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PAPER

Uranium isotopic analysis in unpurified solutions by ICP-MS†

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Mass spectrometry is a widely used tool for analysis of uranium isotopic composition. For solution based inductively coupled plasma mass spectrometry, uranium isotopes are typically analyzed after purification from complex matrices. In this work, we tested the ability of three mass spectrometers (ThermoScientific iCAP TQ, ThermoScientific Neoma, and Agilent 8900) to analyze uranium isotopes in an unpurified NIST reference material (SRM2780a, Hard Rock Mine Waste) digest solution. Results indicate that $^{235}U/^{238}U$ can be analyzed within 1% of the true value. $^{234}U/^{238}U$ is a more challenging analysis due to low count rates and potential isobar interferences, but strategies to mitigate these effects, such as the use of reaction gases in a collision cell and desolvating nebulizer introduction system, are effective for the triple quadrupole instruments. However, the use of the Neoma MS/MS in reaction mode using O_2 gas was problematic. Nevertheless, analysis of unpurified solutions for quick assessment of uranium isotope compositions is practical, especially when high precision is not required.

1. Introduction

Mass spectrometry analysis of uranium isotopic composition is a widespread practice with applications in nuclear,[1–9] geological,[10–18] biological,[19–23] environmental,[24–29] and materials[30,31] science. Improvements in mass spectrometry technology have led to enhanced precision and lower detection limits that have strengthened understanding of a variety of natural and man-made processes from the micro to the macro scale.[32–37] For bulk sample analysis, two types of mass spectrometers are typically used. Thermal ionization mass spectrometry (TIMS) has been considered the conventional method with decades of supporting method development and high precision analytical data using either partial or total evaporation methods.[38–41] Inductively coupled plasma mass spectrometry (ICP-MS), including quadrupole based single collector and magnetic sector multi collector, is also used for isotopic analysis and improves sample throughput.[42–45] Multi collector instruments have primarily followed the path of TIMS instruments, focusing on the analysis of purified samples.[46,47] Most method development studies regardless of the analytical technique have focused on pure uranium standards and/or sample solutions that have undergone a purification process.[48–53]

Purifications provide two benefits for mass spectrometry analysis by either TIMS or ICP-MS. For samples with high matrix and relatively low uranium contents, the process of purification allows for preconcentration of a relatively small total amount of uranium analyte.[45,46,54–58] The sample load size requirements for TIMS generally requires a high-purity uranium aliquot with techniques used to enhance ionization and detection.[59,60] The presence of additional matrix elements during ICP-MS analysis can create isobaric interferences on uranium masses,[61] as well as impart matrix effects during sample introduction that can affect the accuracy of high precision isotopic data.[46] The drawback of sample purification is the amount of time required, including performing chromatographic separations and concentrating the final uranium aliquot eluted from ion exchange columns. Given technological advances in ICP-MS, especially the use of collision-reaction cells, the potential for reducing or even eliminating the need for extensive purification procedures is becoming more viable.

Here we present uranium isotopic data in purified and unpurified aliquots of a standard reference material from both triple quadrupole and multi-collector ICP-MS instruments. The intention of these analyses is to determine the accuracy of uranium isotopic composition data in unpurified samples and compare performance of the triple quadrupole and multi collector instruments. Purified samples were measured using typical methods associated with high precision analysis to establish a baseline value for uranium isotope ratios in the SRM2780a material, and unpurified analyses were compared to this baseline value to determine accuracy. In doing so, we show that uranium isotopes ($^{235}U/^{238}U$, $^{234}U/^{238}U$) can be analyzed accurately (within 1% and 10% of the true values, respectively) without prior purification. This uncertainty is sufficient to determine whether uranium isotopes in a sample are nominally

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natural or have been altered from the natural isotopic composition, as well as a determination of whether the $^{234}U/^{238}U$ is near secular equilibrium. Thus, analysis of uranium isotopes without purification can be useful when high precision is not required.

2. Analysis of uranium isotopes in unpurified matrices

All sample preparation and analytical methods were carried out in either the Ultratrace Laboratory or Radiation Detection Laboratory at Pacific Northwest National Laboratory. All acid reagents were diluted from Optima Grade, and all H_2O used was 18.2 MΩ cm. Analytical experiments were conducted to test the accuracy and precision of uranium isotopic ratios in an unpurified digest compared to high-precision analyses of purified uranium fractions. Samples were prepared from a primary solution containing of NIST SRM2780a (Hard Rock Mine Waste). Uranium isotopes (^{234}U, ^{235}U, and ^{238}U) were analyzed in purified and unpurified aliquots on the ThermoScientific NeptunePlus MC-ICPMS, ThermoScientific Neoma MC-ICPMS (and later upgraded to the Neoma MS/MS), Agilent 8900 QQQ-ICPMS, and ThermoScientific iCAP TQ ICPMS. Accurate isotope ratios were measured as metal ions on the MC-ICP-MS instruments, and metals, oxides, or double oxides on the QQQ-ICPMS. Analysis of double oxides on the Neoma MS/MS was also attempted. Unpurified NIST2780a solutions were diluted to match the uranium concentration of standards.

2.1 Preparation of the NIST SRM2780a solution

NIST SRM2780a contains a certified uranium concentration of 4 mg kg^{-1}. The material also contains relative high abundances of Al, Si, S, and Fe (mass fractions 8.43, 24.1, 8.85, and 8.75%, respectively).[62] Approximately 10 grams of material were weighed into a clean glass beaker, and the sample was placed into an oven at 110 °C for two hours to dry. After cooling the dry weight was recorded. The aliquot was then quantitatively transferred to a Teflon beaker using 33 mL of concentrated (16 M) nitric acid (HNO_3). This solution was dried, then 20 mL of aqua regia (3 : 1 volume ratio of concentrated hydrochloric acid (HCl) : HNO_3) was added and the sample was refluxed for one hour, then dried. The sample was then transposed to nitrate using three sequential additions and dry downs of 10 mL of concentrated HNO_3. This was followed by three sequential additions and dry downs of 10 mL, 20 mL, and 10 mL of concentrated (29 M) hydrofluoric acid (HF). The sample was again transposed to nitrate using three sequential additions and dry downs of 10 mL of concentrated HNO_3. Then a 1 : 1 mixture of concentrated HNO_3 and concentrated (9.5 M) perchloric acid ($HClO_4$) was added and the sample was dried, followed by two more additions and dry downs of 10 mL of concentrated $HClO_4$. The HF step was repeated, then the $HClO_4$ step was repeated. The sample was transposed to chloride using sequential additions and dry downs of 10 mL of concentrated (11 M) HCl, followed by two sequential additions and dry downs of 30 mL of 2 M HCl. The sample was then quantitatively transferred to a pre-weighed 2 liter PFA bottle containing 150 mL of H_2O using concentrated HCl, and the sample was diluted to provide approximately 2 L of 2 M HCl containing a final concentration of 4.84 mg of sample per g of solution.

2.2 Purification of uranium

Two purification schemes were testing for purification of uranium from a digest of SRM2780a. The first purification test involved AG1-X8, 100–200 mesh anion exchange resin using methods similar to those previously published.[18,63,64] Two mL of resin were loaded into a column made from a disposable pipette tip. The resin was cleaned with washes of H_2O, 9 M HCl, and 1 M HCl, and H_2O, then conditioned with 7.5 M HNO_3. The sample was loaded in 7.5 M HNO_3, then the bulk sample matrix was eluted with additional washes of 7.5 M HNO_3. Thorium (Th) was eluted with 9 M HCl, then U was eluted with 1.2 M HCl. The uranium fraction was transposed to 2% HNO_3 in preparation for analyses on the NeptunePlus and Neoma MC-ICPMS instruments. The uranium chemical yields of this procedure from literature studies is near quantitative. Procedural blanks were not explicitly processed during the separation of the SRM2780a material in this study, however blanks processed using the same or similar chemistries during the time period of this study were < 12 pg.

The second purification scheme used a 2 mL Eichrom UTEVA, 50–100 mesh resin cartridge and a vacuum box. UTEVA resin extraction methods improve sample processing times and blank contributions.[49,65,66] The resin was cleaned using 0.02 M HNO_3 and conditioned with 3 M HNO_3. The sample was loaded in 3 M HNO_3, then the resin was washed with 3 M HNO_3 and 4 M HCl to remove the bulk sample matrix. Uranium was eluted with 0.02 M HNO_3. The uranium fraction was transposed to 2% HNO_3 in preparation for analysis. The uranium chemical yields of this procedure from literature studies is near quantitative. Procedural blanks were not explicitly processed during the separation of the SRM2780a material in this study, however blanks processed using the same or similar chemistries during the time period of this study were typically lower than instrumental background. The estimated procedural blank is <2 pg.

2.3 Isotopic analyses

Instrument setup and acquisition parameters for the unpurified sample analyses are provided in Table 1. In general, the Agilent 8900 was configured to provide the most rapid isotopic analysis, whereas the iCAP was configured to optimize performance of isotopic composition analysis resulting in longer analysis times. The running configurations for each instrument are described in more detail below.

2.3.1 NeptunePlus MC-ICPMS. Purified uranium was introduced into the plasma using a dual cyclonic spray chamber (wet plasma mode). Uranium isotopes were analyzed in static mode using a combination of Faraday cups and ion counters. The ^{238}U and ^{235}U were measured on the H3 and H1 Faraday cups attached to 10^{11} ohm resistors, and the ^{234}U was measured using the central secondary electron multiplier/retarding potential quadruple (SEM/RPQ). The purified SRM2780a

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Table 1 Acquisition parameters for ICP-MS instruments

Instrument	Agilent 8900	iCAP	iCAP	Neoma	Neoma MS/MS
Sensitivity spec (kcps per ppb ^{238}U)	1000	330	330	3100	3100
Introduction	Spray chamber	Spray chamber	Aridus II	Spray chamber	Spray chamber
Acquisition time (s)	90	300	1010 (long)	160	160
			101 (rapid)		

uranium fraction was diluted to provide $\sim 7 \times 10^7$ counts per second (cps) ^{238}U. Beam intensities were measured for 40 cycles of 4.134 second integrations. Mass bias and faraday-ion counter gain were externally corrected using a 10 ppb solution of NIST CRM-129a analyzed adjacent to the sample. Blanks were analyzed before and after the sample and standard analyses.

2.3.2 Neoma MC-ICPMS. Four methods were used for analysis of uranium isotopes on the Neoma and were conducted both before and after the addition of the MS/MS component of the instrument. For all methods on the Neoma, blanks are continuously monitored (*i.e.*, after every sample and standard analysis). In addition, pure "sample-standard bracketing" was not employed to reduce the amount of standard material required for the analyses. In most cases only one standard was analyzed at the beginning of the analytical sequences.

Method one used an Apex Ω desolvating system to introduce purified uranium solutions into the plasma (dry plasma). Uranium isotopes were analyzed in static mode on Faraday cups, with ^{238}U and ^{235}U measured on the L1 and H1 cups with 10^{11} ohm resistors, and ^{234}U measured on the L2 cup with a 10^{13} ohm resistor. The SRM2780a uranium fraction was diluted to provide $>1 \times 10^9$ counts per second ^{238}U ($\sim$10 ppb). Beam intensities were measured for 40 cycles of 4 second integrations. Mass bias was externally corrected using solutions of either U030a or NIST CRM-129a.

Methods using traditional nebulization included analyses of both purified and unpurified fractions of SRM2780a. Samples were introduced into the plasma using a dual cyclonic spray chamber (wet plasma). Uranium isotopes were analyzed in static mode using a multiple ion counting array (nuclear package). ^{234}U and ^{235}U were measured on SEMs and ^{238}U was measured on a compact discrete dynode (CDD) ion counter. In addition, isotopes were measured in dynamic mode using the center SEM/RPQ. Purified fractions were diluted to provide $\sim 4 \times 10^5$ counts per second ^{238}U ($\sim$100 ppt). Beam intensities for ^{234}U were $\sim$22 cps at this concentration. Unpurified fractions were tested at multiple dilutions to evaluate matrix effects on sensitivity. Beam intensities were measured for 40 cycles of 4 second integrations. Mass and detector bias was externally corrected using 100 ppt solutions of either U030a or NIST CRM-129a. In dynamic mode, no detector bias correction is required, and no mass bias correction was applied.

Uranium isotopes were also measured as double oxides using O_2 (0.05 mL min^{-1}) as a reaction gas in the collision/reaction cell. This method was tested to compare the mass shifting capabilities of the Neoma MS/MS to the triple quadrupole instruments. Uranium double oxide ions were measured in static mode using the multiple ion counting array. ^{234}U and

^{235}U were measured on SEMs and ^{238}U was measured on a CDD ion counter. Mass and detector bias was externally corrected using 100 ppt solutions of NIST CRM-129a. Discrepancies in isotopic compositions (reported below) were investigated using mass scans from 228 amu to 272 amu covering the range of masses from thorium metal to uranium double oxide.

2.3.3 8900 QQQ-ICPMS. Purified and unpurified fractions of SRM2780a were introduced into the plasma using a Scott spray chamber with a Peltier cooler. Uranium isotopes were analyzed as metal ions in single quadrupole mode. For MS/MS mode, uranium isotopes were introduced as a metal ions (U$^+$) into the reaction cell where nitric oxide (0.4 mL min^{-1}) was utilized to form primarily double oxides (UO$_2^+$) for detection. ^{234}U, ^{235}U, and ^{238}U were analyzed at *m/z* 266, 267, and 270, respectively. Both modes utilized the following acquisition parameters: 3 replicates per sample, 10 seconds/replicate for each isotope, and 100 sweeps/replicate. Due to the slower transit time when a reaction gas is utilized in MS/MS mode, a wait time offset of 30 ms was utilized between each mass jump. Samples and standards were diluted to provide maximum count rate on ^{238}U in single quadrupole mode while keeping it below the threshold for analog counting mode ($<1.7 \times 10^6$ cps) on the detector. Mass bias was externally corrected using a 100 ppt solution of CRM-129a analyzed at the beginning of each session. Blanks were monitored periodically.

2.3.4 iCAP TQ ICPMS. Unpurified fractions of SRM2780a were introduced into the plasma using either Scott spray chamber with a Peltier cooler or an Aridus II desolvating nebulizer. Uranium isotopes were analyzed as metal ions in single quadrupole (SQ) mode. For TQ mode, uranium isotopes were introduced as metal ions (U$^+$) into the reaction cell where oxygen gas (0.2 mL min^{-1}) was utilized to form single and/or double oxides (UO$_2^+$) for detection as single or double oxides. Both SQ and TQ modes used normal resolution. ^{234}U, ^{235}U, and ^{238}U single oxides were analyzed at *m/z* 250, 251, and 254, respectively. ^{234}U, ^{235}U, and ^{238}U double oxides were analyzed at *m/z* 266, 267, and 270, respectively. Both modes utilized the following acquisition parameters: 10 replicates per sample, 1 second/replicate for each isotope, and 10 sweeps/replicate. The dwell time (seconds/replicate) was also modified in some cases to increase the counting time (up to 5 seconds) on the lower abundance isotopes. Samples and standards were diluted to provide $\sim$200–500 ppt of uranium in the sample solution, and mass bias was externally corrected using CRM-129a analyzed at the beginning of each session or every three sample analyses depending on the number of sample analyses. Blanks were monitored continuously throughout analytical sequences (in between every sample and standard analysis).

3. Results

3.1 Purified fractions

Results of analyses of purified fractions of NIST2780a are provided in Table 2 and shown in Fig. 1. No systematic differences were observed between the two purification methods within uncertainty, and the values reported in Table 2 are averages of values measured from both purification processes as available. The high-precision analyses of SRM2780a (a combination of 15 analyses from the Neptune and Neoma) gave an average $^{235}U/^{238}U$ of 0.007255 ± 0.000003 and $^{234}U/^{238}U$ of 0.0000630 ± 0.0000001 (uncertainties are 2 standard error). The $^{235}U/^{238}U$ is in good agreement with the assumed value for natural uranium as measured in CRM960 (0.0072549 ± 0.0000008 (ref. 67)). The $^{234}U/^{238}U$ indicates secular disequilibrium in this reference material giving a $(^{234}U)/(^{238}U)$ activity ratio of 1.146 assuming the secular equilibrium $^{234}U/^{238}U$ of Cheng et al., 2013 (54.970×10^{-6}). Analyses of uranium isotopes using all other methods gave $^{235}U/^{238}U$ from 0.00723 to 0.00728, and $^{234}U/^{238}U$ from 0.000063 to 0.000066.

3.2 Unpurified solutions

Results of analyses of unpurified solutions of NIST2780a are provided in Table 3 and shown in Fig. 2. Analyses of the unpurified solutions using the multiple ion counting (MIC) method on the Neoma gave $^{235}U/^{238}U = 0.00731 \pm 0.00008$ and $^{234}U/^{238}U = 0.000075 \pm 0.000009$ (1σ, $n = 5$). After installation of the MS/MS module, analyses of the unpurified solutions using the MIC method gave $^{235}U/^{238}U = 0.00727 \pm 0.00003$ and $^{234}U/^{238}U = 0.000069 \pm 0.000002$ (1σ, $n = 7$). Single collector mode gave $^{235}U/^{238}U = 0.00722 \pm 0.00012$ and $^{234}U/^{238}U = 0.000065 \pm 0.000011$ (1σ, $n = 2$). The analysis of the double oxides gave values significantly different than any other method, $^{235}U/^{238}U = 0.0147 \pm 0.0008$ and $^{234}U/^{238}U = 0.107 \pm 0.011$ (1σ, $n = 9$). The origins of these discrepancies are discussed below, and mass scans across the 228 amu to 272 amu range are provided in the ESI file.† Analyses of uranium isotopes on the triple quadrupole instruments gave $^{235}U/^{238}U$ from 0.00718 to 0.00732, and $^{234}U/^{238}U$ from 0.000055 to 0.000075.

4. Discussion

4.1 Comparison of purified and unpurified results

One benefit of the purification process is the ability to concentrate an analyte that is typically found in $\mu g \ g^{-1}$ quantities or less in sample materials. Analyses using Faraday cups benefit from this process, whereby uranium that is purified from a solution containing a dissolved reference material is purified and concentrated. The NIST2780a solution used in this study contained $\sim$4.84 mg of soil per gram of solution. NIST2780a contains a certified uranium concentration of 4.0 mg kg^{-1}, giving a uranium concentration in the digest solution of 0.019 $\mu g \ g^{-1}$ (19 ppb). This concentration is above that used for high precision uranium isotopic analysis on the Neoma (10 ppb) but is accompanied by the soil matrix that can include more than 1000 ppm of additional elements (primarily major elements such as Al, Fe, K) in solution. Although not tested in this study, the impacts of matrix effects and interferences would likely prevent any ability to measure uranium isotopes with high precision in unpurified samples.

Analyses of the $^{235}U/^{238}U$ in unpurified NIST2780a solution produced accurate results (within 1%) compared to the high precision value measured in the purified fractions using Faraday cups. No systematic biases exist between the different mass spectrometers, indicating that accurate results can be achieved using either the single collector ICP-MS (iCAP, 8900) or multiple ion counting methods on the MC-ICP-MS (Neoma). However, compared to the results of purified samples, results tend to be biased towards higher $^{234}U/^{238}U$ (10–20%), except for the $^{234}U/^{238}U$ measured in TQ mode on the iCAP with the spray chamber that is biased low. This is likely a result of a combination of interferences and relatively low count rates on the minor ^{234}U isotope. Potential improvements could be achieved by increasing total integration times on the low abundance ^{234}U isotope.

4.2 Origins of discrepancies in unpurified digests

Analyses of uranium isotopic ratios in unpurified samples are problematic due to the presence of matrix elements that can

Table 2 Analyses of NIST2780a purified using AG1-X8 and UTEVA resins

Instrument	Introduction	Method	$^{235}U/^{238}U$	$1\sigma^a$	$^{234}U/^{238}U$	$1\sigma^a$	n
Agilent 8900 (rapid)	Spray chamber	SQ	0.00723	0.00001	0.000065	0.0000004	2
Agilent 8900 (rapid)	Spray chamber	TQ-NO	0.00727	0.00001	0.000066	0.000002	2
iCAP	Aridus II	SQ	0.00728	0.00003	0.000064	0.000001	6
iCAP	Aridus II	TQ-O_2	0.00724	0.00002	0.000063	0.000001	6
Neptune	Spray chamber	Faraday-IC	0.007248	0.000001	0.0000631	0.0000005	1
Neoma	ApexΩ	Faraday	0.007259	0.000012	0.0000632	0.0000001	2
Neoma	Spray chamber	MIC	0.00727	0.00002	0.000064	0.000003	5
Neoma MS/MS	ApexΩ	Faraday	0.007255	0.000004	0.0000629	0.0000002	12
Neoma MS/MS	Spray chamber	MIC	0.00724	0.00023	0.000065	0.000007	1
Neoma MS/MS	Spray chamber	SC	0.007242	0.000016	0.000063	0.000002	2
Average and 2StdErr of faraday measurements	—	—	0.007255	0.000003	0.0000630	0.0000001	15

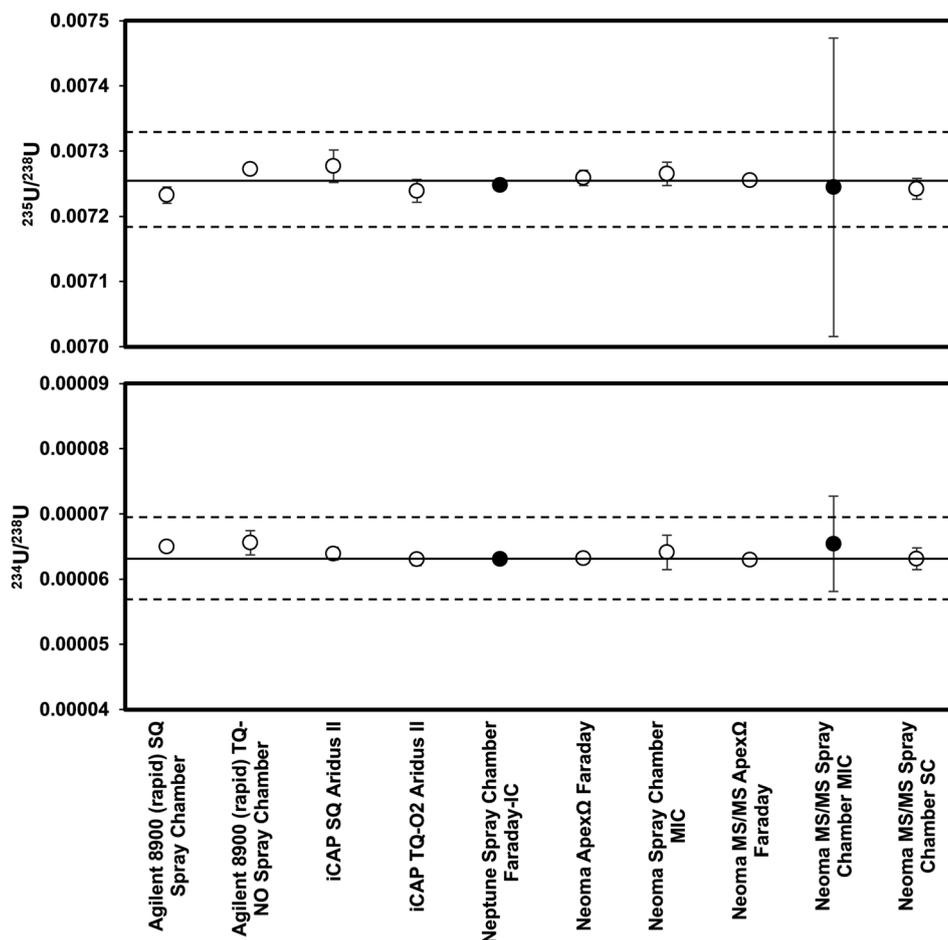^{a} For $n = 1$, the standard deviation from the single measurement is reported.

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Fig. 1 $^{235}U/^{238}U$ (top) and $^{234}U/^{238}U$ (bottom) in purified aliquots of NIST SRM2780a compared to the high precision value (black solid lines) and 1% and 10% deviations (dashed lines), respectively. Filled circles indicate $n = 1$, and open circles indicate $n > 1$. SQ = single quad; TQ = triple quad; IC = ion counter; MIC = multiple ion counting; SC = single collector.

form molecular species in the argon plasma, leading to interferences at uranium masses. This is supported by the high-biased $^{234}U/^{238}U$ ratios in the unpurified digests. Mass shifting the uranium isotopes using gases in the collision cell for measurement as oxides or double oxides mitigates the bulk of

the effects of these interferences. However, especially for the minor ^{234}U isotope, we found no significant difference between single quadrupole and triple quadrupole measurements on the iCAP using the Aridus II. This can likely be attributed to the enhanced sensitivity afforded by using the desolvating

Table 3 Analyses of unpurified NIST2780a

Instrument	Introduction	Method	$^{235}U/^{238}U$	$1\sigma^a$	$^{234}U/^{238}U$	$1\sigma^a$	n
Agilent 8900 (rapid)	Spray chamber	SQ	0.00718	0.00017	0.000068	0.000007	1
Agilent 8900 (rapid)	Spray chamber	TQ-NO	0.00727	0.00015	0.000065	0.000012	1
iCAP TQ	Spray chamber	SQ	0.00728	0.00006	0.000075	0.000004	3
iCAP TQ	Spray chamber	TQ-O_2	0.00721	0.00003	0.000055	0.000005	3
iCAP TQ	Aridus II	SQ	0.00726	0.00001	0.000065	0.000001	3
iCAP TQ	Aridus II	TQ-O_2	0.00732	0.00001	0.000065	0.000002	3
iCAP TQ (rapid)	Aridus II	SQ	0.00728	0.00002	0.000063	0.000004	3
iCAP TQ (rapid)	Aridus II	TQ-O_2	0.00722	0.00004	0.000061	0.000005	3
Neoma	Spray chamber	MIC	0.00731	0.00008	0.000075	0.000009	5
Neoma MS/MS	Spray chamber	MIC	0.00727	0.00003	0.000069	0.000002	7
Neoma MS/MS	Spray chamber	SC	0.00722	0.00012	0.000065	0.000011	1
Neoma MS/MS	Spray chamber	MS/MS O_2	0.0147	0.0008	0.107	0.011	9

^{a} For $n = 1$, the standard deviation from the single measurement is reported.
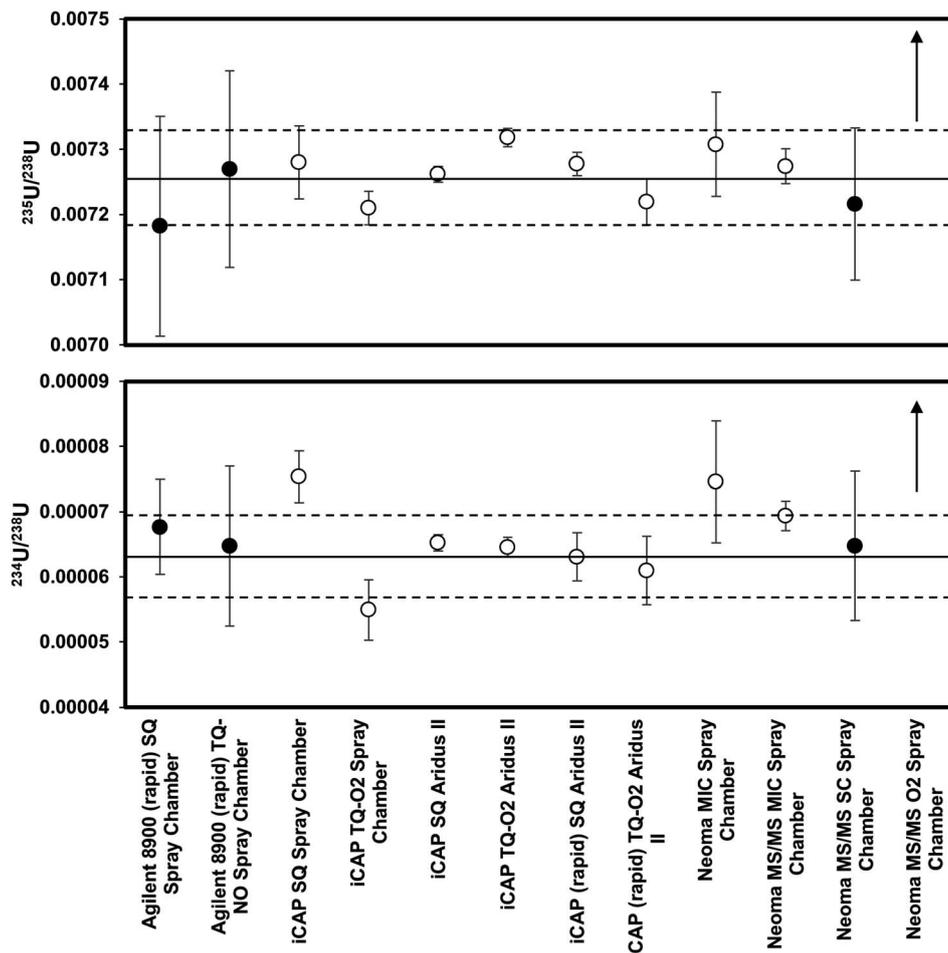
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Fig. 2 $^{235}U/^{238}U$ (top) and $^{234}U/^{238}U$ (bottom) in the unpurified NIST SRM2780a digest compared to the high precision value (black solid lines) and 1% and 10% deviations (dashed lines), respectively. Filled circles indicate $n = 1$, and open circles indicate $n > 1$. All ICP-MS analyses produced $^{235}U/^{238}U$ within 1% of the high precision value. In general, $^{234}U/^{238}U$ were within 10% of the high precision value. In some cases, results were biased high, likely due to molecular interferences that have an outsized impact on the ^{234}U due to relatively low count rates. However, the iCAP TQ analyses using the spray chamber with O_2 in the collision cell produced low-based $^{234}U/^{238}U$. Other than generally low count rates on the ^{234}U, the reasons for the low bias were not immediately clear. SQ = single quad; TQ = triple quad; IC = ion counter; MIC = multiple ion counting; SC = single collector.

nebulizer. In addition, the use of a desolvating nebulizer reduces oxide and hydride formation rates, which would decrease the impacts of some molecular interferences that form in the plasma (e.g., lead nitrides or oxides).[61]

Analyses of uranium isotopes as double oxides in "MS/MS" mode on the Neoma gave spurious results. The origins of these discrepancies are at least two-fold. The band-pass window of the double Wien filter of the Neoma MS/MS is trapezoidal[68,69] with much lower mass resolution compared to the quadrupole-based mass filters on the triple-quadrupole instruments. It is therefore unavoidable to pass thorium through the pre-filter along with the uranium isotopes. We hypothesize that the significant deviations from the high precision isotope ratios, especially in $^{234}U/^{238}U$, are partially the result of the formation of thorium oxide species that also contain additional hydrogen atoms (Fig. 3; additional mass scans are provided in the ESI file†).

Despite using the purest available oxygen gas (99.995% purity), introduction of oxygen into the collision cell raised background levels significantly in blank solutions. For example,

background count rates on ^{234}U were in some cases above 1000 cps, and over 100 cps on ^{235}U (see ESI file†). Typical background count rates are <10 cps for ^{235}U and <1 cps for ^{234}U when measured as metal ions without any gas in the collision cell. Furthermore, a sample with a ^{238}U count rate of 4×10^5 cps would give ^{234}U count rate of ~22 cps (assuming secular equilibrium), making the background issue with collision/reaction gases untenable. This suggests that even the high purity gases introduce additional impurities that make measurements of small ion beams on the ion counters problematic. These impurities (e.g., water) could also be causing the formation of the additional thorium species that cause large deviations in the measured isotope ratios.

4.3 Benefits of triple quadrupole ICPMS for uranium isotope analysis in unpurified digests

The primary benefit of the MC-ICP-MS is the ability to measure relatively high beam intensities simultaneously, allowing for
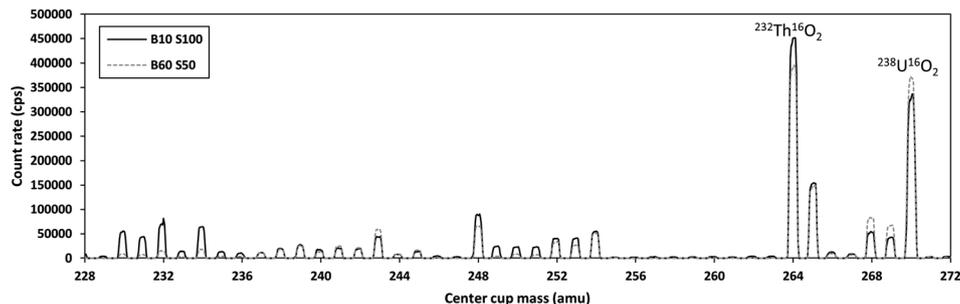
Fig. 3 Mass scan in the NIST SRM2780a digest (diluted to provide ~100 ppt U) from 228 amu to 272 amu with O_2 in the collision/reaction cell at a flow rate of 0.05 mL min^{-1}. Both the Th and U are converted to dominantly double oxide species. The solid black line labeled B10 S100 indicates a pre-filter magnetic field of 10% with the pre-filter slit 100% open. The dashed grey line labeled B60 S50 indicates a pre-filter magnetic field of 60% with the pre-filter slit 50% open. When the B field was set to 10%, the E field was approximately 40 volts. When the B field was set to 60%, the E field was approximately 240 volts. A reduction in beam intensities of the lower mass range (<236 amu) is achieved by changing the pre-filter settings. However, only slight changes are observed in the double oxide mass range of Th and U (>263 amu). Large interfering peaks on the minor uranium isotopes (^{234}U and ^{235}U) persist regardless of the pre-filter setting.

high precision isotopic analysis comparable to TIMS. Given the uncertainties, there is minimal benefit to measuring purified solutions at low concentrations using multiple ion counting on the MC-ICP-MS compared to analysis of unpurified solutions on any of the instruments used in this study. However, analyses of unpurified digests remains unsuitable when high precision is required.

Regardless of the mass spectrometer, precision generally improves when acquisition times are longer and sample consumption is higher. For example, the best precision achieved was using the iCAP equipped with the Aridus II in single quadrupole mode. However, precision of individual analyses across mass spectrometers was similar for ion-counter only measurements (data provided in the ESI file†). Nevertheless, data presented here indicate that triple quadrupole ICP-MS can provide accurate uranium isotopic results that can be acquired without purification, significantly reducing sample preparation time. This "early time" data can be used to enhance sample processing (*e.g.*, provide information for optimized sample/ spike ratios) when higher precision data are required. In addition, this type of analysis can be especially useful when rapid analysis is crucial, such as in emergency response situations. When rapid analyses are required, the analysis times can be minimized (in this case, analysis time per sample was as low as 90 seconds) while maintaining accuracy.

5. Conclusions

Here we presented uranium isotopic composition data measured in an unpurified digest solution of NIST SRM2780a by multi-ion counting ICP-MS (Neoma) and triple quadrupole ICP-MS (8900, iCAP). These data were compared to high precision uranium isotopic data measured in purified fractions by multi-collector ICP-MS (Neptune and Neoma). Results show that triple quadrupole ICP-MS can produce uranium isotopic compositions within 1% of the high precision value for the critical ^{235}U/^{238}U isotope ratio and ^{234}U/^{238}U generally within 10% of the high precision value. These results were generated using

several different conditions (desolvator *vs.* spray chamber, long *vs.* short acquisition times). There is no clear benefit to analyzing unpurified solutions using the multi-ion counting array of the Neoma compared to the iCAP or 8900. Analyses of uranium isotopes as double oxides on the Neoma MS/MS was problematic and requires additional development, potentially in the use of higher purity gases to reduce formation of oxy-hydroxide species. Analysis of uranium isotopes in unpurified solutions can provide a rapid assessment of isotopic composition and can be especially useful when samples are expected to contain an isotopic composition outside of the range of naturally occurring uranium.

Data availability

The data supporting this article have been included as part of the ESI.†

Conflicts of interest

There are no conflicts to declare.

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