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Analysis of Uranium and Plutonium by MC-ICPMS

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Analysis of U and Pu by MC-ICPMS

1.0 PURPOSE

This procedure is written as general guidance for the measurement of elemental isotopic composition by plasma-source inorganic mass spectrometry. Analytical methods for uranium and plutonium are given as examples.

2.0 SCOPE AND APPLICATION

This SOP describes the analysis of bulk samples for elemental isotopic composition by multi-collector inductively coupled plasma mass spectrometry (MC-ICPMS). The MC-ICPMS instrument is an IsoProbe originally manufactured by Micromass, Inc. and now manufactured and supported by GV Instruments, Inc. Analyses are performed on elements purified from samples by various methods.

This procedure is applicable to elements that: (1) are not mono-isotopic; (2) form ions in an argon plasma having +1 charge which are produced with good yield (ions produced/atoms introduced); and (3) have no significant isobaric interferences due to instrumental effects.

Two examples of such elements, uranium and plutonium, are given in this procedure. The analytical principles described for U and Pu may be generalized and adapted for other elements. Only highly purified separated elements may be analyzed by this procedure. While no minimum sample size is specified, the sensitivity of the IsoProbe is sufficient to make isotopic analyses of 10 picogram of uranium and 1 picogram of plutonium. Highly precise results, 0.1% or better at the 95% confidence level, for $^{238}\text{U}/^{235}\text{U}$ and $^{240}\text{Pu}/^{239}\text{Pu}$ are obtained on 50 ng of U and 5 ng of Pu.

3.0 SUMMARY OF METHOD

Samples, dissolved in 2% nitric acid (vol/vol), are nebulized and transported as aerosol with argon carrier gas to the ICP torch where the elements are ionized in the argon plasma. The sample stream passing through the center of the plasma is ionized efficiently; the preponderant ion species formed have +1 charge. The analyte ion beam is defined by a series of two cones as the sample leaves the torch. Mechanical and turbomolecular pumps progressively reduce the pressure behind each of these cones. In the IsoProbe, the range of ion energies produced in the plasma torch is reduced by transporting the beam with a hexapole ion guide through a region of low-pressure argon; a collision cell. The essentially mono-energetic ion beam that emerges from the hexapole collision cell is accelerated by a -6000 V extraction lens and focused with electrostatic lenses. The beam then transits a magnetic sector mass analyzer where ions of different mass/charge ratio are discriminated and focused on the collector array. The IsoProbe has an array of nine Faraday cup collectors, seven continuous dynode (channeltron) pulse counting detectors, and one pulse-counting Daly detector. The ion beam passing to the Daly detector, which is positioned along

the central ion-optic axis, is further energy filtered by a wide aperture retarding potential (WARP) filter to reduce the effects of tailing and scattered ions. Whenever possible, multiple detectors are used to measure isotopic composition by simultaneously collecting the ion beams from the different isotopes. This technique, called simultaneous multi-collection, results in highly precise isotope ratios because variations in the ion beam are seen simultaneously on each of the detectors. Ion beam currents are generally integrated for a total of 100 to 300 seconds, and are recorded as 20 or 30 separate integrations (cycles) of 5 or 10 seconds each. Background is measured on a sample of blank 2% nitric acid prior to sample analysis and standards are measured to determine the mass bias correction and any necessary detector cross-calibration factors (gain factors). The sample data are corrected by background subtraction and for detector gains. Cycle by cycle ratios are calculated and then corrected for mass bias.

4.0 INTERFERENCES AND LIMITATIONS

4.1 SAMPLE MATRIX

Samples for the IsoProbe must be especially pure, as microgram levels of common matrix elements like Ca and Fe can affect the mass bias for elements like uranium and plutonium. The mass bias correction factors determined on pure standard solutions may not accurately reflect the actual mass bias for contaminated samples. Additionally, all samples and standards should be analyzed in the same acid matrix (*i.e.*, 2% nitric acid), because even slight amounts of other acids, for example, trace hydrofluoric acid or sulfuric acid, produce variations in mass bias and can have deleterious effects on sample introduction equipment.

4.2 HYDRIDES and OXIDES

Hydrides and oxides (single hydrogen and single oxygen additions to metal ions), with +1 charge are formed in the ICP torch from the air and water introduced with the sample. In the IsoProbe, these potential interference cluster-ions are significantly reduced in the hexapole/collision cell by collisions with argon. Oxide interferences with uranium and plutonium isotopes are essentially non-existent, but it is possible that Pb-O-O clusters may occur in samples extremely contaminated with lead. Hydrides, on the other hand are more common. For example, $^{238}\text{U-H}$ on ^{239}Pu , $^{235}\text{U-H}$ on ^{236}U , and $^{239}\text{Pu-H}$ on ^{240}Pu are all present at the 1 ppm level. Except for plutonium samples that are extremely contaminated with ^{238}U , corrections for hydride formation are insignificant. The presence of mass 238 in the plutonium mass spectra is monitored and if mass 238 is present at high levels, uranium is confirmed by measuring 238/235. In this case, additional purification of the plutonium fraction may be required.

4.3 ARGIDES

Argides (single argon additions to metal ions), with +1 charge are also formed in the ICP torch. Only argides of platinum or mercury will form interferences

affecting uranium and plutonium, and these metals are generally well separated during purification. While most argides are efficiently removed in the IsoProbe hexapole/collision cell, some argides may also form there. For example, Au-Ar at mass 237 is formed from interaction of the argon plasma with the gold plating on the hexapole rods. Although different rod materials for the hexapole are being considered, at present, the high background at mass 237 prevents the analysis of low-levels of ^{237}Np with the IsoProbe. Also, Pt tipped cones are not recommended for uranium analyses due to formation of Pt argides at the masses of most uranium isotopes. Instead, standard Ni or Al cones are used for uranium and plutonium analyses.

4.4 OTHER ISOBARICS

In special cases, it is possible to measure ^{238}Pu with the IsoProbe, assuming ^{238}U has been almost completely removed from the Pu sample. Even so, measurement of the ^{235}U and knowledge of the $^{238}\text{U}/^{235}\text{U}$ ratio of the sample is necessary to correct the signal at mass 238 for residual uranium contamination.

4.5 RADIOACTIVITY LIMIT

The current limit for handling radioactive material outside of a fume hood in the mass spectrometry laboratory is one microcurie. This limit applies to samples introduced into the IsoProbe. However, activity introduced into the IsoProbe should be kept below about 10^6 dpm, or approximately one-half this limit, to prevent contamination.

5.0 APPARATUS AND MATERIALS

- 6.1 IsoProbe multi-collector ICP-MS (GV Instruments, Inc.)
- 6.2 Cetac Aridus sample introduction system (Cetac Instruments, Inc.)
- 6.3 Cetac ASX-100 autosampler (Cetac Instruments, Inc.)
- 6.4. Polyethylene sample cups, 1.5 ml capacity (Elkay)

6.0 STANDARDS AND REAGENTS

- 6.1 2% nitric acid (vol/vol) prepared from Seastar concentrated nitric acid and ASTM Type II reagent grade water (Seastar Chemical Co.; Milli-Q water, 18 Mohms)
- 6.2 5% nitric acid (vol/vol) prepared from Seastar concentrated nitric acid and ASTM Type II reagent grade water (Seastar Chemical Co.; Milli-Q water, 18 Mohms)
- 6.3 5% nitric acid (vol/vol) + 0.01 M hydrofluoric acid prepared from Seastar concentrated acids and ASTM Type II reagent grade water (Seastar Chemical Co.; Milli-Q water, 18 Mohms)
- 6.4 Natural uranium standard, about 15 ppb, prepared from either NIST SRM 4321C uranium radioactivity solution or NBL CRM 112-A uranium metal standard. These are isotopically equivalent, as both are NBS 960 natural uranium metal.

This standard solution is used to determine the mass bias and relative detector gain factors for uranium analyses.

- 6.5 Isotopic uranium quality control (QC) solutions. These solutions are either prepared from the original NBS materials, or they are the same materials issued by New Brunswick Laboratory (NBL CRMs). Routinely, solutions of both U010 and U005, are used for QC check standards.
- 6.6 NBL CRM 128 Pu isotopic standard. This standard has certified $^{239}\text{Pu}/^{242}\text{Pu}$ of approximately 1.0. Solutions prepared from this CRM are used to determine mass bias and relative detector gain factors for plutonium analyses.
- 6.7 Isotopic plutonium quality control (QC) solutions. These solutions are either prepared from the original NBS materials, or they are the same materials issued by New Brunswick Laboratory (NBL CRMs). Routinely, solutions of NBS SRM 948 (equivalent to NBL CRM 138), are used for QC check standards.

7.0 SAMPLE PRESERVATION AND HANDLING

Samples are analyzed on an 'as received' basis and it is the responsibility of the requestor of the isotopic analyses to arrange for sample preservation and for chemical purification of the element of interest. Only separated elements having a high level of purity may be analyzed with the IsoProbe.

8.0 HEALTH AND SAFETY

This procedure describes activities authorized under Integrated Work Sheet (IWS) 11762 entitled "IsoProbe". Reggie Gaylord is the authorizing individual of this IWS for Chemistry & Materials Science, Chemical Biology & Nuclear Science Division, and Ross Williams is the responsible individual.

9.0 PROCEDURE

Examples of isotopic analyses of uranium and plutonium with the IsoProbe are given below. Isotopic analyses of other elements are made using the same general principles.

9.1 INSTRUMENT OPERATION

Operation of the IsoProbe and acquisition of accurate isotopic composition data requires both a high level of expertise in inorganic mass spectrometry and extensive experience with the instrument itself. That level of expertise and experience is assumed.

9.2 URANIUM ISOTOPIC ANALYSES

- 9.2.1 Samples for isotopic uranium analyses that have been purified for mass spectrometry are dissolved in 3 mL of 2 % nitric acid.
- 9.2.2 Although estimates of the uranium content of the samples are generally available, additional dilutions of the sample solutions are prepared in 1.5 mL polyethylene auto-sampler vials. Generally, 100-fold or 1000-fold dilutions are prepared for initial testing to ensure that the concentration of uranium in the solution introduced to the IsoProbe is less than about 30 ppb. Using readings of the uranium beam intensities from these test solutions, dilutions of the sample are prepared which will give beam intensities of 4 to 7 volts for the most abundant uranium isotope; usually ^{238}U .
- 9.2.3 Standards of natural uranium and QC check samples are prepared to give ^{238}U beam intensities in the range of 4 to 7 volts.
- 9.2.4 Data acquisition programs are selected or created specifically for collection of isotope ratio data using simultaneous multi-collection techniques wherever possible. Generally, Faraday cups are used to determine the intensities of beams from ^{233}U , ^{235}U and ^{238}U and the pulse-counting Daly detector is used to measure the lower intensity beams from ^{234}U and ^{236}U . Utilization of the Daly detector for these isotopes is accomplished by collecting data using two different programs, both in static multi-collection mode.
- 9.2.5 Analyses of 2 % nitric acid using the same data acquisition programs that are used for the sample analysis are made before each sample and subtracted from the sample peak intensities.
- 9.2.6 Analyses of the natural uranium standard (U-Nat) are made at the beginning and end of each batch of samples. U-Nat is also analyzed periodically within the batch, and no more than eight samples are ever analyzed consecutively between analyses of U-Nat. The widely accepted $^{238}\text{U}/^{235}\text{U}$ atom ratio of 137.88 for U-Nat (NBS SRM 960) is used to determine the instrumental mass bias. A formulation of the exponential mass fractionation law is used to calculate average mass bias correction factors for each measured ratio. Corrected isotope ratios are calculated by multiplying the measured ratio by these average correction factors (see calculation section below).
- 9.2.7 The U-Nat analyses are also used to determine the detector cross-calibration factor for the Daly detector relative to the Faraday detector. This factor, denoted the Faraday/Daly gain, is determined using the ^{234}U beam on the Daly detector relative to the simultaneously measured ^{235}U beam on the Faraday detector.
- 9.2.8 Unknown samples are analyzed using the selected data acquisition programs. Between sample analyses, a rinse of the sample inlet system is accomplished by introduction of 2% and then 5% nitric acid for several minutes each. The rinse-out time required to reduce the carry-over signal from the previous sample to blank levels will depend on the sample signal intensities. This time is determined during set up and incorporated in the

analytical protocol. The effectiveness of the rinse-out is determined by measuring the blank intensities as called for in step 9.2.5.

- 9.2.9 Standard reference materials for isotopic uranium are analyzed using the same data acquisition programs as for the samples. At least one of these QC check samples is analyzed for each batch of samples, and no more than eight unknown samples are analyzed before or between the QC check analyses.

9.3 PLUTONIUM ISOTOPIC ANALYSES

- 9.3.1 Samples for isotopic plutonium that have been purified for mass spectrometry are dissolved in 3 mL of 2 % nitric acid.
- 9.3.2 Test dilutions of the Pu sample solutions are prepared in 1.5 mL polyethylene auto-sampler vials. Generally, 100-fold or 1000-fold dilutions are prepared for initial testing to ensure that the concentration of plutonium in the solution introduced to the IsoProbe is less than about 10 ppb. Using readings of the plutonium beam intensities from these test solutions, dilutions of the sample are prepared which will give maximum beam intensities for Pu, no more than about 5 volts for the most abundant isotope; generally ^{239}Pu .
- 9.3.3 Because Pu concentrations are often limited and because high precision isotope ratios depend on maximizing the beam intensities, it is often the case that Pu samples will be analyzed from their original dilutions. The initial 3 mL dilution provides enough volume to repeat the analysis at least one more time if necessary.
- 9.3.4 Data acquisition programs for Pu are selected or created specifically for collection of isotope ratio data using simultaneous multi-collection techniques wherever possible. The option of controlling the beam intensity for Pu by dilution is rare. Instead, working with the beam intensities in the original dilutions, three different data acquisition techniques are most common. From lowest to highest intensity these are: (1) simultaneous pulse counting of all isotopes using channeltron detectors; (2) simultaneous Faraday/Pulse-counting, where only the major isotope(s) ^{239}Pu and ^{240}Pu are collected with the Faraday detector; and (3) simultaneous Faraday multi-collection. Hybrids of these techniques, for example, simultaneous Faraday/Pulse-counting with peak jumping (the so-called multi-dynamic approach) are also quite useful.
- 9.3.5 Solutions of CRM 128 Pu for determination of instrumental mass bias and detector gain calibration and of NBS SRM 948 Pu for QC check samples are prepared at appropriate concentrations to match the beam intensities of the samples.
- 9.3.6 Analyses of 2 % nitric acid using the same data acquisition programs that are used for the sample analysis are made before each sample and subtracted from the sample peak intensities.
- 9.3.7 Analyses of CRM 128 are made at the beginning and end of each batch of samples. CRM 128 may also be analyzed periodically within the batch,

and no more than eight samples are ever analyzed consecutively between analyses of CRM 128. The certified $^{239}\text{Pu}/^{242}\text{Pu}$ atom ratio of CRM128 is used to determine the instrumental mass bias. A formulation of the exponential mass fractionation law is used to calculate average mass bias correction factors for each measured ratio. Corrected isotope ratios are calculated by multiplying the measured ratio by these average correction factors.

9.3.8 Detector cross-calibration factors for the Daly detector relative to the Faraday detector, or for the channeltron detectors relative to the Daly detector are made using CRM 128 or by peak-jumping a ^{239}Pu beam of appropriate magnitude on the different detectors.

9.3.9 Unknown samples are analyzed using the selected data acquisition programs. Between sample analyses, a rinse of the sample inlet system is accomplished by introduction of 2% and then 5% nitric acid + 0.01 M HF solution for several minutes each. The rinse-out time required to reduce the carry-over signal from the previous sample to blank levels will depend on the sample signal intensities. This time is determined during set up and incorporated in the analytical protocol. The effectiveness of the rinse-out is determined by measuring the blank intensities as called for in step 9.3.6.

9.4 CALCULATIONS, DATA ANALYSIS AND REPORTING

9.4.1 Calculations

Isotope ratio data are calculated from the beam intensity data in three steps. First, the raw intensities are corrected by subtracting background intensities as measured on the blank 2% nitric acid and are corrected by the appropriate relative detector gain factors. Second, the required ratios are calculated; and third, the ratios are corrected for instrumental mass bias (see below). Uncertainties on these ratios at the 95% confidence level (2-sigma) are calculated from the standard error on the mean of the replicate ratio analyses (n = number of cycles), the dispersion on the mass bias determinations, and an estimate of the uncertainty due to blank subtraction obtained from counting statistics. For spiked analyses, concentrations of isotopes or elements are calculated from the sample size and spike data.

The blank-corrected isotope ratios are corrected for instrumental mass bias using the exponential mass fractionation law as follows:

$$R_{Corrected}^{x/y} = R_{Measured}^{x/y} \left(\text{mass } x / \text{mass } y \right)^{\beta}$$

where R is the atomic ratio of isotope x to isotope y , and $\text{mass}_x/\text{mass}_y$ is the ratio of their atomic weights. In practice, mass numbers may be used instead of exact masses. The exponential factor, β , is determined from analyses of standards.

$$\beta = \frac{\ln(R_{Standard}^{a/b} / R_{Measured}^{a/b})}{\ln(mass_a / mass_b)}$$

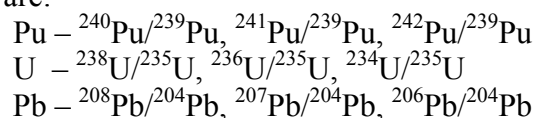
Where the atomic ratio of isotope *a* to isotope *b* in the standard is the known or accepted value.

9.4.2 Data Analysis

Data analysis is the primary responsibility of the requestor of the analyses.

9.4.3 Reporting

Isotopic data are reported in standard formats; generally as atomic ratios relative to a common isotope. Examples of some of these standard formats are:



Report format may be tailored specifically by instructions from the requestor, or by the mass spectrometrists based on expert knowledge and the stated or anticipated use of the data. The units for elemental or isotope concentrations that are calculated from spiked samples are clearly labeled. Uncertainties on each value are reported at the 95% confidence level (i.e., 2-sigma). The QC samples analyzed with each batch are reported with their certified values. Reports are generally transmitted electronically as Excel files. Tables and graphs may also be embedded within Word documents and transmitted electronically also.

10.0 QUALITY CONTROL

- 10.1 Standard reference materials for isotopic uranium are analyzed using the same data acquisition programs as for the samples. At least one of these QC check samples is analyzed for each batch of samples, and no more than eight unknown samples are analyzed before or between the QC check analyses.
- 10.2 NBS SRM 948 Pu standard is analyzed using the same data acquisition programs as for the samples. At least one of these QC check samples is analyzed with each batch of plutonium samples, and no more than eight unknown samples are analyzed before or between the QC check analyses.
- 10.3 The uncertainty on the mass spectrometry results for the QC sample analyses must overlap with the uncertainties on the certified value. If, for any reason, these results do not overlap, the QC analyses have failed, the results are out-of-control and this fact must be pointed out in the data report and explained. Out-

of-control analyses may require that the entire batch of samples be re-analyzed. Determination of whether this is necessary will be made after consultation with the requestor. The mass spectrometry laboratory keeps records of the quality control analyses made with each batch of samples.

11.0 METHOD PERFORMANCE

Highly precise isotope ratio results are obtained with multi-collector ICP instruments. The accuracy of these results depends on the accuracy of the isotope ratio standards that are available for individual elements. All inter-comparisons that have been made with other techniques, for example, thermal ionization mass spectrometry, indicate comparable or enhanced performance by MC-ICPMS.