

Uranium in Urine: Quantification and Isotope Ratio Determination

Key Words

ELEMENT 2, depleted uranium, high resolution ICP-MS, isotope ratios, ultra-trace quantification, uranium, urine

Goal

To demonstrate the capabilities of the Thermo Scientific™ ELEMENT2 HR-ICP-MS for the analysis of uranium in urine to monitor natural, DU (munitions, armor) or enriched uranium (nuclear processing plants) pollution.

The elemental and isotopic analysis of uranium in urine has been previously used to monitor contamination in workers from nuclear power plants^[1] and, more recently, in military personnel exposed to depleted uranium used in modern munitions^[2,3].

The quantification of uranium in urine is complicated by:

- the low concentrations found in urine
- variable amounts of salts in urine.

The second point makes the matrix matching of standards to samples for direct analysis impossible and, in order to normalize all samples to a similar matrix, the analysis of a diluted (or digested) solution is preferable. High instrumental sensitivity is then required to reliably measure the resulting single digit pg g^{-1} uranium concentrations.

While the quantification of uranium is therefore demanding in the diluted sample, uranium isotope ratio determination requires the ultimate in instrumental performance as good precisions for large isotope ratios are required at low concentrations. The abundances of the three naturally occurring U isotopes are shown in Table 1, together with the $^{234}\text{U}/^{238}\text{U}$ and $^{235}\text{U}/^{238}\text{U}$ ratios. The nuclear industry removes the majority of ^{235}U and ^{234}U for use in nuclear fuel rods, leaving behind “depleted uranium” (DU). This material typically has a $^{235}\text{U}/^{238}\text{U}$ ratio of 0.0025, and therefore an increased ^{238}U abundance of approximately 99.75%. In the diluted urine sample matrix however, this analysis is further complicated as minute contaminations of isotopically enriched or depleted uranium must be identified in a much larger quantity of isotopically normal uranium – all this at the pg g^{-1} level.

This report summarizes examples of both concentration and isotopic uranium analyses in urine. All analyses were performed on the Thermo Scientific ELEMENT 2, a single collector double focusing ICP-MS that provides high sensitivity, low background, an extended dynamic range (pre-requisites for quantification over a wide range of uranium concentrations) and flat top peaks (required for precise and accurate isotope ratio measurements). The detection range and isotope capabilities of such instrumentation allow the monitoring of uranium related environmental pollution from natural uranium, DU (munitions, armor) or enriched uranium (nuclear processing plants) by analyzing total uranium content or/and its isotopic composition.

Table 1: Abundances and ratios of uranium isotopes in natural and depleted uranium (DU).

Isotope	Natural abundance	Natural ratio relative to ^{238}U	DU ratio relative to ^{238}U
^{234}U	0.0055%	0.000055	0.00001
^{235}U	0.72%	0.0073	0.0025
^{238}U	99.2745%		

1. Quantification

The quantification of uranium in urine was carried out under ‘hot’ plasma conditions on 20-fold diluted urine samples with reference concentrations of $12 \pm 1 \text{ pg g}^{-1}$ and $99 \pm 7 \text{ pg g}^{-1}$ (kindly supplied by R. Pappas, CDC, Atlanta, USA). For comparison, a commercial quality control sample, Bio-Rad Urine Level 2 (BU2; batch no. 69051), and a sample from a healthy volunteer were analyzed after 20-fold dilution with 5% HNO_3 . The analysis details are summarized in Table 2. Nickel cones were used instead of Pt tipped cones to avoid any contribution from ArPt interferences on the uranium isotopes.

The external calibration curve (with points at 0.1, 1.0 and 10 pg g^{-1}) used for the quantification of uranium in all samples is shown in Figure 1.

Table 2: Analysis details for uranium quantification in urine.

Sample introduction	Nebulizer: Glass Expansion at 1 ml min ⁻¹ (pumped), quartz spray-chamber
Plasma	1200 W, Guard Electrode
Cones	Ni
Sample dilution	20-fold in 5% HNO ₃ ("Baseline" quality, Seastar Chemicals, Canada)
Internal Standard	1 ng g ⁻¹ In
Integration time	In 10 s, U 100 s
Number of scans	250 (5 runs, 50 passes)

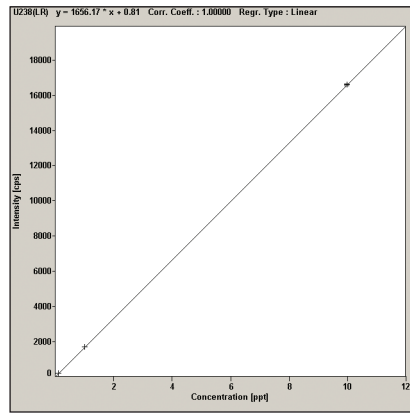


Figure 1: Low level external calibration curve for ²³⁸U

With the Thermo Scientific ELEMENT 2 HR-ICP-MS the combination of:

- high instrumental sensitivity: $\sim 2 \times 10^6$ cps per ng g⁻¹ for ²³⁸U
- low instrumental noise: < 0.2 cps, independent of mass range,

allows for uranium detection limits of < 1 fg g⁻¹ (Table 3). The instrumental detection limit (LoD) was calculated as the concentration equivalent of 3 sigma from ten replicate blank measurements. The counts per second (cps) values for the ten blank measurements are shown in Figure 2. The method detection limit of 16 fg g⁻¹ (taking into account a dilution factor of 20 for the diluted samples) is excellent, since this is by far sufficient for most applications. Recovery of the 10 pg g⁻¹ spiked sample was 94%.

Table 3: Detection limits (LoD) and recovery.

Average blank intensity n=10 [cps]	2.5
Standard deviation n=10 [cps]	0.4
Instrumental LoD [fg g ⁻¹]	0.79
Method LoD [fg g ⁻¹]	16
Recovery for 10 pg g ⁻¹ spike	94%

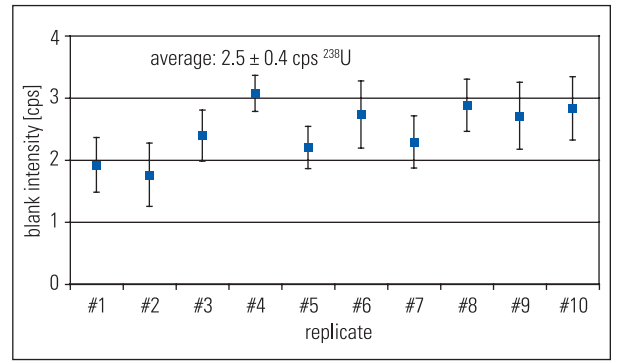


Figure 2: Reproducibility of blank measurements on ²³⁸U

Analysis time was about 2 min, yielding a precision of 1% even in the lowest concentration samples (Table 4). However, in daily routine, the method can likely be shortened to 30 seconds integration time, while still giving high precision results. The results of the concentration measurements are shown in Table 5. The QC samples were analyzed four times, while the Bio-Rad Urine Level 2 quality control and volunteer samples were analyzed once for comparison. The results for the QC samples match the average values previously obtained at CDC and cover a large range of real life concentrations. There is no suggested value for uranium in the Bio-Rad Level 2 quality control sample.

The low concentration of the volunteer sample (3.9 pg g^{-1}) falls within the results from Rodushkin^[4], where the reported large variability of natural U in humans (0.7 – 19 pg g^{-1}) reinforces the need for highly sensitive and precise instrumentation.

Table 4: Precision of individual measurements. Sample "low QC" is diluted 20-fold

Sample	²³⁸ U intensity [cps]	Relative standard deviation
0.1 pg g^{-1}	176.7	1.11%
1.0 pg g^{-1}	1656.7	0.49%
10 pg g^{-1}	16568.3	0.32%
low QC	843.5	0.98%

Table 5: Concentration results

Sample	No. of replicates	U as measured [pg g ⁻¹]	U in original sample [pg g ⁻¹]	Target value samples [pg g ⁻¹]
low QC	4	0.60 ± 0.005	12.0 ± 0.1	11.83 ± 1.15
mid QC	4	5.17 ± 0.056	104 ± 1	98.5 ± 7.2
volunteer	1	0.195	3.9	-
Bio-Rad Urine Level 2	1	2.54	51	-

2. Isotope Ratio Analysis

For these experiments, the Bio-Rad Urine level 1 (BU1) quality control sample was used as the urine matrix.

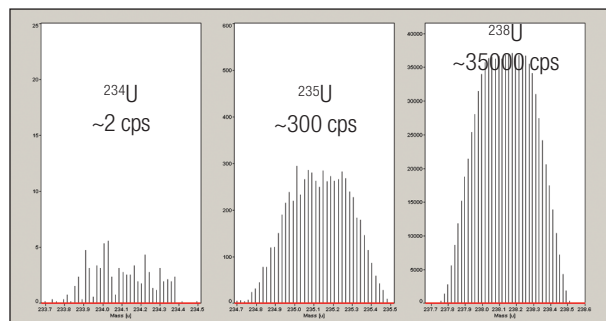


Figure 3: Example spectrum with wide mass windows (BU1, 5-fold diluted).

Results for the $^{235}\text{U}/^{238}\text{U}$ isotope ratio analyses are given in Table 6 and are displayed as a time series in Figure 4. These values have not been corrected by internal or external standards and no outlier rejection has been performed. As expected, the unspiked BU1 quality control sample shows a natural uranium isotope ratio.

The change in isotope ratio in the spiked BU1 sample is much larger than the analytical uncertainty of the measurement. The precision of ± 0.00022 for the spiked BU1 sample, achieved in a 7 minute analysis, allows the detection of $< 5\%$ DU in uranium in urine at natural concentrations. It is clear from these results that even minor amounts of DU can be easily recognized in urine by isotope ratio analysis on the ELEMENT 2 HR-ICP-MS.

The challenge in performing these isotope ratio analyses is to trace small DU contributions in much larger quantities of natural uranium. At ultratrace concentrations this requires a superior sensitivity, low noise, and a stable signal combined with good matrix tolerance. Thus, the ELEMENT 2 HR-ICP-MS makes isotope ratio determinations a sophisticated tool to trace DU contamination.

Table 6: Results for $^{235}\text{U}/^{238}\text{U}$ isotope ratio analyses.

$^{235}\text{U}/^{238}\text{U}$	Average	Standard deviation	Relative standard deviation
1 ng g ⁻¹ spike	0.002020	0.000001	0.07%
BU1	0.00736	0.000018	0.2%
BU1 spiked with DU	0.00673	0.000022	0.3%

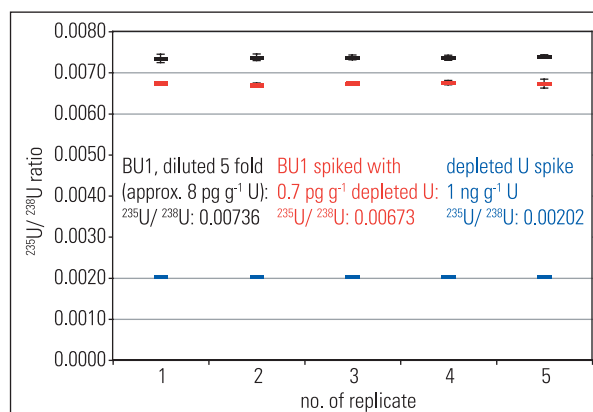


Figure 4: Isotope ratio stability in 5-fold diluted urine samples.

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