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Rapid Determination of $^{235}U/^{238}U$ in Urine Using Q-ICP-MS by a Simple Dilute-and-Shoot Approach

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Abstract

The measurement of uranium (U) isotope ratios in urine provides valuable information about the source of U exposure in humans and can be vitally important in a radiological emergency. This method provides rapid and accurate results for $^{235}U/^{238}U$ at ^{235}U concentrations as low as 0.42 ng/L, which is equivalent to ~200 ng/L of total U for a depleted U (DU) at a $^{235}U/^{238}U$ ratio of ~0.002. The results are within 6% of Certified Reference Materials target values and agree with Department of Defense Armed Forces Institute of Pathology inter-laboratory comparison target values with a bias range of −6.9% to 7.6%.

Keywords

ICP-MS; total uranium; uranium isotope ratio; urine; emergency response

Introduction

Uranium (U) is a very dense metallic element. Three isotopes are naturally occurring: ^{238}U, ^{235}U, and ^{234}U. Other isotopes, such as ^{233}U and ^{236}U, are man-made. Enriched U (EU), which contains elevated levels of ^{235}U, is widely used by military, government, and civilian entities, and is of great public concern because of its widespread application to nuclear power and nuclear weapons [1]. U's availability also makes it an attractive target for terrorist entities to use in dirty bombs and improvised nuclear devices. Because of its presence on active and historical battlefields, both military and civilian personnel have been exposed to depleted U (DU).

The radiation exposure dose determines U's health impact and can be calculated based on the measured U isotope concentrations and biokinetic data, which describes U's biological

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Conflict of interest
The authors declare that they have no competing interest.

half-life and retention in the body. The primary U exposure pathways in humans are ingestion and inhalation. Within a few days of intake, U is mostly eliminated through feces, though a small part of it enters the blood and is excreted in urine [1–3]. Long-term exposure to a large enough amount of U leads to an increased risk of cancer, kidney damage, and liver damage [1, 3]. U can be found in urine for up to several months after exposure [2], and quantitative analysis of "total" U (based on a summation of ^{238}U and ^{235}U) excreted in urine is a common method to assess levels of exposure in humans. However, "total" U concentration provides insufficient information because given equal ^{238}U mass content, the dose from highly EU (~80% ^{235}U) is about 80 times the radiation dose from natural U. Therefore, to determine whether "total" U exceeds the pertinent limit, ^{235}U/^{238}U ratio is a better indicator for U exposure regarding health effects or risks.

Several techniques have been developed for determining U isotope ratios in environmental and biological samples [4–7]. Sector Field Inductively Coupled Mass Spectrometry (SF-ICP-MS) is a sensitive, multi-element mass spectrometry technique that also provides an efficient approach to monitoring U isotope ratios in complex, biological matrices [8–10]. Centers for Disease for Control and Prevention (CDC) has developed a SF-ICP-MS method for accurate determination of U isotope ratios (^{234}U/^{238}U, ^{235}U/^{238}U and ^{236}U/^{238}U) in urine at low total U concentrations [11]. Although this method provides the necessary sensitivity, selectivity, accuracy, and precision, the instrumentation is expensive and complicated to operate. Additionally, it requires time-consuming sample purification procedures involve expensive separation columns and large volumes of hazardous reagents. Therefore, using the SF-ICP-MS method for high-throughput screening in a radiological incident where thousands of individuals must be tested for total U levels may be problematic because of the lack of qualified staff to perform the method.

Q-ICP-MS, a highly selective and sensitive mass spectrometric technique has been applied for precise determination of isotopic compositions of long-lived radionuclides [12–16], including analysis of "total" U and ^{235}U/^{238}U ratio in environmental and biological samples. U mainly exists as ^{238}U (99.27%) and ^{235}U (0.72%) with an ^{235}U/^{238}U abundance ratio of 0.00726 in nature. DU used for military purposes from the U.S. stockpile has a constant ^{235}U/^{238}U isotopic ratio of 0.002 (% RSD < 9) [17].

The goal of this study was to validate a rapid, simple dilute-and-shoot method to determine ^{235}U/^{238}U in urine to address and respond to public health concern related to accidental, environmental, or terrorism-related exposures to U using the PerkinElmer® NexION® 300D Inductively Coupled Plasma Quadrupole Mass Spectrometer (Q-ICP-MS). Compared to previous ICP-MS platforms used (e.g., ELAN® ICP-MS), the NexION® 300D offers better sensitivity and stability along with minimal routine maintenance and cleaning. These factors are very important under extreme demand of high-sample throughput during an emergency response. Though the method on NexION® 300D is not designed to characterize ^{235}U/^{238}U ratios at normal U background level for non-occupationally exposed population, it can serve as a means of identifying people who require medical intervention due to acute U exposure.

In the presented method, patient samples with high measured "total" U concentration are prioritized for determination of the ^{235}U/^{238}U ratio and subsequent U internal dose assessment. From the National Health and Nutrition Examination Survey (NHANES) 1999–2000 trace metals data, the un-weighted, non-creatinine corrected 99th-percentile concentration of total U in urine is 277 ng/L. At concentrations higher than the 99th-percentile, the U isotope ratio $^{235}U/^{238}U$ should be measured. This ratio is important for assessing the radiation exposure dose because it is an indicator of exposure to non-natural isotopes of U. In Table 1, we demonstrate how changes in ^{235}U enrichment level affects the target method sensitivity for determining "total" U in urine.

The speed and simplicity of the presented method, which can easily measure both the $^{235}U/^{238}U$ ratio at "total" U levels greater than approximately 277 ng/L and ^{235}U concentrations as low as 0.55 ng/L at all enrichment levels, becomes the primary consideration in a radiological emergency response involving individuals with high "total" U exposure. In these scenarios, lower precision measurements and higher detection limits for the $^{235}U/^{238}U$ ratio are tolerable. A consequence of this consideration is that the method is unable to measure the $^{234}U/^{238}U$ ratio, which is acceptable since ^{234}U enrichment generally follows that of ^{235}U (^{234}U fractionates in the environment and large variations in the $^{234}U/^{238}U$ ratio can be observed in natural and biological samples). This method is not suitable for measuring the $^{236}U/^{238}U$ ratio, however the $^{235}U/^{238}U$ ratio gives sufficient information about the estimated internal exposure dose.

Experimental

Reagents and sample solutions

We used water deionized (DI) to a level of ≥18 mΩ·cm for all solutions (e.g., as produced by an Aqua Solutions Ultrapure Water System, Aqua Solutions, Inc., Jasper, GA). We prepared all diluent and rinse solutions using double distilled nitric (HNO_3) acid (GFS Chemicals Inc. Columbus, OH). In the rinse solution, we added Triton™ X-100 (Sigma Aldrich, St. Louis, MO), a non-ionic surfactant, which can reduce surface tension of aqueous and used for cleaning the sample introduction system. "Base urine" was collected through anonymous human donations (CDC IRB # 3994) with measured total urine U concentrations of less than 5 ng/L and acidified them to 1% v/v HNO_3. The diluent consists of 2% v/v HNO_3 in DI water. Sample introduction system rinse solution consists of 5% v/v HNO_3 and 0.002% Triton™ X-100 in DI water. This method uses 1 mL of urine sample (mix well before using without filtering). Prepared all samples as 1 mL of urine sample plus 9 mL of diluent, except the method blank (sample blank) which was prepared as 1 mL of DI water and 9 mL of diluent. Spiked serial dilutions of National Institute of Standards and Technology (NIST, Gaithersburg, MD, USA) traceable Pt, Pb, Tl, Hg, and Au single-element stock standards (Inorganic Ventures, Christiansburg, VA) into the urine samples to check if polyatomic interference was formed by using the simple dilute and shoot sample procedure and analyzing them on Q-ICP-MS.

Quality control (QC) materials

As listed in detail in Table 3, we prepared natural U QC solutions by spiking base urine with natural U standard, (High-Purity standard (HPS), North Charleston, SC) traceable to NIST. We prepared low $^{235}U/^{238}U$ ratio QC solutions by spiking base urine with dilutions of Certified Reference Materials (CRM) CRM NBL U005-A, NBL 115 (U.S. Department of Energy (DOE), New Brunswick Laboratory (NBL), Argonne, IL) and a mixture of equal amounts of HPS natural U and NBL U005-A, respectively. We prepared high $^{235}U/^{238}U$ ratio QC solutions by spiking base urine with dilutions of CRM NBL U015 and U150 (U.S. Department of Energy, New Brunswick Laboratory, Argonne, IL) and a mixture of equal amounts of natural U and NBL U015, respectively. Seven $^{235}U/^{238}U$ ratio levels at two different total U concentration levels of QC samples were prepared: low at ~400 ng/L and high at ~5 μg/L, for a total of fourteen pools. The QC materials were characterized 40 times during 20 analytical runs performed over the course of approximately 60 days. Lastly, the QC limits were determined for these materials.

Instrumentation

We used a PerkinElmer® NexION® 300D ICP-MS (PerkinElmer, Shelton, CT) coupled with an SC-4 DX autosampler (Elemental Scientific Inc., Omaha, NE) equipped with a Meinhard quartz nebulizer (Type TQ-30-A3), a quartz cyclonic spray chamber, a 2.0 mm I.D. quartz injector, and nickel sampler and skimmer cones in Standard Mode for all experiments. The instrument operated in single-ion mode with the settings and parameters optimized, detailed in Table 2.

Results and discussion

Interference

Interference and sensitivity problems persist with isotope analysis of U in urine on Q-ICP-MS both at very low total U concentrations and at “elevated” total U concentrations greater than 277 ng/L. The potential spectral interference for ^{235}U and ^{238}U measurement on ICP-MS are polyatomic overlap with $^{195}Pt^{40}Ar$, $^{197}Au^{38}Ar$, $^{199}Hg^{36}Ar$, $^{201}Hg^{34}S$, $^{202}Hg^{33}S$, $^{203}Tl^{32}S$, $^{204}Pb^{31}P$, $^{204}Hg^{31}P$, $^{198}Hg^{37}Cl$, $^{198}Pt^{37}Cl$, $^{200}Hg^{35}Cl$, and $^{198}Hg^{40}Ar$, $^{198}Pt^{40}Ar$, $^{200}Hg^{38}Ar$, $^{202}Hg^{36}Ar$, $^{204}Pb^{34}S$, $^{204}Hg^{34}S$, $^{205}Tl^{33}S$, $^{206}Pb^{32}S$, $^{207}Pb^{31}P$, $^{201}Hg^{37}Cl$, $^{203}Tl^{35}Cl$. These potential polyatomic interferences were investigated through a series of spiking experiments. Hg, Pb, Tl, and Pt were spiked in base urine at concentrations of 5.0 μg/L, 5.0 μg/L, 1.0 μg/L, and 0.5 μg/L, respectively, and did not result in any observable signal increase at mass 235 or 238. We used spiked concentrations significantly above the NHANES 95th percentile of urine Hg, Pb, Tl, and Pt concentrations [18]. No NHANES survey data is accessible for Au, so analysis of a high concentration of Au (5.0 μg/L) [19] was performed and did not yield any visible signal increase on mass 235 or 238. Urine matrix might cause overestimated ^{235}U abundance when using simple dilution on ICP-MS [20, 21]. Reinhard et al., further investigated urine matrix effect and found that organic metabolites in urine form interferences on mass 235, which can create large discrepancies in $^{235}U/^{238}U$ measurement for a number of urine samples on ICP-MS with total U concentrations as high as ~1 ug/L, when only simple diluted vs when U is chemically separated [22]. In some contexts, urine matrix effects will cause a larger than expected bias.

Accuracy and Precision

Method accuracy was evaluated by analyzing diluted urine spiked with CRM solutions from the U.S. DOE NBL and a U standard from HPS traceable to NIST, prepared as bench QC materials for this method. Analysis of two concentration levels of these urine-based bench QC materials (each concentration level had seven ratio levels of $^{235}U/^{238}U$) at the beginning and again at the end of each analytical run. Table 3 shows the method produced agreement for $^{235}U/^{238}U$ with target values for the CRMs provided by the U.S. DOE NBL and HPS, with an analytical bias from 0.16% to 1.66 %. An outlier is the measurement of NBL115 at the low concentration of ~400 ng/L spiked urine sample, where the bias was 5.91%. The increased $^{235}U/^{238}U$ result for the NBL115 urine sample at a low total U concentration via ICP-MS analysis could be the result of the presence of native natural U in the base urine (pooled base urine used for spiking was analyzed for its ^{235}U and ^{238}U content [23]) thus increasing the sample $^{235}U/^{238}U$ ratio versus the $^{235}U/^{238}U$ ratio for this DU spike. Baseline of pooled urine was not corrected as laboratory preference, we use aqueous as sample blank to determine the "real" $^{235}U/^{238}U$ ratio for the patient specimen, and those spiked QC samples need to be handled and analyzed in the same way as patient samples, and this might account for some observed bias for QC samples. For most of the data, the analytical uncertainties (2SD) on Q-ICP-MS are larger than the reported bias leading to the conclusion that the data are accurate, but not precise. The low abundance of ^{235}U in the urine sample also attributed to poorer precision and bias due to the low count signal (~30 cps per ng/L for U) via Q-ICP-MS. Table 3 shows the typical run-to-run precision observed on this Q-ICP-MS method, with the coefficient of variation (% CV) ranged from 1.10% to 5.12% for low concentration QC materials, 0.82% to 1.26% for high concentration QC materials. On the other hand, the % CV for SF-ICP-MS method [11] ranged from 0.79% to 4.67%.

Low-level U Cutoff Concentration Determination

The 5-day Children or Pregnant Women Clinical Decision Guide (C/P CDG) is CDC's primary target level for the sensitivity of its radioanalytical methods. In National Council for Radiation Protection NCRP #161 [24], one CDG level is described as an acute radiation exposure dose which results in a significantly increased lifetime (50-y in adults and 70-y in fetuses and children) risk for stochastic health effects including tumors, genetic effects, and cancers. In an emergency scenario and for the purpose of method development and validation, we assume "spot" (~30 mL) urine will be collected from patients with suspected internal contamination within 5 days post-exposure.

Obtaining accurate results for all CDG level total U ratio combinations is critical. To report accurate ratios (within 15% of the target values required by CDC), we must have accurate, quantitative results for both isotopes. Because this method is generally intended for determination of $^{235}U/^{238}U$ ratio in samples with relatively high (> 277 ng/L) total U content, and because the ratios are of concern across a defined, detectable range of ~0.002–0.95 for $^{235}U/^{238}U$, accurate determination of ^{235}U content (especially at low $^{235}U/^{238}U$ ratios and total U concentration) is important. Figure 1 illustrates the standard deviation as a function of ^{235}U concentration for low concentration (~400 ng/L of total U) and high concentration (~5 μg/L of "total" U) QC materials, expressed by simple linear correction fit along with the determined intercept and slope. Each data point stands for the average of results from 40 analyses. To determine an accuracy requirement for a low ^{235}U level, we used a level of 10 times the standard deviation of the intercept at zero ^{235}U concentration (based on the Low QC plot in Figure 1), which produced an appropriate low-level cutoff concentration for the method [25]. We determined the value to be 0.42 ng/L, much lower than the C/P CDG level of ^{235}U (10.2 ng/L, calculated based on the natural U $^{235}U/^{238}U$ of 0.00726), and equivalent to ~200 ng/L of total U for a DU sample at a ratio of ~0.002, well below our 277 ng/L “elevated” level that calls for performing the U isotope ratio analysis.

Internal Method Comparison

To compare the method described here with CDC’s current SF-ICP-MS method, we used both to analyze the same set of QC samples for $^{235}U/^{238}U$. For the method using SF-ICP-MS, we targeted the concentrations of the QC samples, per the procedure described in [11]. The observed results from both methods showed good agreement with the CRM target values (Table 3) as demonstrated by the acceptable accuracy. Compared to other QC samples, both methods showed increased bias for $^{235}U/^{238}U$ results when U concentration decrease as shown by the biases of 5.41% and 5.91% of NBL115 spiked urine samples containing ~200 ng/L and ~400 ng/L U, respectively. On the other hand, Q-ICP-MS measurement of NBL115 spiked urine sample containing high U concentration showed a smaller bias of 1.48%. The native natural U content in the blank urine (base urine) will affect the $^{235}U/^{238}U$ ratio in low QC concentration spikes more than in high concentration QC spikes. The measurable ^{235}U contributed by the native natural U present in blank urine could explain the high positive bias at low concentrations for depleted NBL115 urine spikes. Table 3 shows that most of the reported bias for the QC materials analyzed on the Q-ICP-MS are slightly more positive than that of the SF-ICP-MS. There are possible causes: an under-correction of the method blank applied to all sample analyses on the Q-ICP-MS, the samples on the Q-ICP-MS not being digested and separated as they are on the SF-ICP-MS and existing possible interference from organic components in urine, lacking mass bias correction to eliminate isotope fractionation effect on Q-ICP-MS and native natural U content of the urine blank (base urine used for spikes) causes observable positive bias for depleted urine spikes and negative bias for enriched urine spikes at low concentrations.

Analysis of samples from the Armed Forces Institute of Pathology (AFIP)

As part of our inter-laboratory collaboration with AFIP on U, the CDC’s Inorganic and Radiation Analytical Toxicology Branch (IRATB) regularly analyzes samples from AFIP as part of the Veterans Administration (VA) DU monitoring program. In this work, we analyzed a set of AFIP samples for $^{235}U/^{238}U$ ratio using both the presented Q-ICP-MS method described here and the SF-ICP-MS method previously described [11]. A correlation plot (Figure 2) of the results from the two methods showed a linear regression with an R^2 of 0.967 (though the DU samples had a narrow $^{235}U/^{238}U$ range, from 0.00204 to 0.00335), which shows good agreement between methods. We also compared the reported results with the AFIP target values. Table 4 shows that over a wide total U concentration range from 0.199 μg/L to 30.6 μg/L (concentrations were determined by using “urine multi-element” in urine on ICP-MS method (DLS 3018) at CDC), the Q-ICP-MS method produced results for $^{235}U/^{238}U$ close to the AFIP target values with an analytical bias from −6.9 % to 7.6 %, though the reported results showed larger standard deviation (especially for urine samples with total U < 0.5 μg/L) than those of SF-ICP-MS method. Even at a total U concentration as low as 0.199 µg/L (depleted U with a $^{235}U/^{238}U$ ratio of ~0.003), the bias of this method was −3.4%, which is better than the bias of −5.1% observed for the method using SF-ICP-MS. However, for all data, the bias on Q-ICP-MS that we report are within 2SD of the analytical uncertainty, though the data are accurate, they are not precise.

Sample throughput

While maintaining high quality results, sample throughput is one of the important considerations in a radiological emergency. This method utilizes a simple dilute-and-shoot sample preparation procedure with minimal reagent, instrument, and personnel training requirements, resulting in a daily throughput of approximately 100 samples per instrument in a 24-hour period. The scalability of the method allows us to surge capacity during a true emergency by using existing Q-ICP-MS instrumentation used in different stable element methods.

Conclusions

We have validated a method for rapid and accurate analysis of $^{235}U/^{238}U$ in urine on a PerkinElmer® NexION® 300D Q-ICP-MS as an alternative to our SF-ICP-MS method for use in emergency response events. This method allows the analysis of $^{235}U/^{238}U$ ratio changes over a broad range of total U concentrations by a simple dilution approach that provides high sample throughput. The analytical method produced good agreement with target values for spiked urine CRM samples, with a bias range of 0.16% to 5.91%. Results obtained using this method for AFIP reference materials had a bias range of −6.9% to 7.6%. The data we present are accurate. The precision of this method is not as good as the SF-ICP-MS method, however, precision is fit for rapid emergence response.

This Q-ICP-MS-based method is simpler and faster than our SF-ICP-MS based method, with high analytical uncertainty using only 1 mL of urine (around 2 mL for the SF-ICP-MS method).

The procedure is appropriate for rapid identification and quantification of $^{235}U/^{238}U$ in urine, it can be used for emergency response involving accidental or terrorism-related elevated U exposures or for evaluating chronic environmental or occupational U exposures.

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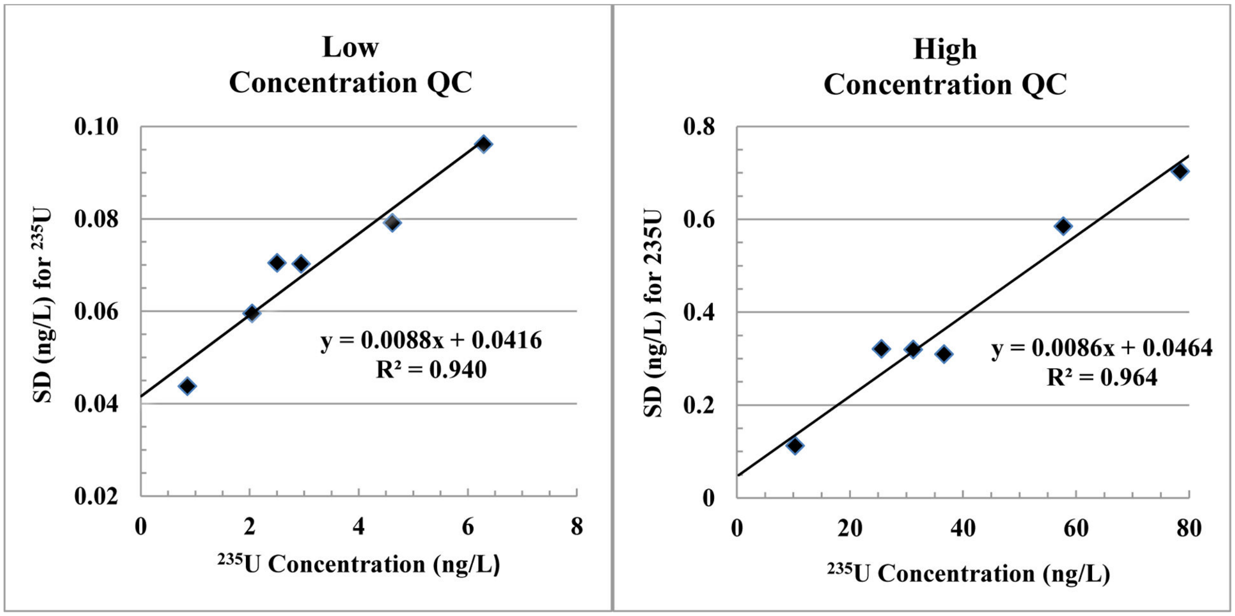

Figure 1.

Low-level U cutoff concentration calculation from determination of the intercept and slope by simple linear correlation for both low and high QC materials

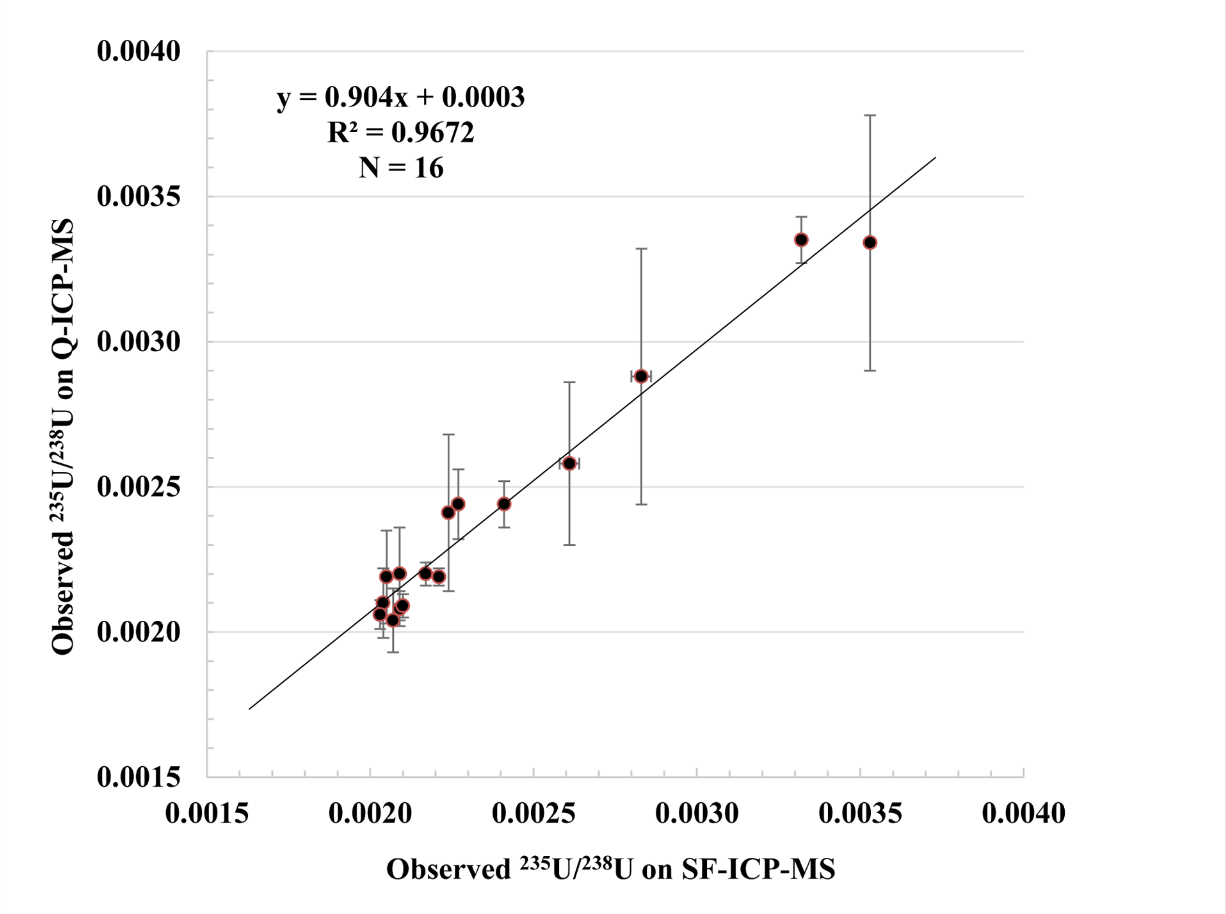

Figure 2.

Method Comparison on Q-ICP-MS and SF-ICP-MS (AFIP samples)

Table 1.

Comparison of 1 C/P CDG 5-day urine concentration of Total U associated with contamination from U at two different enrichment levels

Contamination Source	**Total U Concentration in Urine Corresponds to Total U Activity for 1 C/P CDG at day 5 (ng/L)**
20% EU	255
95% EU	54

Table 2.

Instrument parameters for the PerkinElmer NexION 300D Q-ICP-MS.

RF Power	1.60 kW
Plasma Gas Flow (Ar)	18 L min^{-1}
Auxiliary Gas Flow (Ar)	1.2 L min^{-1}
Nebulizer Gas Flow (Ar)	~ 0.85 – 1.05 L min^{-1}
Detector	Single Channel Electron Multiplier, pulse mode
Pulse Stage Voltage	1100 V
Method Parameters	
Sweeps/Reading	10
Readings/Replicate	1
Replicates	10
Dwell Times	3000 ms for ^{235}U & ^{238}U
Scan Mode	Peak Hopping
RPq	0.25
Dead Time	35 ns
Sample Uptake Rate	0.8 mL min^{-1}
Sample Flush Time	35 s
Speed	−24 rpm
Read Delay Time	15 s
Speed	−18 rpm
Analysis	−18 rpm
Wash Time	90 s
Speed	−24 rpm
Sample Preparation	1:10 dilution in 2% HNO_3

Table 3.

Observed $^{235}U/^{238}U$ accuracy and precision for internal QC materials (N=40)

	CRM T.V. $^{235}U/^{238}U$	**Observed on SF-ICP-MS[d] $^{235}U/^{238}U$**				**Low Conc. Spike (~400 ng/L) $^{235}U/^{238}U$ (Q-ICP-MS)**				**High Conc. Spike (~5 μg/L) $^{235}U/^{238}U$ (Q-ICP-MS)**			
		Average	**1SD**	**Bias(%)**	**%CV**	**Average**	**1SD**	**Bias(%)**	**%CV**	**Average**	**1SD**	**Bias(%)**	**%CV**
NBL115 [a]	0.00203	0.00214	0.00010	5.41	4.67	0.00215	0.00011	5.91	5.12	0.00206	0.00002	1.48	0.97
NBL U005-A [a]	0.00509	0.00512	0.00009	0.59	1.76	0.00512	0.00015	0.59	2.93	0.00513	0.00006	0.79	1.17
NBL U005-A + NU [b]	0.00617	0.00616	0.00008	−0.16	1.30	0.00627	0.00018	1.62	2.87	0.00624	0.00006	1.13	0.96
Natural Uranium [c]	0.00725	0.00727	0.00012	0.28	1.65	0.00737	0.00018	1.66	2.44	0.00734	0.00006	1.24	0.82
NU + NBL U015 [b]	0.0114	0.0114	0.00015	−0.44	1.32	0.0116	0.00020	1.23	1.72	0.0116	0.00012	1.23	1.03
NBL U015 [a]	0.0156	0.0155	0.00028	−0.25	1.81	0.0157	0.00024	1.09	1.53	0.0157	0.00014	0.90	0.89
NBL U150 [a]	0.181	0.177	0.0014	−2.03	0.79	0.181	0.0020	0.16	1.10	0.182	0.0023	0.76	1.26

[a] Internal QC materials made at CDC by spiking CRMs into pooled urine collected anonymously.

[b] Internal QC materials made at CDC by spiking equal mixture of natural uranium standard and CRMs into pooled urine collected anonymously.

[c] Internal QC materials made at CDC by spiking natural uranium standard into pooled urine collected

[d] All materials were prepared at ~200 ng/L [11], except NBLU150, which was prepared at 20 ng/L.

Table 4.

Comparison of CDC results with AFIP target values (T.V.)

Sample ID	Observed Total Uranium Conc. in CDC (μg/L)	AFIP Results $^{235}U/^{238}U$		On SF-ICP-MS $^{235}U/^{238}U$		Bias (%)	On Q-ICP-MS $^{235}U/^{238}U$		Bias (%)
		T.V.	1SD	Observed[a]	1SD		Observed[b]	1SD	
09-116-0002	2.91	0.00327	0.00000	0.00332	0.00001	1.5	0.00335	0.00008	2.4
09-116-0004	0.224	0.00271	0.00001	0.00261	0.00003	−3.8	0.00258	0.00028	−4.8
09-116-0006	30.6	0.00216	0.00001	0.00221	0.00001	2.4	0.00219	0.00003	1.4
09-116-0007	2.24	0.00200	0.00002	0.00207	0.00000	3.4	0.00204	0.00011	2.0
09-116-0008	0.945	0.00207	0.00000	0.00205	0.00000	−0.6	0.00219	0.00016	6.0
09-116-0009	0.877	0.00227	0.00003	0.00227	0.00001	0.2	0.00244	0.00012	7.6
09-116-0013	1.21	0.00213	0.00008	0.00204	0.00001	−4.3	0.00210	0.00012	−1.4
09-116-0015	4.97	0.00204	0.00000	0.00203	0.00000	−0.5	0.00206	0.00005	0.8
09-116-0023	0.462	0.00228	0.00001	0.00224	0.00000	−1.8	0.00241	0.00027	5.7
09-116-0025	4.13	0.00208	0.00003	0.00209	0.00001	0.3	0.00208	0.00006	−0.2
09-116-0026	3.78	0.00244	0.00006	0.00241	0.00001	−1.1	0.00244	0.00008	0.0
09-116-0027	0.199	0.00298	0.00012	0.00283	0.00003	−5.1	0.00288	0.00044	−3.4
09-116-0028	4.28	0.00221	0.00004	0.00217	0.00000	−2.2	0.00220	0.00004	−0.6
09-116-0029	12.7	0.00210	0.00002	0.00210	0.00000	−0.1	0.00209	0.00004	−0.6
09-116-0031	0.347	0.00359	0.00021	0.00353	0.00000	−1.5	0.00334	0.00044	−6.9
09-116-0040	0.997	0.00222	0.00005	0.00209	0.00001	−5.9	0.00220	0.00016	−0.7

[a] Samples were diluted to ~200 ng/L if Total Uranium > 300 ng/L before purified using TRU columns as described previously [11].

[b] All samples were simply diluted to 1 to 10 by diluent before loading on Q-ICP-MS.