# MM800[(a)]

# Ion Exchange and ICP/MS of Uranium in Water

## 1.0 Scope and Application

This procedure can be used to determine U concentration or isotopic-ratio composition in groundwater and drinking water, using ion exchange (IE) and inductively coupled plasma-mass spectrometry (ICP-MS) techniques, at concentrations > 10 pg/mL. The information provided by this procedure will allow for evaluation and determination of $^{235}$U enrichment or depletion.

## 2.0 Summary of Method

The IE and ICP-MS determination of U concentration and isotopic abundance was obtained by adding a $^{233}$U spike solution with known isotopic and elemental concentration to the sample before sample preparation. A 10-mL, 1-bed volume (BV) column of Dowex-1X8 anion exchange resin in the chloride form and 2 M HCl as the mobile phase provides for a U chloro-complex having a distribution coefficient (Kd) of $10^2$ (Kraus and Nelson 1956). This allows for 100 mL of sample solution to be processed. Standard operating procedures for ICP-MS are outlined in section 8.3.

## 3.0 Interferences

Isobaric interferences for U isotopes may be observed for U.S. Department of Energy (DOE) wastes due to the presence of Pu, Pa, and Np. However, these elements may be considered as analogs to the lanthanide elements, which do not produce anion chloro-complexes in HCl solutions. This should be confirmed using a Pu, Pa, and Np spike. Other interferences, due to high mass loading, may also be observed in the presence of elements such as Zn and Fe. However these elements do not produce isobaric interferences for the determination of U using ICP-MS. Table 1 lists possible isobaric interferences for uranium isotopic determination. For more details on interpreting interferences, refer to U.S. Environmental Protection Agency (EPA) Method 6020 CLP-M v. 8.0.

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(a) This method was supplied by O. T. Farmer, G. M. Mong, A. Sharma, and C. J. Cemetson (Pacific Northwest Laboratory, Richland, Washington).

**Table 1.** Isobaric Interferences for Uranium

| Plutonium Element Nuclides: | | | Protactinium Element Nuclides: | | | Neptunium Element Nuclides: | | |
|---|---|---|---|---|---|---|---|---|
| Nuclide | Weight | Half-Life | Nuclide | Weight | Half-Life | Nuclide | Weight | Half-Life |
| $^{236}$Pu | 236.046 | 2.87 y | $^{234}$Pa | 234 | 6.69 h | $^{235}$Np | 235 | 1.085 y |
| $^{237}$Pu | 237.048 | 45.2 d | $^{234m}$Pa | 234 | 1.17 m | $^{236}$Np | 236 | 1.6E05 y |
| $^{238}$Pu | 238.049 | 87.7 y | | | | $^{236m}$Np | 236.05 | 22.5 h |
| | | | | | | $^{238}$Np | 238 | 2.117 d |

## 4.0 Safety

Ordinary laboratory safety procedures are assumed. Waste from DOE sites, either as leachates or as specific chemical separation process material, may contain significant amounts of fission products or actinides. Shielding and radiochemical safe-handling practices are assumed for those instances where radioactivity is suspected.

## 5.0 Apparatus and Materials

### 5.1 Sample Preparation

- Nalgene beaker (250 mL)
- Nalgene cover glass
- adjustable hot plate
- Plastic pipettes (0.1, 1.0, and 10.0 mL)
- Four place balance (0.001 g)
- Milli-pore vacuum Filtration system (0.45-µm)

### 5.2 Ion Exchange

- Column with zero head space (10 mL)
- Dowex 1 X 8 anion resin
- Advanced Gradient Pump (Dionex Corp.)
- DQP Pump (Dionex Corp.)
- Eluent Delivery Module (Dionex Corp.)
- AS40 Autosampler (Dionex Corp.)
- Foxy 200 Fraction Collector (Dionex Corp.)

### 5.3 Inductively Coupled Plasma-Mass Spectrometry

- ICP-MS Fission PQ2
- U5000 Ultrasonic Nebulizer (USN)

## 6.0 Reagents

- American Society for Testing and Materials (ASTM) Type II water (ASTM D1193)
- Concentrated HCl (Seastar)
- Thirty percent $H_2O_2$ (Reagent Grade)
- Concentrated $HNO_3$ (Seastar)
- Natural isotopic U standard {National Institute for Standards and Technology (NIST)}
- Uranium-233 standard

## 7.0 Sample Collection, Preservation, and Handling

This procedure implements processes specified in Method 6020 CLP-M Version 8.0 whenever applicable. Special care should be taken to avoid contamination while collecting samples. All samples should be placed in a sealed container. Proper shielding should be provided to handle the sample safely.

## 8.0 Procedure

### 8.1 Relative Uranium Concentration Procedure

8.1.1 The sample is shaken, and 10 mL of the sample are transferred to a 20-mL plastic sample bottle. Then 0.1 mL of (1:1) $HNO_3$:$H_2O$ are added to the sample.

8.1.2 The ICP-MS is optimized using a 10-ng/mL solution of natural U for a maximum $^{238}$U count rate. Each sample solution is compared to this standard for relative concentration. This procedure will determine the amount of $^{233}$U spike that will be added in the actual sample preparation. The ratio of $^{233}$U/$^{238}$U in the final sample solution is between 0.5 to 1.5. The amount of $^{233}$U spike is determined by the cognizant scientist and should be near the value expected for the sample U concentration or at a minimum at a detectable amount (5 to 10 times the instrument detection limit). If the $^{238}$U is above 0.1 μg/mL in this solution, the sample should be further diluted.

### 8.2 Acid Digestion Procedure for IC and ICP-MS Analysis

8.2.1 One hundred milliliters of a well-mixed sample are transferred to a 250-mL Nalgene beaker.

8.2.2 One milliliter of (1:1) $HNO_3$:$H_2O_2$ and 2 mL of 30% $H_2O_2$ are added to the sample to oxidize U(IV) to U(VI) and break down any organic material.

8.2.3 An appropriate amount of a spike solution of $^{233}$U (as defined by the above procedure) is added to the samples being prepared. The samples are labeled with the sample identification.

8.2.4 The sample is covered with a watch glass or similar cover and heated on a steam bath or hotplate for 2 h at 95°C or until the sample volume is reduced to between 25 and 35 mL.

8.2.5 The sample is cooled and filtered with a 0.45-μm filter to remove insoluble material.

8.2.6 Seventeen milliliters of 12 M HCl are added to the digestion vessel, and the sample volume is adjusted to 100 mL, which will provide an ~2 M HCl sample solution. The sample is now ready for ion chromatography (IC) separation.

## 8.3 Ion Exchange

### 8.3.1 Column Characteristics

The column characteristics are established before any column separation of U. This is initiated by conditioning the resin to the chloride form using 2 to 4 BV of 2 M HCl. A solution of 100 ng/mL of natural U in 2 M HCl is processed through the column and directly into the ICP-MS to determine the number of BV required for U breakthrough (BT). The determination of U BT will establish the volume of sample in 2 M HCl that can be processed with this column. However, this procedure requires that 15 BV be obtained before U BT.

The volume of $H_2O$ necessary to elute a 100-mL (10 BV) U solution off the column should be determined. Initially, the column is conditioned with 2 to 4 BV of 2 M HCl. This is followed by loading 100 mL (10 BV) of a 2 M HCl U solution on the column. In the next step, 2 BV of 2 M HCl are processed; these fractions are diverted to waste. The U is then eluted using $H_2O$ directly into the ICP-MS, and the BV of $H_2O$ required to remove U is determined. These characteristics are used to separate and collect U in groundwater and drinking-water samples. (**Note**: If the $^{233}$U spike solutions are contaminated with Pu, Np, or Pa or the 2 M HCl eluent is contaminated with U, then an IE separation or clean-up can be performed using this procedure. If this is done, then an analysis of the solution is required to determine the U concentration and isotopic abundance of this solution using ICP-MS. The need for any spike cleanup will be displayed in the blank solution if any alteration in the U isotopic ratios after IE separation occurs.) (Kunin 1956; Marcus 1968).

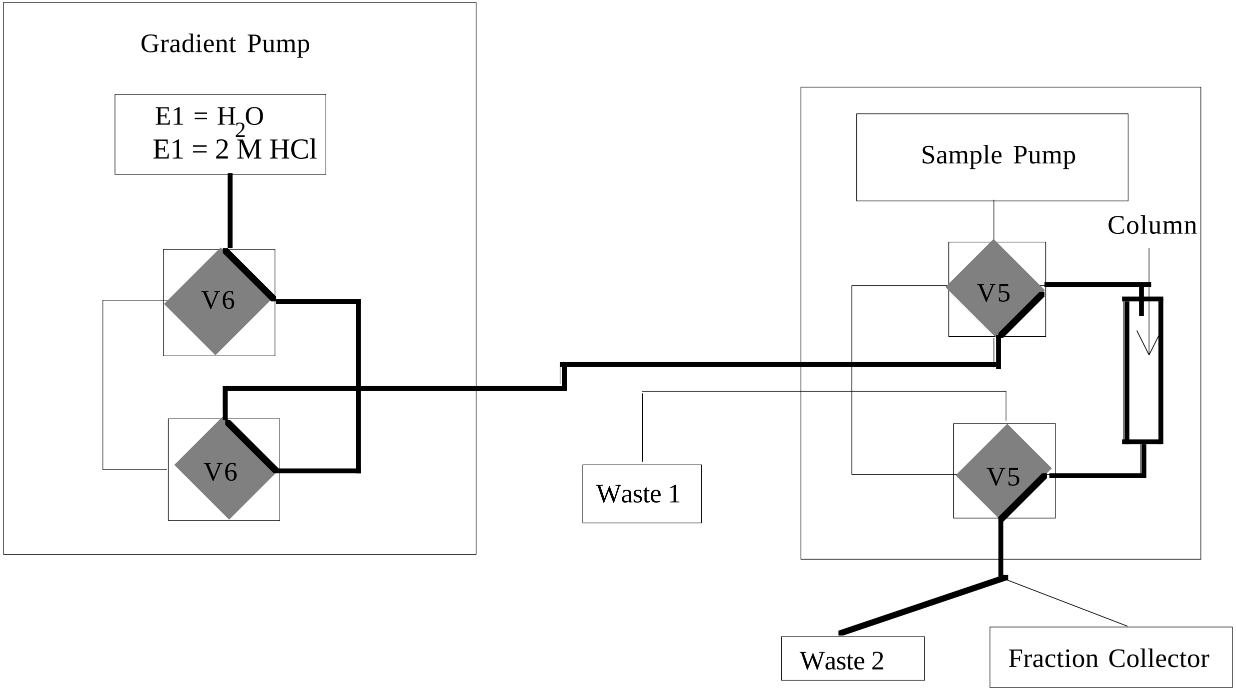
### 8.4 Sample Processing

The system configuration for separating and eluting U is defined in Figures 1 through 4. In Figure 1, the anion column is equilibrated with 20 mL of 2 M HCl to convert the resin to the $Cl^-$ form, with this solution being diverted to waste. In Figure 2, the gradient pump is turned off, and valve 5 is switched to the off position; the sample pump is put inline to the column, and 100 mL of sample are loaded. The output from the column is also diverted to waste. This solution will contain lanthanide elements, actinides, alkali, alkaline earth elements, and most transition elements (Kraus and Nelson 1956; Hudgen 1956). In Figure 3, the gradient pump is turned on, valve 5 is switched to the on position, and the column is washed with 20 mL of 2 M HCl. This is to remove all elements that have little tendency to form chloro-complexes in 2 M HCl. This solution is also diverted to waste. In Figure 4, the eluent is changed to $H_2O$, and U is eluted with 20 mL of $H_2O$. This solution is collected by the fraction collector and is ready for analysis by ICP-MS.

### 8.5 ICP-MS

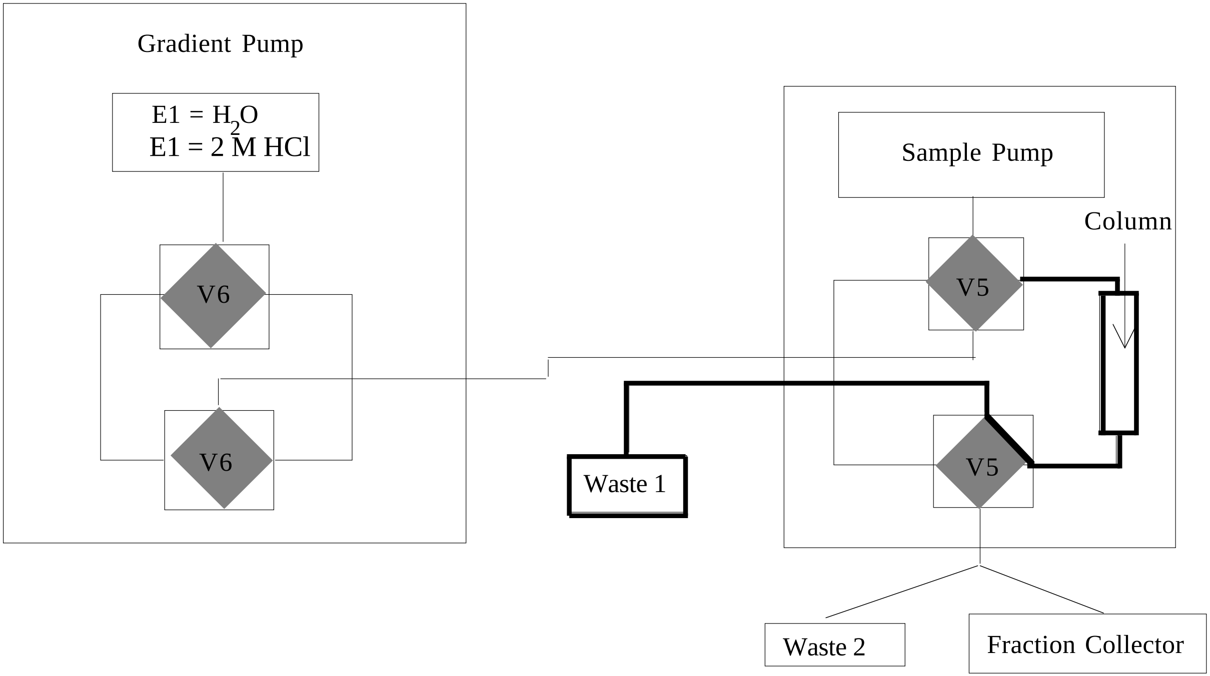
#### 8.5.1 Instrument Detection Limit

The instrument detection limit (IDL) is three times the average of the standard deviations obtained from the analysis of a standard solution (each analyte in reagent water) at a concentration of 3 to 5 times the expected IDL, with seven consecutive measurements. For general purposes, once an IDL has been established, it is valid until either 1) a significant change in instrument response occurs, or 2) there is a major change or repair to the instrument (e.g., a new sample interface or quadrupole); certain projects may have more stringent requirements regarding the frequency and/or protocol of determining the IDL (Marcus 1968).



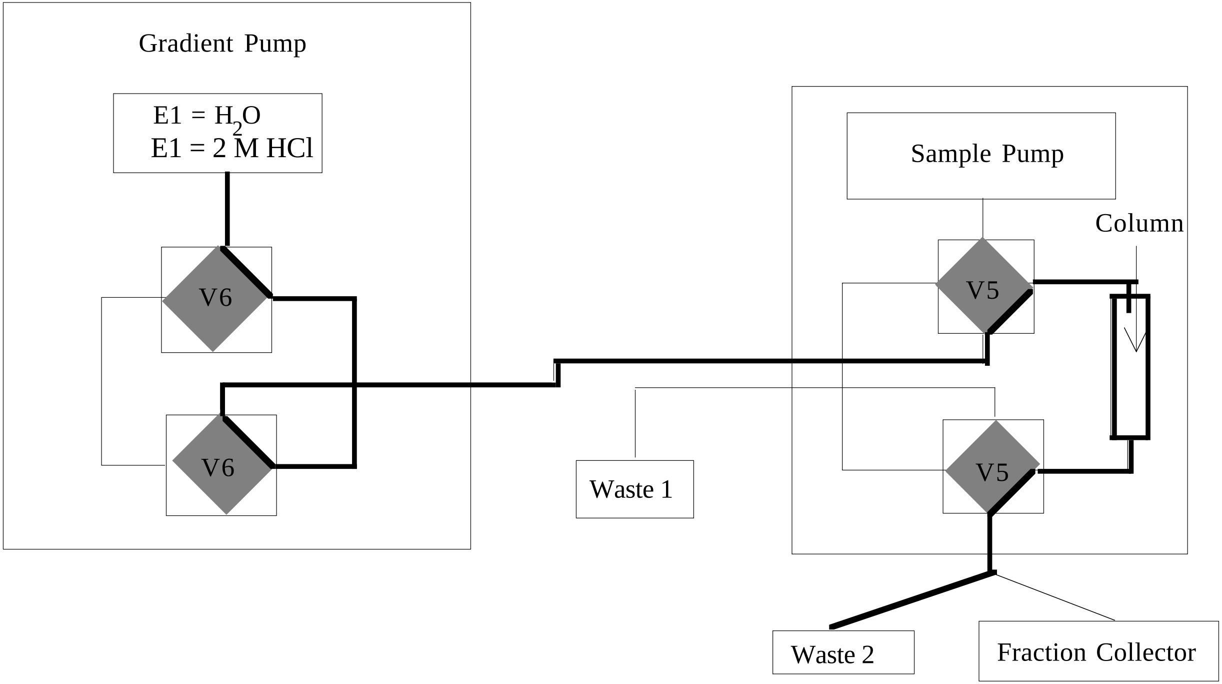
| Time | Gradient Flow | % E1 | % E2 | V5 | V6 | Fraction Collector | Sample Pump Flow |
|---|---|---|---|---|---|---|---|
| 0.0 | 5.0 | 0.0 | 100 | On | Off | Waste 2 | 0.0 |
| 4.0 | 5.0 | 0.0 | 100 | On | Off | Waste 2 | 0.0 |

**Figure 1.** Column Conditioning with 2 M HCl



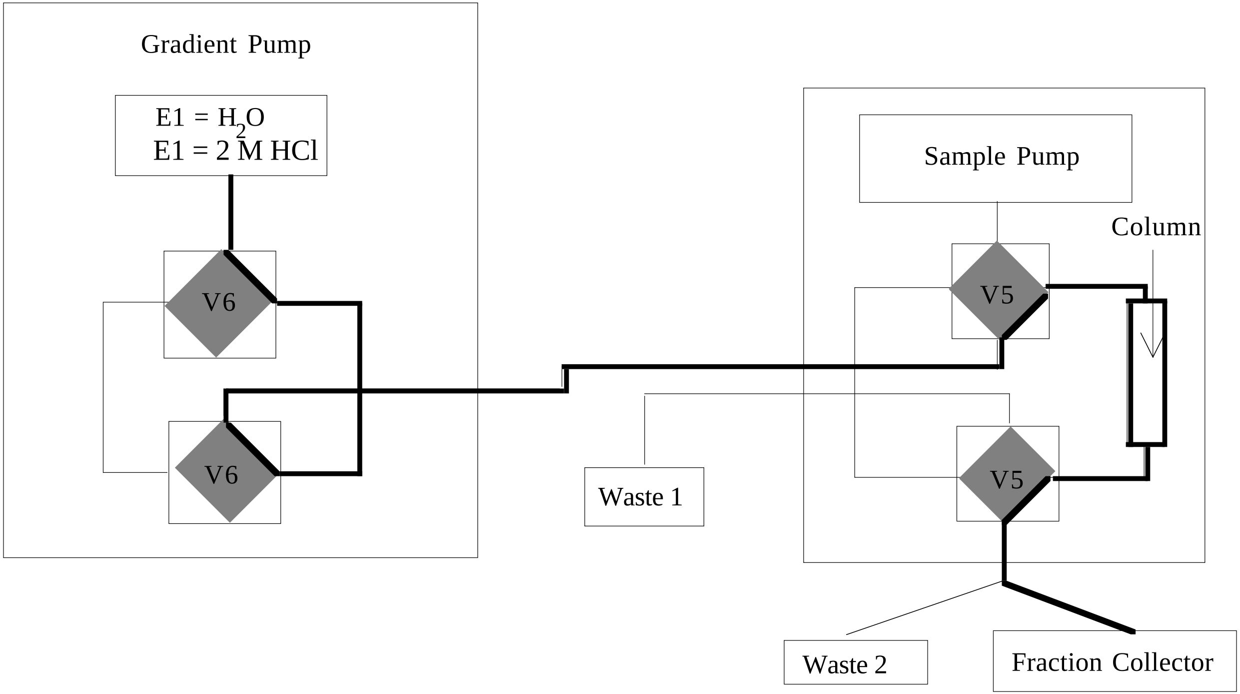
| Time | Gradient Flow | % E1 | % E2 | V5 | V6 | Fraction Collector | Sample Pump Flow |
|---|---|---|---|---|---|---|---|
| 4.0 | 0.0 | 0.0 | 0.0 | Off | Off | Off | 5.0 |
| 24.0 | 0.0 | 0.0 | 0.0 | Off | Off | Off | 5.0 |

**Figure 2.** 100-mL Sample Loading on Column



| Time | Gradient Flow | % E1 | % E2 | V5 | V6 | Fraction Collector | Sample Pump Flow |
|---|---|---|---|---|---|---|---|
| 24.0 | 5.0 | 0.0 | 100 | On | Off | Waste 2 | 0.0 |
| 28.0 | 5.0 | 0.0 | 100 | On | Off | Waste 2 | 0.0 |

**Figure 3.** Wash Column with 2 M HCl



| Time | Gradient Flow | % E1 | % E2 | V5 | V6 | Fraction Collector | Sample Pump Flow |
|---|---|---|---|---|---|---|---|
| 28.0 | 5.0 | 100 | 0.0 | On | Off | On | 0.0 |
| 32.0 | 5.0 | 100 | 0.0 | On | Off | On | 0.0 |

**Figure 4.** Elution of Uranium with $H_2O$

## 9.0 Instrument Operation and Analysis

The following procedures are to be used in conjunction with the VG Plasmaquad operating and user's manuals. The procedures below assume that the instrument is operating and functioning normally.

### 9.1 Normal Operating Conditions

Operating conditions typically change on a daily basis. The following parameters are guidelines for proper instrument performance:

| | |
|---|---|
| Plasma Gas | ~13 L/min (Lpm) |
| Auxiliary Gas | ~0.8 Lpm |
| Nebulizer Gas | ~0.9 Lpm |
| Forward Power | 1250 W |
| Reflected Power | < 5 W |
| Sampling Height (mm above loadcoil) | 12 mm |

### 9.2 Tuning the Instrument

At least 30 min should be allowed for the instrument to equilibrate before analyzing any samples. The ICP-MS is then tuned by aspirating the tune solution and adjusting the lens voltages for optimal sensitivity. The element in the tune solution having the median mass (e.g., In at 115 amu) is typically tuned first, with the low and high masses being tuned subsequently only if their resulting sensitivities are determined to be insufficient.

#### 9.2.1 Instrument Response and Precision Check

The instrument response is determined using the tune solution and shall be at least 1 x $10^6$ counts per sec per ppm at 115.0 amu by pneumatic nebulization (assuming the tune solution contains In) to be considered acceptable for analysis. Tuning an instrument using the ultrasonic nebulizer (USN) (Cetac Model U-5000) enhances instrument response by 10 to 50 times. Therefore a tune solution with element concentrations approximately 1 to 10% that of the pneumatic-nebulizer tune solution is typically used. Both the instrument and the nebulizer must be optimized. The "level" and "tuning" settings on the USN are adjusted to maximize output (indicated on the output meter); output may be slightly compromised, however, to optimize the aerosol density and/or instrument response. The ICP-MS is tuned in the same manner with the USN as with the pneumatic nebulizer. Instrument response using the USN must be at least 5 x $10^7$

cps/ppm at middle mass to be acceptable for analysis. The USN chiller must be running for at least 30 min before data acquisition using the USN and preferably before USN operation.

# 10.0 Calculations

A mass bias correction (MBC) for any isotope of U, relative to $^{233}$U, is determined using a solution having a known U molar concentration.

The following equation (1) represents the calculation for the MBC for $^{235}$U:

$$\mathrm{M\,B\,C} = \frac{\left(\dfrac{\mathrm{CPS}\ ^{235}\mathrm{U}}{\mathrm{CPS}\ ^{233}\mathrm{U}}\right)}{\left(\dfrac{\mathrm{Moles}\ ^{235}\mathrm{U}}{\mathrm{Moles}\ ^{233}\mathrm{U}}\right)} \qquad (1)$$

where

CPS stands for counts per second for the desired U isotope, represented by $^{XXX}$U, obtained from the instrument. These values are corrected for the background signal before insertion in the above equation (1).

## 10.1 Isotopic Mass

The following equation (2) represents U isotopic mass (IM) (in g) calculation in a given sample. It can be used for any available isotope of U that is represented by $^{XXX}$U:

$$\mathrm{IM} = \left[\left(\frac{\dfrac{\left(\mathrm{CPS}\ ^{XXX}\mathrm{U}\right)\left(\mathrm{Moles}\ ^{233}\mathrm{U}\right)}{\mathrm{CPS}\ ^{233}\mathrm{U}}}{\mathrm{MBC}}\right) - Z\right] \bullet \mathrm{At.\ Wt.} \qquad (2)$$

where

$^{XXX}$U = desired U isotope
At. Wt. = atomic weight of U isotope under consideration
Z = moles of $^{XXX}$U/ mole of $^{233}$U (moles of $^{XXX}$U associated with spike)

### 10.2 Isotopic Concentration

The isotopic concentration can be determined by introducing a known amount of $^{233}$U as the spike. The isotopic concentration of any U isotope can be determined relative to $^{233}$U by the following equation (3):

$$\text{IC} = \frac{\text{IM}\left(\text{g}\right)}{\text{Sample Volume}\left(\text{mL}\right)} \qquad (3)$$

### 10.3 Total Uranium Isotopic Mass

The total U IM is the sum of all the observed U isotopes. Since $^{234}$U and $^{236}$U are relatively low in natural abundance, these isotopes can be neglected in total U IM determinations. The following equation (4) is used:

$$\text{Total U} = \sum^{n} \text{IM} = {}^{235}\text{U}(\text{g}) + {}^{238}\text{U}(\text{g}) \qquad (4)$$

where n is the number of U isotopes.

### 10.4 Isotopic Abundance

Once the total U is determined, the isotopic abundance (IA) of any U isotope can be obtained by taking their concentration respective to the total U. This is shown in the following equation (5):

$$\text{IA} = \frac{\text{IM}}{\sum^{n} \text{IM}} \qquad (5)$$

Once IA is known, depletion or enrichment can be determined by comparing the ratio with 0.715, which is the naturally occurring ratio. If the ratio is less then 0.715, U is depleted, and if it is greater then 0.715, it is enriched.

## 11.0 Quality Control

### 11.1 Sample Preparation Check Sample

11.1.1 A matrix sample solution is used having a known concentration and IA of U spiked with $^{233}$U and processed through all steps of the sample-preparation procedure. This solution validates the sample preparation.

## 11.2 Instrument Check Sample

11.2.1 To evaluate the instrument response, a known natural U standard is spiked with a known amount of $^{233}$U. This is followed by performing a preparation check. The data obtained by instrument check (Table 2) and prep-check (Table 3) are listed as follows:

**Table 2.** Instrument Check

| Run No. | $^{235}$U (ppm) | $^{238}$U (ppm) | $^{235}$U (Abundance) | Total (ppm) |
|---|---|---|---|---|
| 1 | 0.00733 | 1.014 | 0.00718 | 1.021 |
| 2 | 0.00716 | 0.999 | 0.00712 | 1.006 |
| 3 | 0.00725 | 0.994 | 0.00714 | 1.001 |
| 4 | 0.00720 | 0.995 | 0.00718 | 1.003 |
| 5 | 0.00717 | 1.000 | 0.00712 | 1.008 |
| 6 | 0.00738 | 1.025 | 0.00714 | 1.033 |
| 7 | 0.00718 | 0.994 | 0.00717 | 1.001 |

**Table 3.** Preparation Check

| Run No. | $^{235}$U (ppm) | $^{238}$U (ppm) | $^{235}$U (Abundance) | Total (ppm) |
|---|---|---|---|---|
| 1 | 0.0193 | 2.682 | 0.00715 | 2.701 |
| 2 | 0.0188 | 2.612 | 0.00715 | 2.631 |
| 3 | 0.0189 | 2.612 | 0.00717 | 2.630 |
| 4 | 0.0190 | 2.644 | 0.00712 | 2.663 |
| 5 | 0.0188 | 2.620 | 0.00713 | 2.639 |
| 6 | 0.0195 | 2.697 | 0.00719 | 2.716 |
| 7 | 0.0191 | 2.639 | 0.00718 | 2.658 |

## 12.0 Method Performance

The average, standard deviation, and % RSD for instrument check samples and prep-check samples were calculated for establishing the method performance. These values are listed in Table 4 as follows:

**Table 4.** Instrument and Preparation Checks

**Instrument Check**

| Variable | $^{235}U$ (ppm) | $^{238}U$ (ppm) | $^{235}U$ Abundance | Total (ppm) |
|---|---|---|---|---|
| Average | 0.00722 | 1.003 | 0.00715 | 1.010 |
| Standard Deviation | 0.0001 | 0.0110 | 0.00002 | 0.0111 |
| % rsd | 1.16 | 1.10 | 0.35 | 1.10 |

**Preparation Check**

| Variable | $^{235}U$ (ppm) | $^{238}U$ (ppm) | $^{235}U$ Abundance | Total (ppm) |
|---|---|---|---|---|
| Average | 0.01905 | 2.643 | 0.00716 | 2.663 |
| Standard Deviation | 0.003 | 0.0314 | 0.00003 | 0.0317 |
| % rsd | 1.35 | 1.19 | 0.35 | 1.19 |

## 13.0 References

Hudgen, J. E. 1956. “Ion Exchange in Analytical and Radiochemistry.” *Ion Exchange and Chromatography in Analytical Chemistry*. Fifty-Ninth Annual Meeting Papers. ASTM Special Technical Publication No. 195. American Society for Testing and Materials, Philadelphia, Pennsylvania, pp. 11-26.

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