standards (Charleston, SC). The U test solution can be traced to a U isotopic reference material (CRM 129a, New Brunswick Laboratory, Argonne, IL), provided by High Purity Standards and employed in all studies directed towards characterizing the isotope ratio measurement performance. The certified <sup>235</sup>U/<sup>238</sup>U value for the CRM is 0.0072614. While there are numerous examples of isobaric interferences in the lower mass range that would benefit from high mass resolution, the Orbitrap data system does not allow the quadrupole mass filters to transmit ions of m/z < 50 Da to the C-trap.

## Optimization of ion sampling conditions

In comparison with the previously described coupling with the Exactive version of the Orbitrap, there are fundamental differences in how ions are sampled in the Lumos implementation. Parameters effecting the initial de-clustering of the desired metal ions, removal of solvent-related ligands, and focusing/transfer of ions to the C-trap assembly are quite different with the Lumos ion funnel assembly versus S-lens optical elements used on prior experiments and instruments. Therefore, a directed optimization exercise was undertaken to understand the roles of those in-source dissociation and ion funnel rf focusing voltages. A cursory evaluation of the analyte species' responses to the microplasma operating conditions was first performed, confirming that the most intense and stable ion signals were achieved at the same conditions previously employed.

In-source collisional dissociation, affected by the potential applied to the ion transfer capillary (ITC), has long been proven to be an essential tool for removal of loosely-bound solvent species in ESI- and APCI-MS.<sup>26,27</sup> The same has been found in the sampling of the LS-APGD microplasma. Using the multielement test solution at a concentration of 500 ng mL<sup>-1</sup>, the role of the ITC potential on the response of the test elements was evaluated. As seen in Fig. 2a, the responses of the elements that are typically monitored as atomic ions are very similar, increasing with ITC potential (effectively CID energy) to a maximum at a potential of 80 V. The general result is the removal of solvent molecules to yield bare metal ions and to remove small water clusters from filling the Orbitrap, allowing more analyte ions to enter the trap. Beyond the 80 V level, it is believed that a general loss in throughput occurs. Notably different from the other test elements, the response for  $UO_2$  shows a continuous increase. It is interesting to note that of the analytes in the present suite, only uranium presents itself most prominently as a molecular species  $(UO_2^+)$ . Herein lies a defining difference between this plasma source and what would be seen using an ESI source. In this case, the degree of solvent molecule attachment to the UO<sub>2</sub><sup>+</sup> ion is far more extensive than the other metal ions, and the level



Figure 2. Roles of ion sampling/transfer conditions on analyte responses. a) Role of in-source CID potential on analyte species signals, b) role of in-source CID potential on the fractional contributions of Ba molecular species, and c) role of ion funnel rf potential on analyte throughput. Conditions: discharge current = 30 mA, solution flow rate =  $30 \ \mu L \ min^{-1}$ , and sheath gas flow rate =  $0.5 \ L \ min^{-1}$ , analyte concentrations =  $500 \ ng \ mL^{-1}$ , each.

of de-clustering continues at higher voltages. Also presented in Fig. 2a is the response of the "spectral background" (267.0-267.1 for <sup>235</sup>U and 270.0-271.1 for <sup>238</sup>U), which takes the general form of  $(H_2O)_nH^+$ , and was measured by averaging all of the signals in the spectrum and subtracting the analyte ion signals. In this case, it is clear that these cluster species are indeed effectively reduced using in-source CID.

As removal of solvent molecules is the primary purpose of in-source CID, there are benefits to be seen in terms of dissociation of undesirable inorganic species. In the case of the LS-APGD source, the presence of the 2% HNO<sub>3</sub> provides a rich source of nitrates (NO<sub>3<sup>-</sup></sub>) which can be associated with metal cations. Likewise, hydroxide (OH<sup>-</sup>) is also prevalent within the plasma through the dissociation of  $H_2O$ . Of the elements in the test mixture, Ba<sup>+</sup> illustrates the case of a very reactive metal ion towards both of these species. Molecular BaNO<sub>3</sub><sup>+</sup> and BaOH<sup>+</sup> species are initially prominent in the spectra with low CID potentials applied. As shown in Fig. 2b, the application of higher in-source CID potentials dramatically reduces the contributions of these species, to the point that the atomic isotopic distribution then dominates the Ba mass spectra. On closer consideration, the relative responses of the two species is guite telling relative to the gas phase processes. The data imply that BaNO<sub>3</sub> first dissociates to yield Ba<sup>+</sup>, which can then react with OH<sup>-</sup> in the gas phase to form BaOH. Ultimately, both species are dramatically reduced in this stage, with the yield of the desired Ba+ increasing to the maximum at 80 V.

The final optical element effecting the transport of analyte ions to the mass analyzer is the ion funnel. Originally described by Smith et al.,<sup>28</sup> the ion funnel consists of a series of ring electrodes of decreasing diameter, to which a radio frequency (rf) and

d.c. potential is applied. The role of the funnel is to focus a spatially dispersed ion cloud exiting the ITC into the primary entrance aperture of the mass analyzer. What is desired are rf conditions (d.c. held constant) which yield high ion throughput without imparting any intraspecies biases. As seen in Fig. 2c, this goal is readily achieved for the test element ions produced by the LS-APGD. Each of the ion species increases in response to rf potential to a very broad maxima occurring between ~100 – 125 V. The parallel responses, and broad range of tunability ensure a level of experimental robustness to minor variations in operation conditions.