Supporting Information for: Considerations for Uranium Isotope Ratio Analysis by Atmospheric Pressure Ionization Mass Spectrometry

Thomas P. Forbes* and Christopher Szakal
National Institute of Standards and Technology, Materials Measurement Science Division, Gaithersburg, MD, USA
* Corresponding author: E-mail: thomas.forbes@nist.gov; Tel: 1-301-975-2111

Supporting Information Table of Contents

Experimental Methods

Supplemental Figures and Data
Figure S1. Schematic representation of the hybrid QTOF mass spectrometer. Figure S2. Isotope ratio as a function of in-source CID. Figure S3. Isotope ratio and peak areas as a function of spectra averaging number. Figure S4. Extracted ion chronograms as a function of spectra averaging number. Figure S5. Extracted ion chronograms of 5 × 3 Hz vs 5 × 1 Hz for multiple injection masses. Figure S6. Extracted ion chronograms of 3 Hz vs 1 Hz for multiple injection masses. Figure S7. Isotope ratio as a function of (a) spectra rate (b) the averaging time scale. Figure S8. Extracted ion chronograms for 5 average spectra as a function of spectral rate. Figure S9. Extracted ion chronograms of multiple spectral acquisition settings. Figure S10. Example mass spectra of chemical noise in minor isotope region. Figure S11. Extracted ion chronograms of UO₂ isotopes and chemical noise. Figure S12. Peak areas of as a function of injected mass for 1 Hz and 3 Hz spectra rates.

Experimental Methods
Single-element uranium dilutions. The standard ICP-MS solution was certified for mass of U, however, the uranium existed as UO₂²⁺ in solution. Dilutions of the uranium standard (10 ppm of U) were created for (4000, 1000, 400, 100, 40, 10, 4, 1) ppb of U. Given that UO₂⁺ was observed as the dominant ion in the mass spectra and all isotope ratios were measured as $^{235}$UO₂²⁺/$^{238}$UO₂⁺, concentration and injected mass values were converted to UO₂ (4536, 1134, 453.6, 113.4, 45.36, 11.34, 4.536, 1.134) ppb UO₂ and (22680, 5670, 2268, 567.0, 226.8, 56.70, 22.68, 5.670) pg UO₂.

Baseline subtraction. The determination of peak areas from extracted ion chronograms and subsequently isotope ratios incorporated a baseline subtraction. The instantaneous baseline background levels at the extracted ion m/z value were measured immediately prior to and following each discrete sample injection (i.e., counts per second, cps). These before and after background levels were averaged and multiplied by the duration (i.e., in seconds) of the peak of interest to give an approximation of the baseline background counts during the discrete sample injection. This background value (counts) was subtracted from the overall peak area (counts).

S-1
Supplemental Figures and Data

Figure S1. Schematic representation of the hybrid quadrupole time-of-flight (QTOF) mass spectrometer†. Inset represents the location of in-source collision induced dissociation (CID) between the two ion funnels. Adapted from image provided by Bruker Daltonic GmbH (Bremen, Germany).

† Certain commercial products are identified in order to adequately specify the procedure; this does not imply endorsement or recommendation by NIST, nor does it imply that such products are necessarily the best available for the purpose.

Figure S2. Isotope ratio \( ^{235}\text{UO}_2^+ / ^{238}\text{UO}_2^+ \) as a function of in-source CID energy for 567 pg UO\(_2\) injections for spectra acquisition of \(5 \times 3\) Hz. Data points and uncertainties represent the average peak area ratios and expanded standard deviations \((k=2)\) of seven replicate injections at each in-source CID energy.
Figure S3. (a) Isotope ratio ($^{235}\text{UO}_2^+ / ^{238}\text{UO}_2^+$) and peak areas of (b) $^{238}\text{UO}_2^+$ and (c) $^{235}\text{UO}_2^+$ as a function of spectra averaging number for 567 pg UO$_2$ injections for spectra rate of 3 Hz. Data points and uncertainties expressed as averages and expanded standard deviations (k=2) of replicate injections.

Figure S4. Examples of extracted ion chronograms (XICs) for $^{238}\text{UO}_2^+$ ($m/z$ 270) and $^{235}\text{UO}_2^+$ ($m/z$ 267) from 567 pg UO$_2$ injections as a function of spectra averaging number for a 3 Hz spectra rate.
Figure S5. Examples of extracted ion chronograms (XICs) for $^{238}$UO$_2^+$ ($m/z$ 270) and $^{235}$UO$_2^+$ ($m/z$ 267) for UO$_2$ injections of (a) 5670 pg (b) 567 pg, and (c) 56.7 pg at (i) $5 \times 3$ Hz and (ii) $5 \times 1$ Hz.
Figure S6. Examples of extracted ion chronograms (XICs) for $^{238}\text{UO}_2^+$ ($m/z$ 270) and $^{235}\text{UO}_2^+$ ($m/z$ 267) for $\text{UO}_2$ injections of (a) 5670 pg (b) 567 pg, and (c) 56.7 pg at (i) 3 Hz and (ii) 1 Hz with no averaging.
Figure S7. (a) Isotope ratio ($^{235}$UO$_2^+$/^{238}$UO$_2^+$) as a function of spectra rate for 567 pg UO$_2$ injections and 5 spectra averaging. (b) Isotope ratio ($^{235}$UO$_2^+/^{238}$UO$_2^+$) as a function of the averaging time scale for 567 pg UO$_2$ injections of a series of variable spectra rates for 5 spectra averaging and variable spectra averaging for 3 Hz spectra rate. Data points and uncertainties expressed as the averages and expanded standard deviations (k=2) of replicate injections.

Figure S8. Examples of extracted ion chronograms (XICs) for $^{238}$UO$_2^+$ (m/z 270) and $^{235}$UO$_2^+$ (m/z 267) for 567 pg UO$_2$ injections as a function of spectra rate and 5 spectra averaging.
Figure S9. Examples of extracted ion chronograms (XICs) for $^{238}\text{UO}_2^+$ ($m/z$ 270) and $^{235}\text{UO}_2^+$ ($m/z$ 267) from 567 pg $\text{UO}_2$ injections for a number of spectra averaging and spectra rates, maintaining constant averaging timescale ($t_{ave} = 1.5$ s).

Figure S10. Examples of mass spectra in the region around $^{235}\text{UO}_2^+$ ($m/z$ 267) from (a) blank injections prior to the analysis of (i) 56.7 pg, (ii) 567 pg, and (iii) 5670 pg injection replicates and (b) $\text{UO}_2$ injections of (i) 56.7 pg, (ii) 567 pg, and (iii) 5670 pg (Figure S10(b) matches mass spectra insets from Figure 5 with the intensity scale adjusted for visualization and comparison with S10(a)).
Figure S11. Examples of extracted ion chronograms (XICs) for $^{238}\text{UO}_2^+$ (m/z 270.04) and $^{235}\text{UO}_2^+$ (m/z 267.03) and a chemical noise peak (m/z 267.12) for UO$_2$ injections of (a) 5.67 pg (b) 56.7 pg, and (c) 567 pg and (d) 5670 pg at 3 Hz with no averaging.

Figure S12. Peak areas of (a) $^{238}\text{UO}_2^+$ and (b) $^{235}\text{UO}_2^+$ as a function of UO$_2$ injection mass 1 Hz and 3 Hz spectra rates. Data points and uncertainties expressed as the averages and expanded standard deviations (k=2) of seven replicate injections. Uncertainties are smaller than data points.