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Determination of $^{234}U/^{238}U$, $^{235}U/^{238}U$ and $^{236}U/^{238}U$ Isotope Ratios in Urine Using Sector Field Inductively Coupled Plasma Mass Spectrometry (SF-ICP-MS)

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Abstract

Quantification of the isotopic composition of uranium in urine at low levels of concentration is important for assessing both military and civilian populations' exposures to uranium. However, until now there has been no convenient, precise method established for rapid determination of multiple uranium isotope ratios. Here we report a new method to measure $^{234}U/^{238}U$, $^{235}U/^{238}U$ and $^{236}U/^{238}U$. It uses solid phase chelation extraction (via TRU columns) of actinides from the urine matrix, followed by measurement using a magnetic sector field inductively coupled plasma mass spectrometer (SF-ICP-MS - Thermo Element XR) equipped with a high efficiency nebulizer (Apex PFA microflow) and coupled with a membrane desolvating introduction system (Aridus II™). This method provides rapid and reliable results, and has been used successfully to analyze Certified Reference Materials (CRM).

Introduction

Uranium is a radioactive element naturally present in the environment from very low to high concentrations. CDC's National Health and Nutrition Examination Survey (NHANES) has historically monitored exposure of the US population to uranium through measurements of total uranium in urine using inductively coupled plasma mass spectrometry (ICP-MS).[1, 2]

Various studies indicate that military personnel who were exposed to aerosols of depleted uranium (DU) exhibit no clinically significant uranium related health effects.[3–5] However, the epidemiology community needs further experimental data to evaluate and assess the adverse health effects after chronic exposure to DU, because long-term effects that might result in cancer and birth defects remain unknown,[6, 7] and because of increased possibility of military and civilian personnel being exposed to DU and enriched uranium (EU) during military conflicts and radiological/nuclear terrorist attacks. Because of differences in analytical sensitivities for, and specific activities of, the various isotopes of uranium, monitoring total urine uranium concentrations, though a powerful biological indicator for uranium exposure, is not sufficient. Therefore, if total uranium concentration exceeds the pertinent limit, the need to more closely monitor radiological contamination of these people

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requires isotopic analyses. For reference, the unweighted, non-creatinine corrected 95th percentile concentration of total uranium in urine from the NHANES 2009–2010 cycle is 0.036 μg/L,[1] and the Nuclear Regulatory Commission recommends intervention if a uranium worker has a urine uranium concentration greater than 15 μg/L.[8]

Measurable individual levels of uranium reflect sums of recent and accumulated exposures, including those from various sources of natural uranium (NU), and possibly from DU and EU exposures. Urine uranium analysis is the least invasive approach to assess such exposures. EU is a critical component of the fuel in many nuclear reactors and nuclear weapons. It is a class of uranium in which the percent composition of ^{235}U is enriched to within the range of 0.9% to 85% or more through the process of isotope separation. DU, on the other hand, is a by-product of this enrichment process. The DU used for military purposes has a rather constant ^{235}U/^{238}U isotopic ratio of 0.002, compared to 0.00725 for natural uranium, and a ^{234}U/^{238}U isotopic ratio of 0.00001, compared to 0.000055 for natural uranium. The presence of ^{236}U in DU or EU is not universal; it may be introduced into the manufacturing process by recycling of spent fuel from plutonium production. Depending on manufacturing history, ^{236}U could be an indicator of the presence of DU or EU, but it should not generally be used for this purpose.[14] In any case, the DU used by U.S. Forces shows a rather constant ^{236}U/^{238}U isotopic ratio of 0.00003, compared to $< 10^{-10}$ for natural uranium.[9–13]

Several advanced instrumental techniques are available for isotope ratio measurements. Geological scientists consider Thermal Ionization Mass Spectroscopy (TIMS) and Multi-Collector (MC) ICP-MS to be the ultimate tools for U isotope ratios determination since they provide the most precise results.[15–18] Health physics' lower precision measurement requirements make SF-ICP-MS the standard accepted method for uranium isotope ratios analysis in this discipline.[17,18] SF-ICP-MS is a sensitive, multi-element technique that provides an efficient approach to biomonitoring multiple metals in complex, large scale biological matrices. However, significant challenges, including polyatomic interferences, matrix effects and low sensitivity for ultra-low concentrations are common for urine uranium isotope ratio analyses by SF-ICP-MS.[19, 20] CDC has published methods designed to address some of these problems and improve urine uranium isotope ratio (for ^{235}U/^{238}U) analysis accuracy at low concentrations in urine.[20, 21] However, rapid and reliable determination of ^{234}U/^{238}U and ^{236}U/^{238}U in urine samples still remains challenging, as the ^{234}U and ^{236}U isotopes have very low abundance relative to ^{235}U and ^{238}U.

This study aimed to develop, characterize and validate a new SF-ICP-MS method for uranium isotope ratio analysis to achieve rapid and accurate quantification of uranium isotope ratios of ^{234}U/^{238}U, ^{235}U/^{238}U and ^{236}U/^{238}U in one practical method.

Experimental

Reagents and solutions

Prepare all nitric (HNO_3) and hydrofluoric (HF) acid solutions from double distilled acids (GFS Chemicals Inc. Columbus, OH). Use water deionized to ≥18 mΩ·cm for all solutions (e.g., as produced by an Aqua Solutions Ultrapure Water System - Aqua Solutions, Inc.,

Jasper, GA). Collect contributions for base urine pools from healthy volunteers with measured total urine uranium concentrations of < 5 ng /L, and acidify them to 1% v/v HNO_3. Prepare natural uranium QC solutions by spiking base urine with dilutions of a uranium standard, (SPEX Industries, Inc., Edison, NJ) traceable to the National Institute of Standards and Technology (NIST, Gaithersburg, MD, USA). Prepare aqueous CRM solutions by dissolution of uranium oxide CRMs in powder or pellet form.[22] Prepare low uranium ratio QC solutions by spiking base urine with dilutions of CRM NBL U005-A, NBL 115 (U.S. Department of Energy, New Brunswick Laboratory, Argonne, IL) and a mixture of natural uranium and NBL U005-A. Prepare high uranium ratio QC solutions by spiking base urine with dilutions of CRM NBL U015 (U.S. Department of Energy, New Brunswick Laboratory, Argonne, IL) and mixture of natural uranium and NBL U015.

Sample preparation

The optimum urine sample volume is 2 mL unless the total uranium concentration is greater than 300 ng/L or less than 100 ng/L. For samples with uranium concentrations higher than 300 ng/L, use 1 mL (or less, depending on the uranium concentration) of the sample, diluted to ~ 200 ng/L for analysis. Use 4 mL or more of the sample, as appropriate, if the total uranium concentration is less than 100 ng/L. Acidify urine sample by adding 375 μL concentrated HNO_3 per mL of (diluted, if appropriate) urine sample using 4 mL polystyrene sample cups (VMR, Suwanee, GA) prewashed with 5% v/v HNO_3. Pour the contents into individual 0.22g TRU resin (Eichrom, Darien, IL) solid phase extraction columns, previously washed extensively with ≥18 mΩ·cm water , 10% v/v HNO_3 (30 mL) and 5% v/v HF (30 mL × 2) and equilibrated with 10% v/v HNO_3 (5 – 6 mL). Next wash each column with two to five mL 10% v/v HNO_3, pouring each wash through the column, followed by two 5 mL 10% v/v HNO_3 column washes to force unretained ions through each column. Elute the uranium from the samples into acid-cleaned 4 mL polystyrene conical bottom sample cups (Thermo-Fisher Scientific, Suwanee, GA) with 2 mL 5% v/v HF, or proportionately higher volumes for dilution purposes. The reagent blank for this method is 5% v/v HF (Figure 1).

Instrumentation

This method measures Uranium isotope ratios using an extended dynamic range high resolution ICP-MS model Element XR (Thermo Fisher Scientific, Bremen, Germany), which is a double focusing magnetic sector field inductively-coupled-plasma mass spectrometer with a high performance, discrete dynode, dual mode secondary electron multiplier detector and a high current (for percent level content) faraday detector (Mascom, Bremen, Germany). It uses the ICP-MS, equipped with nickel sampler and skimmer cones and a CD-2 guard electrode, in triple mode. The sample introduction system consists of a computer controlled ASX-112 (Cetac, Omaha, NE) autosampler and Aridus II™ (Cetac, Omaha, NE) desolvation unit. Samples self-aspirate from the autosampler into the desolvation unit through an Apex perfluoroalkoxy (PFA) 100 μL/minute nebulizer (ESI, Omaha, NE, or equivalent). Sample desolvation occurs within the AridusII™ unit in a PFA spray chamber (Cetac, Omaha, NE) set at 110 °C. With the aid of argon sweep gas and nitrogen gas for sensitivity enhancement, the sample passes through a semi-permeable membrane coil set at 160°C. Optimize flow rates as needed, with argon sweep gas at ~ 2–7

L/min and nitrogen gas at ~ 3–9 mL/min. The desolvated sample exits the desolvating unit into a 1.8 mm I.D. sapphire injector and a standard quartz torch, and then into the mass spectrometer.

Optimization of the SF-ICP-MS measurement procedure

Some method parameters are crucial for the precision of uranium isotope ratios determination by SF-ICP-MS. Table 1 reflects optimized method parameters, including numbers of method passes, runs and samples based on the precision of the measurement of uranium isotope ratios. Further, the method requires the performance of individual run experimental parameter optimizations with respect to maximum ion intensity of ^{238}U and minimum uranium oxide formation rate using a tuning solution containing natural uranium. Table 1 also contains summary examples of these optimized operating conditions.

Results and discussion

Sample recovery

The sample separation protocol uses solid phase chelation extraction (SPE), with TRU columns for separation of the actinides from the urine matrix, which is a modification of previously published methods for determination of uranium isotope ratios in urine.[20, 21, 23] Because the Aridus II™ demonstrates exceptional signal stability, and in order to avoid introduction of interference or contamination into the samples, this method uses no tracer (or internal standard). SPE separation recovery is evaluated by analyzing the spiked internal quality control material both before and after running the sample material through the columns. The recoveries are acceptable, at approximately 90% to 104%. We use a 5% v/v HF solution as the reagent and instrument blank for this method since it is the sample matrix introduced to the ICP/MS, and the results obtained for blank samples (2 mL of water), which underwent exactly the same chemical separation procedure as the urine samples, showed very similar cps to 5% v/v HF.

Improvement in sensitivity using the Aridus II™

Sensitivity requirements for ^{234}U and ^{236}U are extremely stringent, and this limits the utility of SF-ICP-MS measurements. In order to determine possible improvement of instrumental sensitivity by use of an Aridus II™, we analyzed a 5 ng/L tuning solution which contained natural uranium. The Aridus II™ sensitivity for uranium is approximately 10 times higher than that of a Meinhard® quartz nebulizer (Type TQ-30–43) and the quartz cyclonic spray chamber (~3.0×10^5 cps/ppt versus 3.0×10^4 cps/(ng/L). The acid trap bottle (1M NaOH), connected to the sweep gas output line of the Aridus II™, affects the back pressure of the instrument's introduction system, and has a significant effect on instrument sensitivity. The position of this gas line under the surface of the NaOH solution is very important and must be checked/optimized for best instrument performance.

SEM "Triple" mode used

Previous CDC methods, [20, 21] in which the target ^{238}U eluent concentration from the TRU column is ~ 40 ng/L, use one detection mode (Secondary Electron Multiplier, or SEM, in counting mode) for the $^{235}U/^{238}U$ isotope ratio measurement.[20, 21] For this method, we

increased the target ^{238}U eluent concentration from the TRU column to ~200 ng/L because of the extremely different isotopic abundances among ^{234}U, ^{235}U, ^{236}U, and ^{238}U. Thus, the "counting mode only" method, with its limited dynamic range, is no longer practical. This method uses the "Triple" mode, where both SEM Counting and Analog detection modes are used, to perform the analysis. Counting mode is used for the low abundance ^{234}U, ^{235}U and ^{236}U isotopes and analog mode is used for ^{238}U. It is important to run a short, separate method before each batch of analysis with ^{238}U at about 2 to 4 million cps in "Triple" mode for >10 scans, which updates the analog conversion factor (ACF), i.e., the factor between SEM counting and analog detection modes (for cross calibration between modes). Optimal samples per peak for this method is 600, and 1% of the Mass Window (see Table1) is used to avoid continuous automatic ACF updates for all analyses.

Abundance sensitivity correction

The abundance sensitivity of the instrument is critically important for the $^{236}U/^{238}U$ measurement since ^{236}U is present only in very small proportion relative to ^{238}U. The abundance sensitivity during the experiments was 2.3×10^{-6}, which was calculated by averaging the measured $^{236}U/^{238}U$ ratio of the spiked natural uranium internal quality control material during the QC characterization of this method. $^{236}U/^{238}U$ ratio results for all samples in this method are mathematically corrected for abundance sensitivity.

The contribution of ^{235}UH to the ^{236}U signal

The Aridus II™ desolvating system reduces the contribution of $^{235}U^{1}H$ to the ^{236}U signal. We used the signal at mass $M = 239$ (due to $^{238}U^{1}H^{+}$) to estimate the significance of any remaining $^{235}U^{1}H^{+}$ contribution to the ^{236}U signal at mass $M = 236$. Our experiments showed that this hydride contribution to the $^{239}U/^{238}U$ signal, with an average value of 1.2×10^{-5}, is equivalent to $< 1 \times 10^{-7}$ for the analytically more important $^{236}U/^{238}U$ ratio, and can therefore be ignored for this method.

Linearity range

CDC's procedures require investigation of the uranium isotope ratios in patient urine samples when the study protocol calls for it, or if a urine specimen is determined to have an 'elevated' total uranium concentration. For this method, based on the known ^{238}U concentration in the urine sample determined by the other available methods, the volume of urine sample loading on the TRU column is determined to target the uranium concentration of the column eluent at approximately 200 ng/L (as is, diluted or pre-concentrated). Thus, the linearity range requirement is not critical as long as the total U concentration is < 300 ng/L. However, we tested the linearity range using aqueous solutions of CRM NBL U005-A, with total uranium concentrations ranging from 5 ng/L to 400 ng/L, and calculated the corresponding concentrations of ^{234}U, ^{235}U, ^{236}U and ^{238}U based on the certified uranium isotope ratios of NBL U005-A for comparison. The results are summarized in Figure 2.

Precision and accuracy

We performed analyses of aqueous CRM solutions from the U. S. Department of Energy's New Brunswick Laboratory, and the observed uranium isotope ratios were in good

agreement with the certified values. Table 2 shows this, along with the typical precision observed at low, medium and high ratios of daily quality control materials that were analyzed at the beginning, in the middle and at the end of each analytical run.

Limit of Detection

The method was best optimized for a total uranium concentration between 100 ng/L and 300 ng/L. Limit of detection (LOD) determination is not critical for this method since it is generally intended for ratio determination in samples with relatively high (> ~200 ng/L) total uranium content, and because ratios present are of concern across a defined, detectable range (~0.2–95% for $^{235}U/^{238}U$). However, in order to confirm the concentration range for which reliable uranium isotope ratios may be determined, we prepared three urine pools with lower concentrations (spiked with CRM NBL U005-A, at 50 ng/L, 100 ng/L and 150 ng/L of total uranium) than that of the target total uranium concentration (200 ng/L) and analyzed these samples during the internal quality control materials' characterization procedure. Analyses at all of these concentration levels showed good precision. However, samples with a total uranium concentration of < 100 ng/L (~3.54 pg/L of ^{234}U, and ~1.18 pg/L of ^{236}U) had a trend of increased ratio RSD and might therefore require more volume for pre-concentration. Samples with uranium concentrations > 300 ng/L may be pre-diluted with 1 mL of 5% v/v HNO_3 or less to 200 ng/L, depending on uranium concentration (Figure 3).

Conclusions

We have successfully developed a method for determining uranium isotope ratios of $^{234}U/^{238}U$, $^{235}U/^{238}U$ and $^{236}U/^{238}U$ in urine using solid phase chelation extraction and a high sensitivity sample introduction system, coupled with a SF-ICP-MS. This approach is a rapid and sensitive method for analyzing uranium isotope ratios at low levels in people.

The Triple mode (SEM) method used here allows measurement of low and high ion signals at the same time, thereby facilitating accurate measurement of isotopic signature ratios of NU, DU and EU for the low abundance isotopes (e.g., $^{234}U/^{238}U$, $^{235}U/^{238}U$ and $^{236}U/^{238}U$) simultaneously in one analytical method.

A significant advantage of this method is that the volume of a urine sample loaded on the TRU column can be adjusted, based on the sample's known uranium concentration, to reach the target uranium eluent concentration of ~ 200 ng/L. The analysis requires only 2 mL of urine sample that has a total uranium concentration of ~100 ng/L to ~300 ng/L.

As can be seen in Table 2, the method produced good agreement for different uranium isotopes with target values for the CRMs provided by the U.S. Department of Energy's New Brunswick Laboratory. Except for $^{234}U/^{238}U$ of NBL115 spiked urine sample, bias was lower than 5.4% in all cases. The increased $^{234}U/^{238}U$ result for NBL115 urine sample might be caused by the uranium transferred by the difference between the spiked uranium concentration and the natural uranium content existed in the base urine. The very low abundance of ^{234}U in the urine sample also attribute to a high bias, due to the low count signal.

Although the method's efficient uranium separation scheme effectively eliminates most molecular ion sources of interference, the instrument's systematic abundance sensitivity error for measuring the $^{236}U/^{238}U$ isotope ratio must be mathematically corrected.

This procedure may be used for rapid and accurate identification and quantification of uranium isotopes in urine when people are suspected of having been exposed to depleted or enriched *vs.* environmental (natural) uranium, or for evaluating chronic environmental exposure or other non-occupational exposures.

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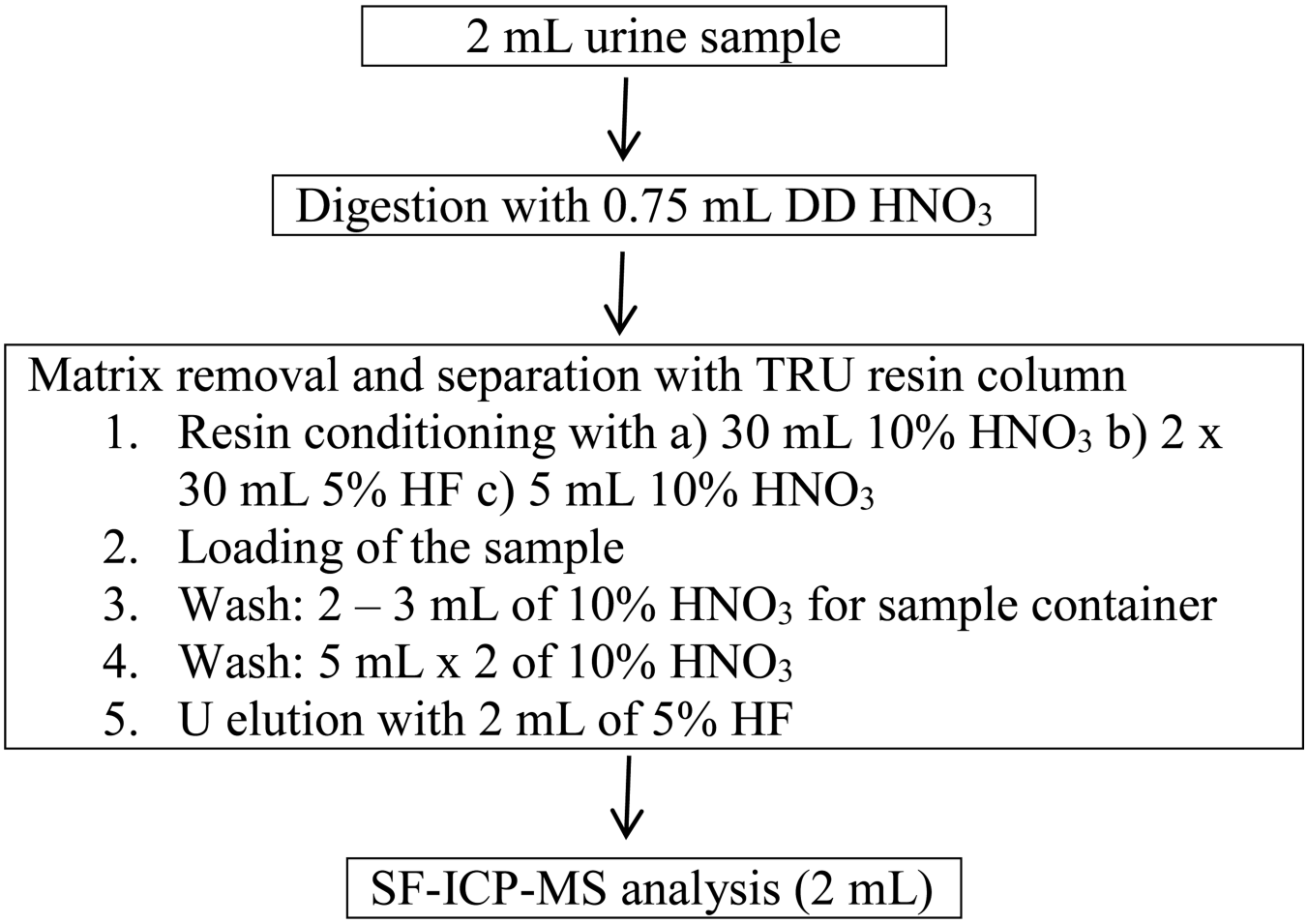

Figure 1.
Sequential sample preparation procedure for U isotopes determination.

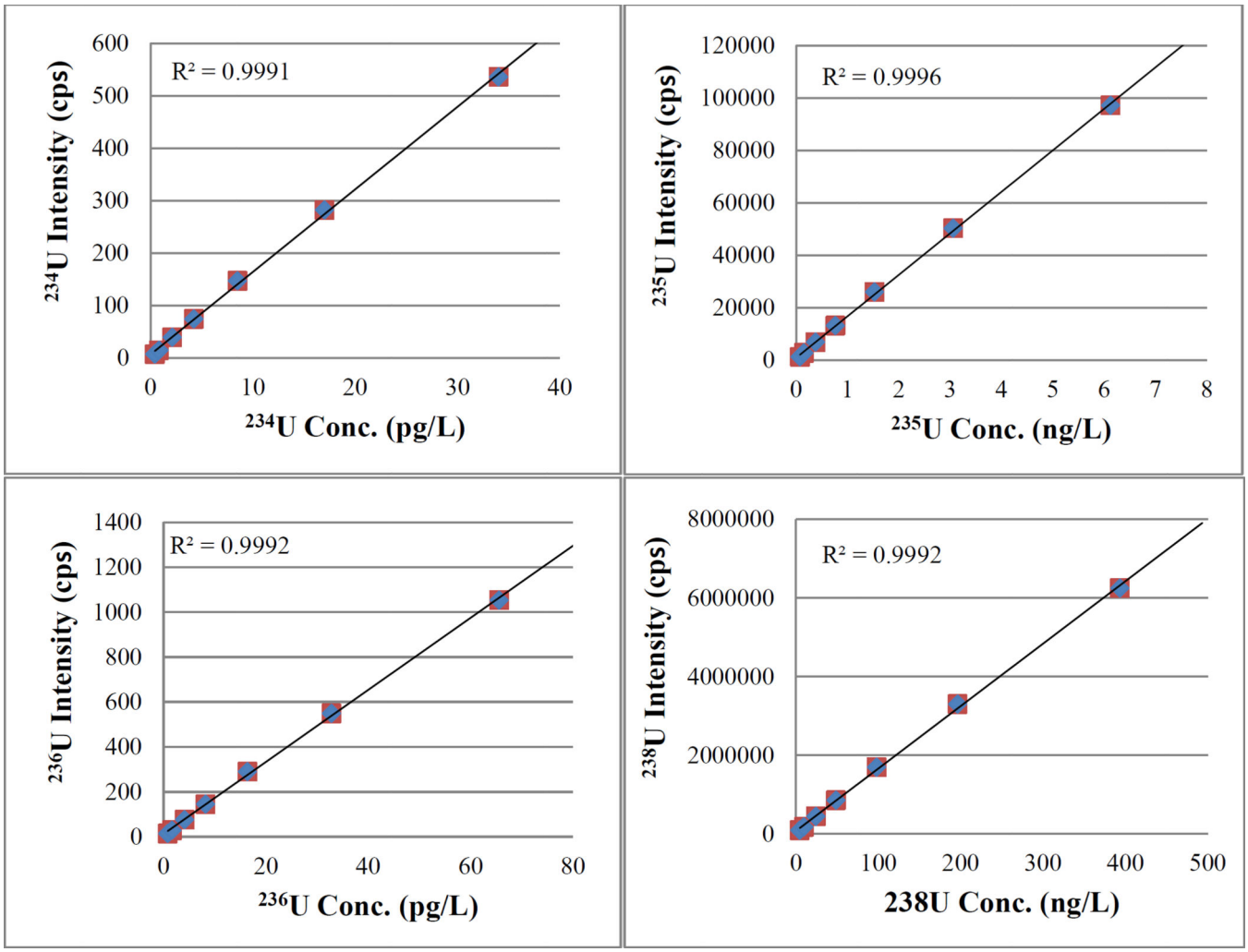

Figure 2.
Typical uranium isotopes intensity (cps) vs. concentration

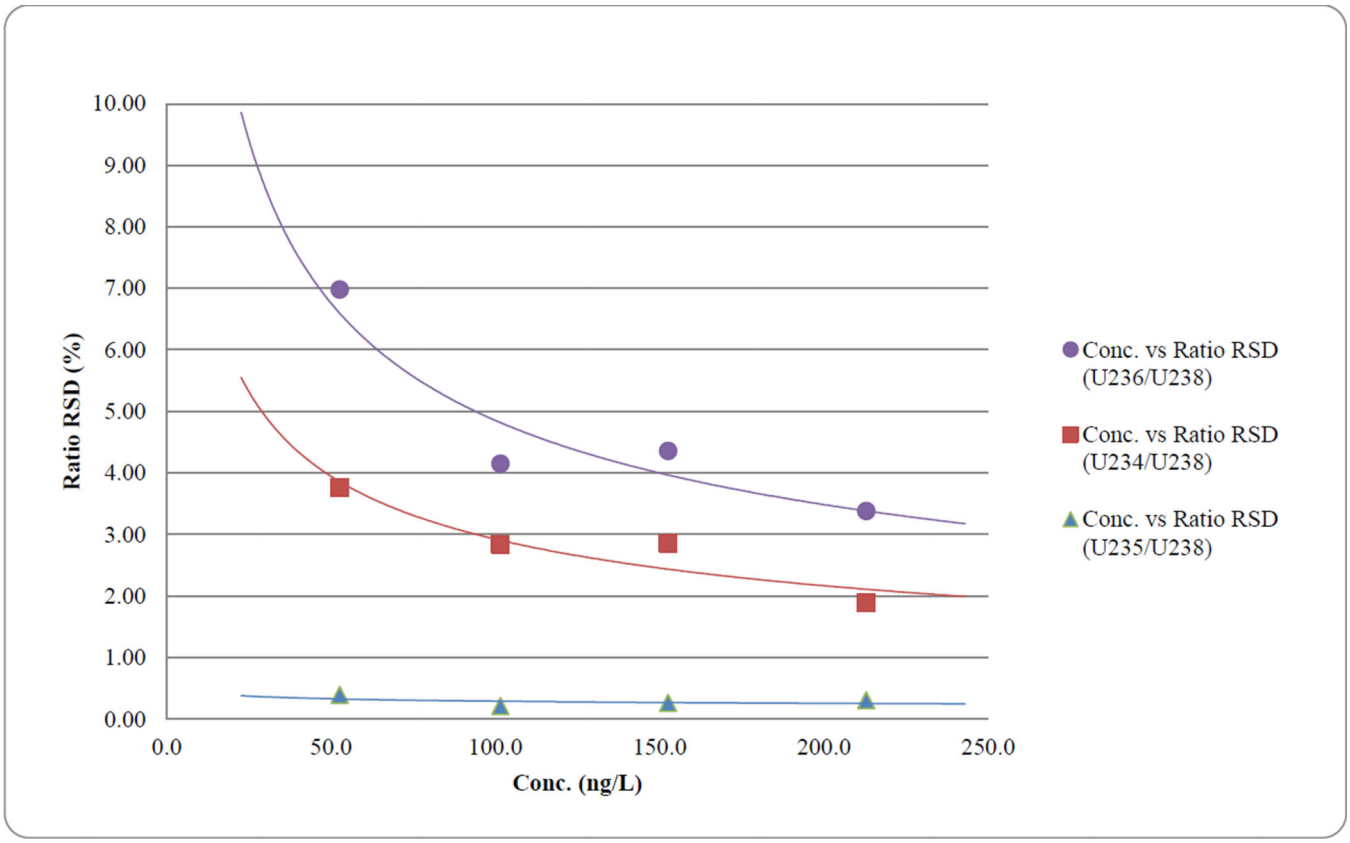

Figure 3.
Total uranium concentration and average of ratios RSD (N=20 runs) for CRM NBLU005-A spiked Urine samples

Table 1

Instrumental conditions and data acquisition settings for SF-ICP-MS measurements

RF Power (KW)	1.2 – 1.3
Cooling Gas flow (L/min)	16
Auxiliary Gas flow (L/min)	0.9
Sample Gas flow (L/min)	0.7 – 0.8
Lenses (V)	Optimized as needed
Sample Take up time (min)	2.1
Wash (min)	3
Pump Speed During Wash (rpm)	1
LR Runs/Passes	3* 2500
Detection Mode	Triple
Measurement Units	CPS
Scan Type	ESCAN
Scan Optimization	Speed
Number of Pre-Scans	5
Intergration Type	Average
Res. Switch Delay (s)	2
Resolution	300
Mass Window (%)	1
Setting Time (s)	0.001
Sample Time (s)	0.002
Sample Per Peak	600
Search Window (%)	1
Intergration Window (%)	1
Measured Isotopes	^{234}U, ^{235}U, ^{236}U, ^{238}U

Table 2

Observed uranium isotope ratios among-run precision for CRM and internal quality control material

		$^{234}U/^{238}U$				$^{235}U/^{238}U$				$^{236}U/^{238}U$			
	N	**Average**	**2SD**	**CRM T.V.**	**Bias (%)**	**Average**	**2SD**	**CRM T.V.**	**Bias (%)**	**Average#**	**2SD**	**CRM T.V.**	**Bias (%)**
NBL U005-A[a]	19	0.0000354	0.0000028	0.0000342	3.5	0.00504	0.00006	0.00509	−1.0	0.0000115	0.0000016	0.0000119	−3.4
Natural Uranium[c]	19	0.0000543	0.0000028	0.0000550	−1.3	0.00717	0.00008	0.00725	−1.1	0.0000000	0.0000016	<1.0E-10	-
NBL U015[a]	19	0.0000858	0.0000022	0.0000863	−0.6	0.01527	0.00026	0.01556	−1.9	0.0001636	0.0000036	0.0001667	−1.9
NBL115[b*]	40	0.0000098	0.0000020	0.0000076	28	0.00214	0.00020	0.00203	−5.4	0.0000318	0.0000022	0.0000323	−1.5
NBL U005-A[b*]	40	0.0000358	0.0000018	0.0000342	4.7	0.00512	0.00018	0.00509	0.6	0.0000118	0.0000010	0.0000119	−0.8
NBL U005-A + NU[e*]	20	0.0000451	0.0000016	0.0000446	1.1	0.00616	0.00016	0.00617	−0.2	0.0000057	0.0000008	0.0000060	−5.0
Natural Uranium[d*]	40	0.0000547	0.0000018	0.0000550	−0.5	0.00727	0.00024	0.00725	0.3	0.0000000	0.0000008	<1.0E-10	-
NU+ NBL U015[e*]	20	0.0000714	0.0000046	0.0000706	1.1	0.01136	0.00030	0.01141	−0.4	0.0000833	0.0000030	0.0000834	−0.1
NBL U015[b*]	40	0.0000872	0.0000038	0.0000863	1.0	0.01552	0.00056	0.01556	0.3	0.0001659	0.0000064	0.0001667	−0.5

[a] Aqueous dilutions (200 ng/L) of CRMs from the U.S. Department of Energy, New Brunswick Laboratory.

[b] Internal quality control materials made at CDC by spiking CRMs in pooled urine collected anonymously.

[c] Aqueous dilutions (200 ng/L) of natural uranium standard from the SPEX Industries, Inc..

[d] Internal quality control materials made at CDC by spiking natural uranium standard in pooled urine collected anonymously.

[e] Internal quality control materials made at CDC by spiking mixture of natural uranium standard and CRM in pooled urine collected anonymously.

[*] All internal quality control materials were prepared at ~200 ng/L (after TRU columns separation)

[#] Average of $^{236}U/^{238}U$ was corrected for abundance sensitivity mathematically.