An inter-comparison exercise on the application of ICP-MS techniques for measurement of long-lived radionuclides

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Abstract

Inductively coupled plasma (ICP) spectrometry techniques are widely used in the fields related to environmental monitoring, nuclear waste disposal and management, radioecology and tracer studies, as well as nuclear forensics and nuclear emergency preparedness. Especially ICP mass spectrometry (ICP-MS) is playing an important role for determination of low-level long-lived radionuclides and their isotopic ratios. ICP optical emission spectrometry (ICP-OES) is commonly used for determining stable elements (Al, Fe, Ca, etc.) and cannot perform isotopic ratio measurement with desirable precision and at low analyte concentrations. Therefore ICP-OES is often used as a supplementary technique to ICP-MS in the analysis, for instance, to screen the matrix composition of a sample, or to determine Sr and Y chemical yield in the Sr-90 analysis, etc.

Among the Nordic countries, there are probably less than 20 ICP-MS instruments which are currently applied in the nuclear field for the measurement of radionuclides and their isotopic ratios. Due to different application purposes and technical background of the analysts, each ICP lab has different set-ups and experiences in running these instruments. More efficient application of ICP-MS will be achieved when these experiences are well shared among these labs. Also, for newly established ICP labs or scientists/students in the Nordic countries to quickly build up the competence in operating their instruments in practice, hands-on experience is very valuable. Therefore, within the Nordic-ICP project, an inter-comparison exercise was performed during 2016, which was focused on the measurement of uranium and plutonium isotopes in certified reference material by ICP-MS in combination with radiochemical separation. This report summarizes the results and conclusions obtained base on this inter-comparison exercise.

Key words

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Introduction

Inductively coupled plasma (ICP) spectrometry techniques are widely used in the fields related to environmental monitoring, nuclear waste disposal and management, radioecology and tracer studies, as well as nuclear forensics and nuclear emergency preparedness. Especially ICP mass spectrometry (ICP-MS) is playing an important role for determination of low-level long-lived radionuclides and their isotopic ratios. ICP optical emission spectrometry (ICP-OES) is commonly used for determining stable elements (Al, Fe, Ca, etc.) and cannot perform isotopic ratio measurement with desirable precision and at low analyte concentrations. Therefore ICP-OES is often used as a supplementary technique to ICP-MS in the analysis, for instance, to screen the matrix composition of a sample, or to determine Sr and Y chemical yield in the Sr-90 analysis, etc.

Among the Nordic countries, there are probably less than 20 ICP-MS instruments which are currently applied in the nuclear field for the measurement of radionuclides and their isotopic ratios. Due to different application purposes and technical background of the analysts, each ICP lab has different set-ups and experiences in running these instruments. More efficient application of ICP-MS will be achieved when these experiences are well shared among these labs. Also, for newly established ICP labs or scientists/students in the Nordic countries to quickly build up the competence in operating their instruments in practice, hands-on experience is very valuable. Therefore, within the Nordic-ICP project, an inter-comparison exercise was performed during 2016, which was focused on the measurement of uranium and plutonium isotopes in certified reference material by ICP-MS in combination with radiochemical separation. The participating institutes in this inter-comparison exercise included FOI CBRN Defence and Security, Sweden; Center for Nuclear Technologies (Nutech), Technical University of Denmark (DTU), Denmark; Laboratory of Radiochemistry, University of Helsinki (UH), Finland; Centre for Environmental Radioactivity, Norwegian University of Life Sciences (NMBU) Norway; ALS Life Sciences Division, ALS Scandinavia AB, Luleå, Sweden, and Department of Chemistry, Norwegian University of Science and Technology (NTNU), Norway

DTU Nutech has one ICP-QQQ triple quadrupole ICP-MS (Agilent 8800), one quadrupole ICP-MS (X-II series, Thermo Scientific) and one ICP-OES (VISTA AX, Varian). The two ICP-MS are used for low-level environmental samples. Different sample introduction systems are used including Apex Q, Ultrasonic nebulizer (U5000AT+, CETAC) and Scott-type double-pass spray chamber together with concentric nebulizer depending on the sample type

and radionuclides interested. The quadrupole ICP-MS was installed in 2003. The ICP-QQQ was installed in 2015, and currently Ni-tipped cone together with x-lens is used for measurement of long-lived radionuclides (mostly actinides). The ICP-OES is most often used for determinations of stable elements including calcium, aluminum, sulfur, etc., as well as the yield determination for yttrium purification in Sr-90 analysis.

The radio-analytical laboratory at FOI is equipped with two ICP-SFMS (Element 2 and Element XR, Thermo Scientific) and one ICP-OES (iCAP 7400, Thermo Scientific), apart from the radiometric instrumentation. ICP-MS is used for the determination of long-lived radionuclides and a large range of elements, as well as for isotope ratio measurements. The two ICP-SFMS are used for different samples, one is dedicated for low level samples and the other one is mainly used for samples with tougher matrices. Different sample introduction systems are used depending on the application of interest. Most commonly, a Twister spray chamber and a Conikal nebulizer is used together with a demountable torch, equipped with a quartz injector, and nickel cones (all from GlassExpansion, Melbourne, Australia). For some applications where oxide and hydroxide formation are necessary to keep as low as possible, ARIDUS II (Teledyne CETAC Technologies, Omaha, NE, USA) is used in order to achieve a dry plasma. The ICP-OES is most often used for yield determinations of strontium and yttrium.

ALS currently operates 13 ICP-SFMS (HR-ICP-MS, ELEMENT, ELEMENT2 and ELEMENT XR, all from ThermoScientific), 2 MC-ICP-MS (NEPTUNE and NEPTUNE PLUS, all from ThermoScientific), 3 ICP-OES and multitude of sample preparation/separation methods.

NTNU has two ICP-MS instruments. One is ICP-SFMS Element 2 from Thermo 2004 model. Sample introduction system includes SC2 DX auto sampler (Elemental Scientific) with prepFAST 400 inline dilution system, PFA nebulizer and PFA cyclonic spray chamber with Peltier cooling from ESI, sapphire demountable torch and Al skimmer and sample cones. The other is ICP-QQQ triple quadrupole ICP-MS (Agilent 8800), 2016 model. The sample introduction system used most often includes an SC2 DX auto sampler (Elemental Scientific) with prepFAST 500 inline dilution system, PFA nebulizer and quartz Scott spray chamber with Peltier cooling, quartz torch and Ni skimmer and sample cones.
NTNU has experience in U and Pu isotope measurements as well as in environmental and biological samples. The ICP-SFMS instrument at NTNU is used for analyses of various

elements in different matrices covering surface water, sea water, silica, oil, vegetation, animal tissues, feather, sediments, soil. NTNU also carries out Pb-isotopic measurement in sediment.

UH has access to Q-ICP-MS (Agilent 7800), MC-ICP-MS (Nu Plasma from Nu Instruments) and SF-ICP-MS (AttoM from Nu Instruments) for measurement of natural radionuclides (e.g., uranium isotopes) as well as anthropogenic radionuclides (e.g., ^{240}Pu, ^{239}Pu). The Q-ICP-MS has newly arrived; both MC-ICP-MS and SF-ICP-MS have been previously used for uranium isotope measurements.

At NMBU three ICP-QQQ triple quadrupole ICP-MS (Agilent 8800) are utilized for the determination of long-lived radionuclides and a large range of elements, as well as for isotope ratio measurements. At very low concentration levels, AMS in Australia or Spain is utilized.

This report summarizes the results and conclusions obtained base on this inter-comparison exercise.

Experiment

Materials

A certified reference material NBL CRM 103-A Pitchblende Ore – Silica Mixture Uranium Standard (U 0.04992 ± 0.00078 Wt.%) from New Brunswick Laboratory (NBL) was used in the inter-comparison exercise to perform the uranium isotopic ratios (^{234}U/^{235}U, ^{235}U/^{238}U, ^{234}U/^{238}U) measurement. This material was prepared by milling and blending NBL CRM 6-A Pitchblende Ore (67.91 ± 0.05 Wt.% U_3O_8) with silica (99.9% SiO_2) to obtain a uniform mixture of desired uranium concentration. NBL CRM 103-A is not certified for uranium isotope amount ratios, but the material has natural uranium isotopic composition, hence the IUPAC observed range of natural variations for uranium[10] has been used in this inter-comparison. A certified reference material IAEA-384 Fangataufa Lagoon sediment was used for determination of the concentration of ^{239}Pu and ^{240}Pu and their isotopic ratio. This material was collected by IAEA-MEL in July 1996 in Fangataufa Lagoon (French Polynesia), where nuclear weapon testing had been carried out.

Sample preparation for uranium isotope ratio measurements

At DTU Nutech, prior to the ICP-MS measurement for uranium isotopic ratios, 50-100 mg of NBL CRM 103-A was dissolved using about 2 ml of concentrated HF and 2 ml of concentrated HNO_3 with addition of 200 µl of concentrated HCl. Thereafter the NB CRM 103-A solution was diluted with 0.3-0.5 M HNO_3 to an appropriate concentration.

At FOI, about 100 mg of NBL CRM 103-A was dissolved in 2 ml of concentrated HF, 2 ml concentrated HNO_3 and 200 µl of concentrated HCl. Thereafter the NBL CRM 103-A solution was diluted in 0.28 M HNO_3 to appropriate concentration.

At ALS, MW-assisted digestion using HNO_3+HF mixture was used for the sample preparation: 50 mg of NBL CRM 103-A or 250 mg of IAEA-384 were dissolved with 2 milliliter of concentrated HF and 2 ml concentrated HNO_3 in closed Teflon vessels at 600 W RF power for 25 minutes. Digests were evaporated to dryness and re-dissolved in 0.3 M HNO_3. Thereafter the NBL CRM 103-A solution was diluted in 1.4 M HNO_3 to appropriate concentration.

AT NTNU, the sample was diluted down to appropriate concentration, in the preliminary test, only with 0.1M HNO_3. However, the sample solution obtained was not clear, and analytical result was very unstable with high deviation, indicating that the solution was inhomogeneous. Afterwards, the sample was diluted with 0.5 M HNO_3 + 0.25% v/v HF, wherein clear solutions were obtained. For the ICP-MS measurement, two sample solutions with different concentrations (approx. 50 and 350 µg/l) were made.

At NMBU, approximately 0.08 g of NBL CRM 103-A (n=3) were digested in PTFE tubes with 2.5 ml of concentrated nitric acid for 40 minutes at 260 degrees C in an UltraWave from Milestone. The samples were diluted to 25 ml with de-ionized water after digestion. The U_3O_8 is soluble and the SiO_2 is only slightly soluble in this procedure.

At UH, 0.002 g of pitchblende NBL CRM 103-A was weighed to a Teflon beaker and 5 ml of conc. HNO_3 (s. p.) was added. The mixture was nearly boiled for 2 hours. The solution was filtered through a membrane filter (Acrodisc® Syringe Filter, 0.2 µm Supor® Membrane, Pall Life Sciences) and diluted to 100 ml with H_2O. This solution was ready for measurements. Two subsamples of this solution were measured.

Pre-separation of IAEA-384 for plutonium measurement

Plutonium contained in IAEA-384 material was pre-separated at DTU and distributed to participating institutes for measurement. The chemical separation procedure for purification of plutonium at DTU is summarized as follows. 2 g of IAEA-384 sediment was spiked with 0.2528g of 0.1037 Bq/kg ^{242}Pu tracer and dissolved directly with 20 ml of 8 M HNO_3. A 4 ml of anion exchange column was packed and preconditioned with 20 ml of 8 M HNO_3. The dissolved sample solution was loaded onto the anion exchange (AG 1×4, 50-100 mesh) column, and the column was washed with 60 ml of 8 M HNO_3 followed by 40 ml of 9 M HCl.

The Pu was eluted with 50 ml of 0.5 M HCl and the eluate was evaporated to dryness. The Pu residue was dissolved with 12 ml of 0.5M HNO_3, and each 2 ml of aliquot was transferred to a scintillation vial and delivered to ICP-MS measurement in each institute.

Radiochemical separation for IAEA-384

Raw IAEA-384 material was also processed in participating institutes to perform the inter-comparison of radiochemical analysis for Pu determination. The radiochemical separation procedures used in this inter-comparison are summarized below.

At DTU, 0.2 g of IAEA-384 sediment was spiked with 0.1g of 0.1037 Bq/kg ^{242}Pu tracer and digested with 40 ml aqua regia at 200 °C for 2 hours. After filtration, 1 mg of Fe was added to form $Fe(OH)_3$ co-precipitation with the addition of NH_3 to pH 8-9. After centrifugation, the residue was dissolved with 2 ml conc. HCl and diluted to 100 ml. In total of 300 mg of $K_2S_2O_5$ was added with stirring for 20 min. to reduce Pu to Pu(III). NH_3 was added to adjust the sample to pH 8-9 and the precipitate was centrifuged. 3 ml of concentrated HNO_3 was added to dissolve the residue and the sample was finally adjusted to 3 M HNO_3 for chromatographic purification. 2 of TEVA (100-150 µm) column was packed and preconditioned with 20 ml of 3 M HNO_3. The dissolved sample solution was loaded onto the TEVA column, and the column was washed with 60 ml of 8 M HNO_3 followed by 40 ml of 9 M HCl. The Pu was eluted with 50 ml of 0.5 M HCl and the eluate was evaporated to dryness. The Pu residue was dissolved with 5 ml of 0.5M HNO_3, and measured with ICP-QQQ instrument.

At FOI, the reference material IAEA-384 was first checked for moisture content. 1 g of IAEA-384 sediment was mixed with 3 g lithium metaborate ($LiBO_2$, Claisse, ultra-pure grade, Gammadata, Uppsala, Sweden) and thereafter spiked with about 10 pg of ^{242}Pu (NIST SRM 4334G). The sample mixture was first pre-oxidized at 650°C for 1 hour prior to fusion for 15 minutes at 1050°C. The melt was allowed to cool before mixing with 100 ml of 1.4 M HNO_3 and thereafter the melt was dissolved under stirring and heat. When dissolved, PEG2000 was added to a concentration of 0.0002 M and thereafter the sample volume was evaporated to half the volume, leading to a sample matrix of 2.8 M HNO_3. The sample was left over night to allow silica to flocculate and thereafter the sample was filtrated using filter paper (Munktell filter paper No. 00M). The sample filtrate was heated to 90°C and thereafter 375 mg NH2OH·HCl was added. After cooling, 900 mg $NaNO_2$ was added to assure that all plutonium was oxidized to Pu(IV). 2 ml TEVA (Triskem) columns were packed in-house by

in 3 ml cartridges (Isolute reservoir 3 ml, Biotage, Uppsala, Sweden). 20 µm polyethene frits (Biotage) were used to keep the TEVA resin in the reservoir. The column was pre-conditioned with 5 ml 3 M HNO_3 and then the sample was added. The column was rinsed with 10 ml 3 M HNO_3, followed by 10 ml of 9 M HCl and 20 ml 3 M HNO_3. Plutonium was eluted in 5 ml 0.01% hydroxylethylidene diphosphonic acid (HEDPA, purum, Merck Millipore, Stockholm, Sweden). The eluted plutonium was measured with an Element XR ICP-SFMS with the RPQ filter activated.

At UH, three parallel subsamples (about 1 gram of each) of IAEA-384 reference sediment were weighed. 26 mBq (177 pg) of [242]Pu was added to each sample as a yield tracer. The samples were dissolved with the mixture of conc. HNO_3 (30 ml) and HCl (10 ml) on a hotplate for 6 hours. The sample solution was filtrated and evaporated to dryness. Radiochemical separation of Pu from the disturbing matrix and other radionuclides was performed according to the method described [1]. In general, after dissolving the sample in 10 ml of 1 M $Al(NO_3)_3$ + 3 M HNO_3, 2 ml of 0.6 M ferrous sulfamate solution and ~ 150 mg of ascorbic acid were added. After 15 minutes, the sample solution was loaded into UTEVA-column (preconditioned with 5 ml of 3 M HNO_3). The UTEVA column was washed with 10 ml of 3 M HNO_3. The effluent of the sample loading and washing solution were loaded onto a TRU column (preconditioned with 5 ml of 2 M HNO_3). The TRU column was washed with 5 ml of 2 M HNO_3, 5 ml of 0.1 M $NaNO_2$ + 2 M HNO_3, 3 ml of 0.5 M HNO_3, 2 ml of 9 M HCl, 20 ml of 4 M HCl and 10 ml of 0.1 M HF + 4 M HCl, respectively. Pu was finally eluted with 10 ml of 0.1 M $NH_4HC_2O_4$ and evaporated to dryness. 2 ml of conc. HNO_3 was added to the residue and re-evaporated into dryness. The separation procedure with UTEVA- and TRU-columns was repeated. After elution from TRU-column, the ammonium oxalate solution containing Pu was evaporated into dryness with addition of a few drops of H_2O_2 and conc. HNO_3 (s.p. grade). The residue was dissolved to 10 ml of 5 % HNO_3 (s.p.) and filtered through a membrane filter (Acrodisc® Syringe Filter, 0.2 µm Supor® Membrane, Pall Life Sciences). Blank samples were processed similarly with the sediment samples. Blank samples and acid blank of 5% HNO_3 were included to the measurement sample set. Two of three subsamples had very low radiochemical yield (< 10%).

At ALS, pre-packed 2 ml UTEVA columns were used for Pu separation from matrix. Briefly, digested, evaporated and re-dissolved IAEA-384 in 3M HNO_3 was loaded on columns followed by 12 ml 3 M HNO_3 and 4 ml 9.6 M HCl matrix wash followed by Pu elution in 8

ml of 5 M HCl+0.05M oxalic acid. ^{242}Pu spike (NIST SRM 4334G) was used as yield monitor of entire procedure.

At NMBU, Approximately 1 g of IAEA 384 (n=3) was weighed directly in to a PTFE digestion tube and added 12 mL of concentrated nitric acid and 4 mL of 48 % (w/w) hydrofluoric acid. 24.1 pg of ^{242}Pu was added as a yield monitor. The samples were digested (UltraClave IV, Milestone Ltd) at a temperature of 260 °C for 40 minutes. After digestion, the samples were transferred to PTFE beakers and left to evaporate to dryness on a sand-bath. Matrix separation was performed according to the method described in [2]. The eluate from the separation was evaporated to dryness, and taken up in 7 ml 0.8 M HNO$_3$ + 0.2 M HF for analysis. One sample was lost in the separation and one had very low yield (<10 %).

The pre-purified Pu sample was diluted 1+3 with 0.8 M HNO$_3$ + 0.2 M HF before analysis.

Instrumentation, measurement and calculations

DTU

At DTU Nutech, the instrumentation used throughout the work was an ICP-QQQ (Agilent 8800). Both uranium and plutonium measurement, standard introduction system consisted of MicroMist nebulizer and Scott-type double pass spray chamber, together with Ni skimmer cone and x-lens were used. Typical sensitivity of the instrument is about 0.7 cps per ppq of ^{238}U. The uptake of the sample was performed at a flow rate of 20 µL/min with a standard peristaltic pump equipped in the ICP-QQQ instrument. A ^{242}Pu standard solution was diluted from NBL-CRM 130 (New Burnswick Laboratory, Argonne, IL, USA). Standard solution of uranium were diluted to different levels from a 1000 ppm U standard (Scientific Standards) and used for calibration purposes. All standard solutions and samples were diluted to appropriate concentrations using MQ water (Starilum) and concentrated nitric acid (VWR).

For the measurement of uranium at DTU Nutech, the instrument was controlled for mass bias using the standard solution NBL-112a with a concentration of 50 ppb. The major isotope amount ratio $n(^{235}U)/n(^{238}U)$ was determined in a sample diluted to achieve a maximum intensity of 1 x 10^6 counts/s at m/z 238. The minor isotope amount ratio $n(^{234}U)/n(^{235}U)$ was measured in a sample diluted to achieve an intensity of about 1 x 10^6 counts/s at m/z 235 and thereafter amount ratio $n(^{234}U)/n(^{238}U)$ was calculated from the ratios of $n(^{235}U)/n(^{238}U)$ and $n(^{234}U)/n(^{235}U)$. For the measurement of plutonium, a 0.5 M HNO$_3$ as a blank, ^{242}Pu (4.09 ppt) standard and ^{238}U (1ppb) standard was measured in parallel with the purified Pu fraction (in

0.5 M HNO$_3$). 1 ppb In (as InCl$_3$) was added into each sample and used as an internal standard to calibrate the efficiency of instrument. The signal at m/z 240 and 242 were corrected for contributions from blank levels and the signal at m/z 239 was corrected for contributions both from blank and ^{238}UH. Mass bias correction was not performed for ^{239}Pu and ^{240}Pu, whereas average isotope amount ratios (n=5) of n(^{239}Pu)/n(^{242}Pu) and n(^{240}Pu)/n(^{242}Pu) were calculated based on the intensities measured by ICP-MS. Thereafter the activity concentration of ^{239}Pu and ^{240}Pu in the raw sample were calculated by multiplying the total amount of ^{242}Pu tracer spiked in the sample with ^{239}Pu/^{242}Pu and ^{240}Pu/^{242}Pu isotopic ratios, respectively.

FOI

At FOI, the instrumentation used throughout the work was an ICP-SFMS (Element XR, Thermo Scientific, Bremen, Germany). For the plutonium measurements, the retarding potential quadrupole lens of the ICP-SFMS was activated to reduce the peak tailing of the instrument, whilst for the uranium measurements the RPQ lens was inactivated. The instrument was tuned for maximum uranium intensity whilst keeping the uranium oxide formation as low as possible. The typical sensitivity is about 2 cps per ppq of ^{238}U with the RPQ lens inactivated. When using the instrument with the RPQ lens active, the typical sensitivity is decreased with about 10%, see Table 2. The automatic dead time correction was disconnected as this correction was performed post-acquisition. The sample introduction systems used consisted of a Conikal nebulizer, a Twister spray chamber, a standard torch and nickel cones (all from GlassExpansion, Melbourne, Australia).

For the determination of uranium and plutonium at FOI, the instrument was controlled for mass bias and spectral interference at m/z 239 from ^{238}U using the certified reference material IRMM-073/7 (IRMM, Institute for Reference Materials and Measurements, Geel, Belgium). IRMM-184 was used as a quality control sample. The raw data was extracted from the instrument to avoid non-linearity effects as published earlier [3] and data reduction thereafter was done off-line in order to correct detector dead time of the individual, averaged signal intensities. The detector dead time and its associated uncertainty, was determined to 73,1(1,4) ns, with the 70 ns nominal dead time setting on the ion detection board using IRMM-073/5 (IRMM, Institute for Reference Materials and Measurements, Geel, Belgium) by a method described by Appelblad and Baxter [4]. Following the dead time correction, the intensities were corrected for contributions from blank levels, and thereafter mass bias corrected ratios for $n(^{234}$U)/$n(^{238}$U), $n(^{235}$U)/$n(^{238}$U), $n(^{240})$Pu/$n(^{239})$, $n(^{239})$Pu/$n(^{242})$ and $n(^{240})$Pu/$n(^{242})$Pu were

calculated using the Russell equation [5]. For the separated plutonium sample, the signal at m/z 239 was also corrected for contributions from ^{238}UH and peak tailing from ^{238}U prior to mass bias correction. The reported results for ^{239}Pu and ^{240}Pu were corrected for moisture in IRMM-384. All uncertainties were evaluated in accordance with ISO/GUM (1995) using the software GUM Workbench [GUM].

ALS

At ALS Luleå lab, ICP-SF-MS (ELEMENT XR, Thermo Scientific) was used for both plutonium and uranium measurement in this work. For the uranium ratio measurement, a 'Stable' sample introduction system (from MC-ICP-MS NEPTUNE) equipped with a Micromist nebulizer and standard cones were used. RPQ (Retarding Potential Quadrupole) lenses was activated to improve abundance sensitivity. This set-up offers a typical sensitivity of 1.2 cps per ppq of ^{238}U and ^{238}U/^{238}U^{1}H ratio of >60 000. For the plutonium isotope measurement, Apex introduction system equipped with a PFA nebulizer and X skimmer cone was used. RPQ was also activated with a typical sensitivity of > 6 cps per ppq for ^{238}U. Standard solutions of U0002 CRM, IRMM-184, CRM130 and 1000-ppm U standard (Scientific Standards) were used for tailing and spectral interference corrections as well as for calibration purposes.

At ALS, mathematical corrections for UH and tailings was performed based on experimental factors deduced by analyzing U0002 CRM. Mass bias was assessed using IRMM-184 (natural U). Concentration was determined using external calibration with diluted CRM130 (Pu) and Scientific Standards 1000 ppm U solutions.

UH

Two ICP-MS instruments at the Geological Survey of Finland (GTK), Espoo, were used in this inter-comparison for UH, including Nu AttoM Single-Collector ICP-MS and Nu Plasma Multi-Collector ICP-MS (Nu Instruments Ltd., Wrexham, UK). Both instruments have been used for measuring uranium isotopes from solid and liquid samples, but no previous attempt for measuring plutonium isotopes had been made. Assumed limit of detection (LOD) was < 20 ppq for Pu and U before the sample measurements.

Nu AttoM Single-Collector ICP-MS instrument was used for determination of ^{239}Pu and ^{240}Pu. The sample introduction system consisted of an autosampler, peristaltic pump,

Meinhard nebulizer and a cyclonic spray chamber without cooling. Nickel skimmer and sampler cones were used and the typical sensitivity for ^{238}U is 2 cps per ppq.

In determination of ^{240}Pu and ^{239}Pu, the samples have been bracketed using a CPI^{TM} single element solution of 1ppb of U in 2% HNO_3, meaning that the U standard solution was measured between every sample measurement. A blank has been measured before every sample and standard. Analyses were performed in deflector jump mode using 80 sweeps of 500 cycles at low resolution. The following isotopes have been measured: ^{238}U, ^{235}U, ^{239}Pu, ^{240}Pu, ^{242}Pu and half masses at 239.5 and 240.5. The dwell time was 1ms for each isotope. Washing time was 120 s and a further 60 s of sample uptake was allowed before measurement started. The results have been calculated using an in house excel data reduction program. The natural ratio of ^{238}U/^{235}U has been used to calculate the mass bias and tailing and applied for correcting ^{240}Pu/^{239}Pu.

A linear regression through the half mass 239.5 and 240.5 was made, to calculate the tailing on ^{239}Pu and ^{240}Pu. The acid blank was subtracted from the counts. The fractionation factor was calculated, based on the ^{235}U/^{238}U ratio (set at 0.0072527). The fractionation factor was used to correct for the mass bias on ^{240}Pu/^{239}Pu ratio.

The undiluted subsamples of pitchblende have been analyzed for U isotopes using the NBL112a standards [7] diluted down to 30 ppb, into a disposable 2ml beaker in 1.0 to 1.5 ml of 2% HNO_3. The analyses were carried out by using a desolvator nebulizer and an 80μl Meinhard concentric quartz nebulizer.

The analyses of uranium isotopes were carried out by using a Nu Plasma Multi-Collector ICP-MS (Nu Instruments^{TM}) at low mass resolution ($\Delta m/m = 400$). The uranium measurements were performed in dynamic mode and consists of 1 block of 12 integrations of 15s (2 cycles for the two isotopes ratio) and 1s (3 cycles for the tail corrections). A 5 min wash using HNO_3 (2%) has been used between U isotopes measurements. Two Faraday detectors have been used for ^{238}U and ^{235}U and one ion counter has been used for ^{234}U, ^{233}U and tail corrections in U isotope measurements. The samples have been standard bracketed using the NBL112a standard [7] in order to correct for mass fractionation and Faraday cup to ion counter gain. The nonlinearity of the ion counter is known to vary in time and should thus be checked at regular intervals (at least twice a year). Peak tailing has been corrected using an exponential function after dynamic measurements at three different half-masses 232.5, 233.5 and 234.5 on the same ion counter used for the determination of ^{234}U and ^{233}U. The international uranium standard UO10 has been used for quality control at the beginning and at the end of each run.

NTNU

At NTNU, ICP-SFMS (Element 2, Thermo) was used for uranium measurement. The sample introduction system included an SC2 DX auto sampler (Elemental Scientific) with prepFAST 400 inline dilution system, PFA nebulizer, PFA cyclonic spray chamber with Peltier cooling from ESI, and sapphire demountable torch. Al skimmer and sample cones were used for the measurement. The typical sensitivity was approx. 0.8 cps per ppq for ^{238}U. ^{235}U and ^{238}U was measured in analog mode, and ^{234}U was measured in counting mode. The UH$^+$ formation at m/z=236 from ^{235}U was approx. 0.01%. At NTNU, two subsamples were measured after dissolution with HF. For mass bias correction, IRM-184 was used with appropriate concentrations versus tested sample. The sample was as earlier described diluted with 0.5M HNO3 and 0.25% HF v/v, to concentration at approx. 50 and 350 µg/l.

NMBU

At NMBU, A triple quad ICP-MS (Agilent 8800 ICP-QQQ-MS) with a quartz Micromist nebulizer and a Peltier cooled (2 °C) Scott double pass spray chamber was used for the analysis of both Pu and U.

Plutonium analysis: Uranium still present in the sample solution after the single step extraction chromatography was mass shifted to mass m+16 and m+32 through reaction with 0.32 mL/min CO$_2$ in the reaction cell, allowing for unreacted Pu to be analysed on mass (here: 239, 240, 242) with negligible remaining UH$^+$ interference. The concentrations of Uranium are, in all samples, estimated at m+16 for control of the UH$^+$ interference. No correction equation was applied to the results, as the concentrations of U were low. The octapole bias was kept close to zero (-1 V) to prevent increased formation of PuO$^+$. For increased sensitivity, an s-lens was used and the mass balance of the quadrupoles was set to 92 % (240 amu/260 amu). Typical sensitivity in no-gas mode is about 1.5 cps per ppq for ^{238}U. Due to bureaucratic difficulties, it proved impossible to obtain an isotopic plutonium standard for isotope calibration and mass bias determination. We therefore chose to use IAEA 135 as an isotopic standard material for mass bias correction. CRM IAEA 135 is a well-documented reference material, issued in 1993, but regrettably without a reference value for the ^{240}Pu/^{239}Pu atom ratio. However, we have found 22 papers documenting the ^{240}Pu/^{239}Pu atom ratio in the material with 49 individual results. Outlier analysis rejected two of these results, and we used the average of the remaining results as an isotopic standard for mass bias correction in the

current work. The concentrations of ^{239}Pu and ^{240}Pu were calculated from ^{240}Pu/^{242}Pu and ^{239}Pu/^{242}Pu multiplied by total amount of added ^{242}Pu.

Uranium analysis: Due to high concentrations of Uranium in the sample, the instrument was tuned to low sensitivity and with x-lens installed. The samples were analyzed in MS-MS mode, where Q1=Q2, and with no gas present in the reaction cell. NBL CRM 129A was used for mass bias correction for the Uranium atom ratios.

Table 1. Instrumentation conditions used in each institute for the inter-comparison exercise.

	DTU	FOI		ALS		NTNU	UH		NMBU
Instrument model	Agilent 8800 ICP-QQQ	Element XR ICP-SFMS		Element XR ICP-SFMS		Element 2 ICP-SFMS	Nu Plasma MC-ICP-MS	AttoM double-focusing ICP-SFMS	Agilent 8800 ICP-QQQ
Radionuclides measured	^{234}U, ^{235}U, ^{238}U, ^{239}Pu, ^{240}Pu, ^{242}Pu	^{234}U, ^{235}U, ^{238}U	^{238}U, ^{239}Pu, ^{240}Pu, ^{242}Pu	^{234}U, ^{235}U, ^{238}U	^{239}Pu, ^{240}Pu, ^{242}Pu	^{234}U, ^{235}U, ^{238}U, ^{239}Pu, ^{240}Pu, ^{242}Pu	^{234}U, ^{235}U, ^{238}U	^{239}Pu, ^{240}Pu, ^{242}Pu, ^{238}U	^{234}U, ^{235}U, ^{238}U, ^{239}Pu, ^{240}Pu, ^{242}Pu
Auto-sampler	AS X-520 (CETAC))	No	No			SC2 DX	ASX110	ASX260	AS X-520 (CETAC))
Sample uptake	High-precision 10-roller three channel peristaltic pump	Self-aspired nebulization	Self-aspired nebulization	Peristaltic pump	Apex introduction system	PrepFast system	Peristaltic pump	Peristaltic pump	ISIS 2
Nebulizer	MicroMist (Borosilicate glass)	Conikal nebulizer	Conikal nebulizer	MicroMist nebulizer	PFA nebulizer	PFA-ST (50-700 µl/min)	Meinhard and Desolvating nebulizer (DSN) (50-100 µl/min)	Meinhard nebulizer	MicroMist quartz
Spray chamber	Quartz, low volume, Scott-type double-pass	Twister spray chamber	Twister spray chamber	Cyclonic spray chamber	Cyclonic spray chamber	Quartz baffled micro cyclonic with dual gas inlet type ESI-ES-3452-111-11	Cyclonic spray chamber	Cyclonic spray chamber	Quartz, Scott-type double-pass
Cooling	In-house groundwater cooling system	No cooling of spray chamber	No cooling of spray chamber	No cooling	No cooling	PC^{3x}-Peltier cooling and heated system	No cooling of spray	No cooling of spray Double pass spray chamber	Peltier cooled at 2 C
Torch	Quartz, ShieldTorch system	Quartz, shield torch system	Quartz, shield torch system	Quartz, ShieldTorch system	Quartz, ShieldTorch system	Quartz demountable with o-rings			Quartz, ShieldTorch system
Injector	2.5 mm ID injector	2.2 mm ID injector	2.2 mm ID injector	2.5 mm ID injector	2.5 mm ID injector	Quartz 2.5 mm with o-rings, ES-1024-0250			2.5 mm ID injector

Sample cone	1mm diameter orifice, Ni cone	Ni sampler, TF1001-Ni	Ni sampler, TF1001-Ni	Nickel sample cone	Nickel sample cone	Alunium ES-3000-18032	Nickel sample cone		1 mm Pt cone
Skimmer cone	0.4 mm diameter orifice, stainless steel base with Ni tip	Ni skimmer, TF-1002A-Ni	Ni skimmer, TF-1002A-Ni	X skimmer cone	X skimmer cone	Alunium type X-Skimmer ES-3000-1805X	Nickel skimmer cone		0.4 mm Ni, s-lens for Pu and x-lens for U
RF generator	27 MHz, 500-1600 W power	1200 W	1200 W	1400 W	1400 W	1350 W Power			1550 W
RPQ voltage applied		No	Yes	No	Yes				
Typical sensitivity	0.7 cps/ppq ^{238}U	2 cps/ppq ^{238}U	1.8 cps/ppq ^{238}U	1.2 cps/ppq ^{238}U	6 cps/ppq ^{238}U	0.8 cps/ppq ^{238}U	2 cps/ppq ^{238}U	2 cps/ppq ^{238}U	1.5 cps/ppq ^{238}U with s-lens
Typical noise, cps				< 0.2	< 1				
Calibration solution	NBL-112a (U), CRM-130 (Pu), Scientific Standards 1000 ppm U solution	IRMM-073/7 (mass bias, ^{238}UH and ^{238}U tailing correction)	IRMM-073/7 (mass bias, ^{238}UH and ^{238}U tailing correction))	CRM U0002 Ultra Scientific	CRM U0002	PS-ClBrI (Elemental Scientific, Inc), IRMM-184 (mass bias correction)	NBL112a (mass fractionation and Faraday cup to ion counter gain)	CPI^{TM} single element U solution (mass bias, ^{238}UH and ^{238}U tailing)	NBL CRM 129A for mass bias U
Quality solution		IRMM-184	IRMM-184	IRMM-184		PS-70 (Elemental Scientific, Inc)	UO10 international standard		
Correction factor for m/z 239 from UH and peak tailing (=CPS$_{239}$/CPS$_{238U}$)	1/14892	1/104000	1/104000		1/100000				None

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Individual laboratory performance evaluation and scoring

Based on the ISO 13528 (ISO 13528) and IUPAC-CITAC recommendation [8], two tests including *z*-score and *zeta*-score were used to evaluate the individual performance of individual laboratory.

z-score is calculated according to the following equation:

$$z = \frac{x-X}{\sigma_t} \times 100\% \tag{1}$$

where *x* is the participant's result, *X* is the assigned value, is the standard deviation set externally for the performance assessment. The standard deviations (σ_t) were set to be 0.05*X* for $^{234}U/^{235}U$ and $^{235}U/^{238}U$, $^{240}Pu/^{239}Pu$ atomic ratios, 0.005*X* for $^{235}U/^{238}U$ atomic ratio and 0.2*X* for ^{239}Pu and ^{240}Pu activity. The performance is considered to be acceptable if $|z| \leq 2$. A $|z|$ from 2 to 3 indicates that the results are of questionable quality. If $|z| > 3$, the analysis was considered to be out of control.

Optimally, the ISO 13528 standard for profession testing [8,9], the *zeta*-score methodology should be used in evaluation of results in an inter-comparison. The *zeta*-score is calculated according to:

$$zeta = \frac{x-X}{\sqrt{u_x^2+u_X^2}} \tag{2}$$

where *x* is the participant's result, *X* is the assigned value, u_x is the standard uncertainty of a participant's result, and u_X is the standard uncertainty of the assigned value. The performance is considered to be acceptable if $|zeta| \leq 2$. A $|zeta|$ from 2 to 3 indicates that the results are of questionable quality. If $|zeta| > 3$, the analysis was considered to be out of control.

Results and discussion

Six laboratories within the project participated in the inter-comparison exercise. One triple-quadrupole ICP-MS (ICP-QQQ), one multi-collector ICP-MS (MC-ICPMS) and four high resolution sector field ICP-MS (ICP-SFMS) instruments were used during the exercise. The results achieved from the inter-comparison exercise are presented in Table 2 for uranium isotopic ($^{234}U/^{235}U$, $^{235}U/^{238}U$ and $^{234}U/^{238}U$) ratios in CRM NBL-103A, and in Table 3 for plutonium isotopes (^{239}Pu and ^{240}Pu) massic activity and $^{240}Pu/^{239}Pu$ atomic ratio in reference material IAEA-384. The value of *n* in bracket is the number of replicates for the individual

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ICP-MS measurement. All uncertainties for the results obtained in this work are expanded uncertainties as obtained after uncertainty propagation with a coverage factor $k=1$.

Uranium isotopic ratios

Five labs reported the results on uranium isotopic ratio in NBL CRM 103-A (Table 2). However, as the reference material used for this inter-comparison is not certified, there is no value available, either for X or u_X. As the reference material used is of uranium natural composition, the IUPAC observed range of natural variations for uranium could be used [10]. Because the number of participants in this inter-comparison is very small, we used the average of the IUPAC observed range of natural variations given in the publication, and the standard deviation for the upper and lower level of the range.
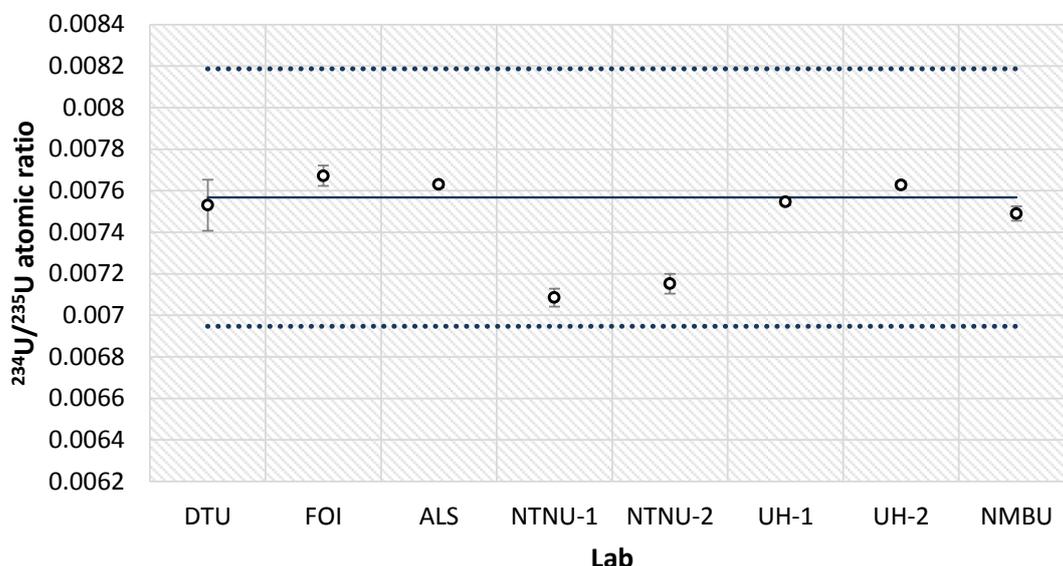
Figure 1 ^{234}U/^{235}U isotope ratios from the measurement of the reference material NBL CRM 103-A. The solid and dotted lines represent the observed average and variation of natural uranium, respectively [10]. The error bars of the results represent the expanded uncertainty with a coverage factor, $k=1$.
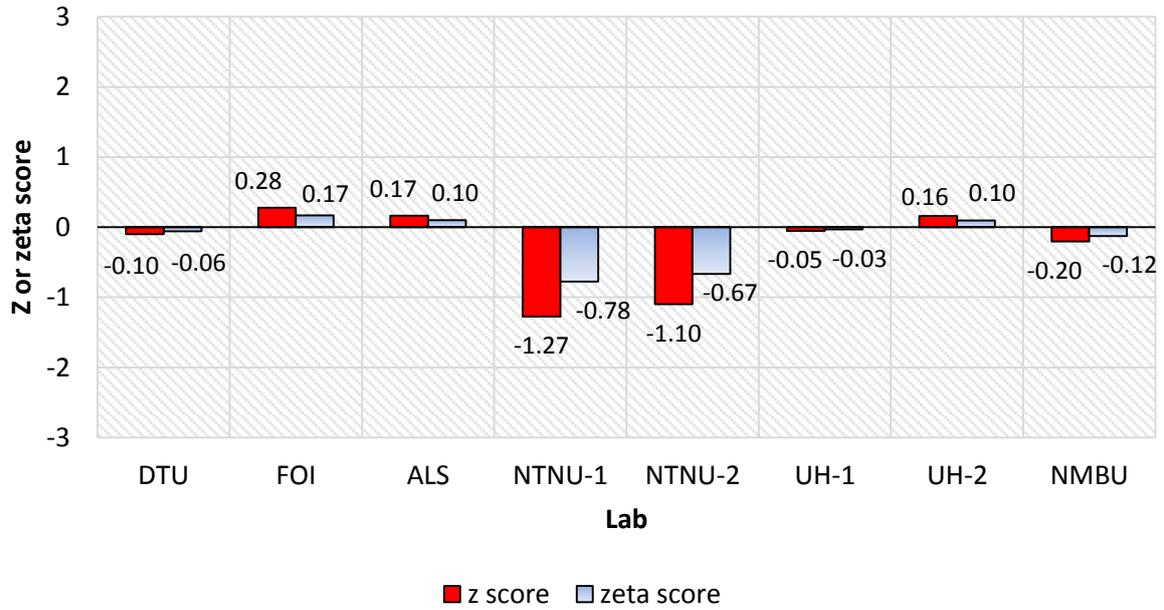
Figure 2 *Z*-score and *zeta*-score calculated for $^{234}U/^{235}U$ atomic ratios from the measurement of the reference material NBL CRM 103-A.
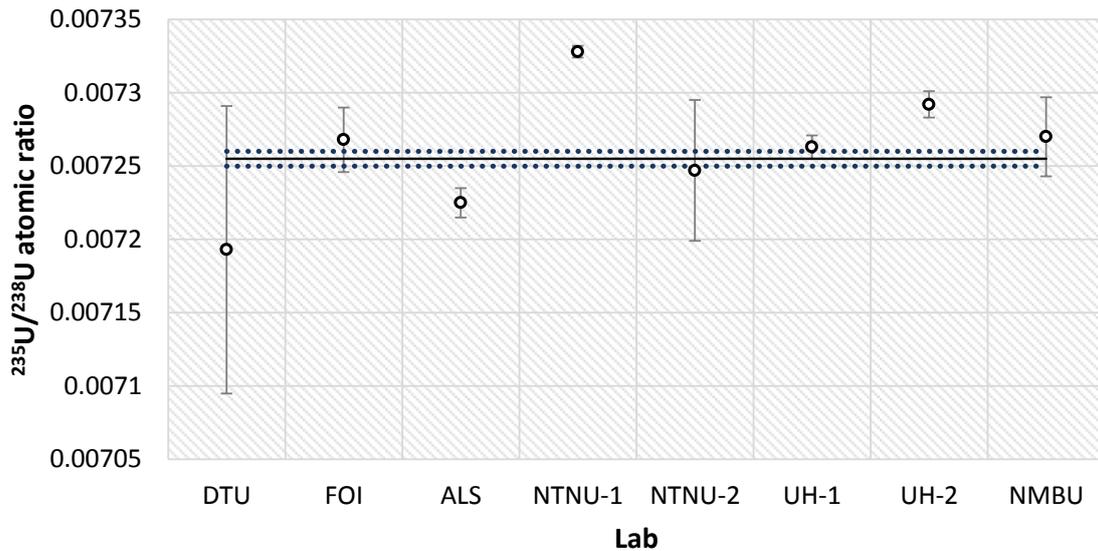
Figure 3 $^{235}U/^{238}U$ isotope ratios from the measurement of the reference material NBL CRM 103-A. The solid and dotted lines represent the observed average and variation of natural uranium, respectively [10]. The error bars of the results represent the expanded uncertainty with a coverage factor, *k*=1.
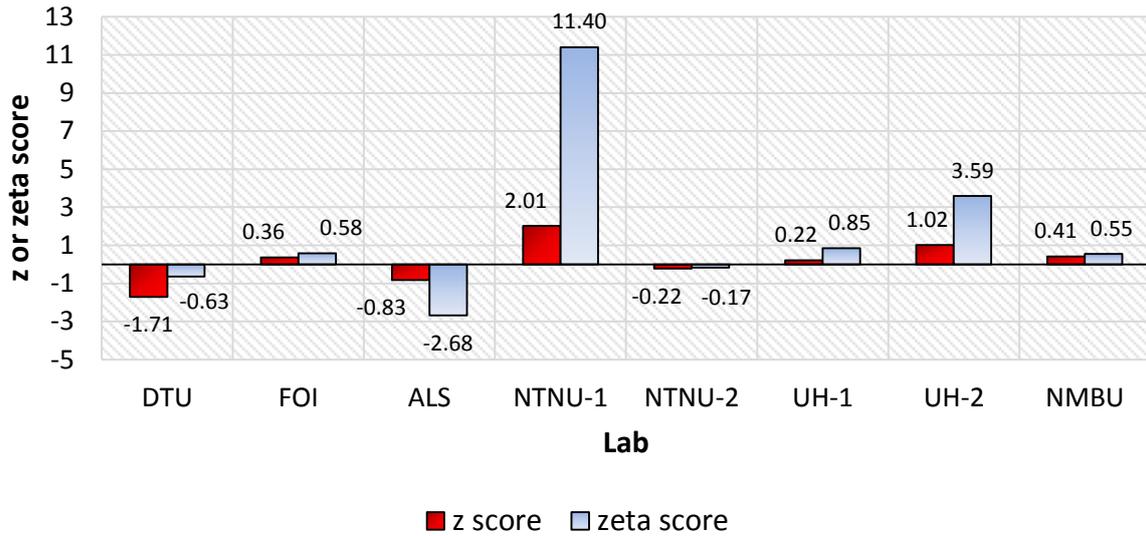
Figure 4 Z-score and *zeta*-score calculated for $^{235}U/^{238}U$ atomic ratios from the measurement of the reference material NBL CRM 103-A.
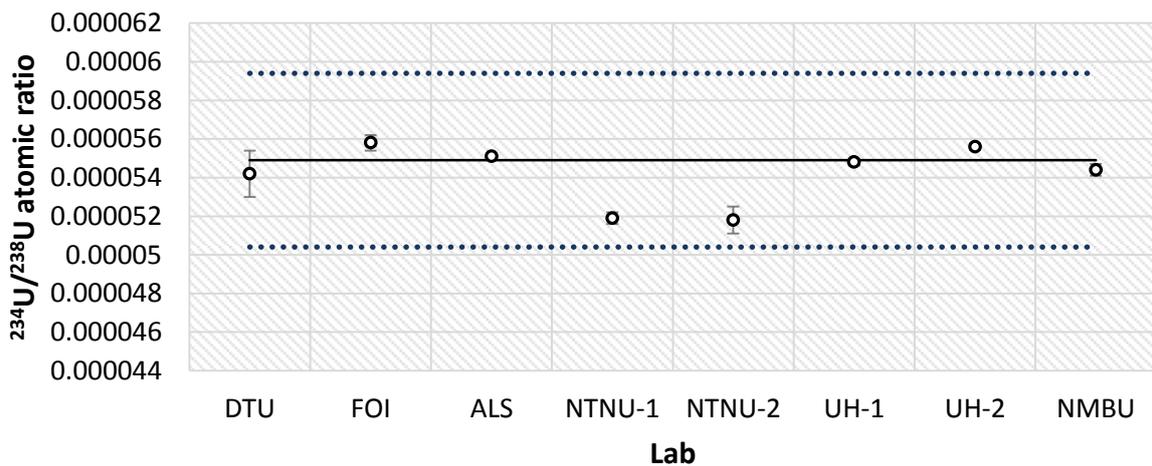
Figure 5 $^{234}U/^{238}U$ isotope ratios from the measurement of the reference material NBL CRM 103-A. The solid and dotted lines represent the observed average and variation of natural uranium, respectively [10]. The error bars of the results represent the expanded uncertainty with a coverage factor, *k*=1.
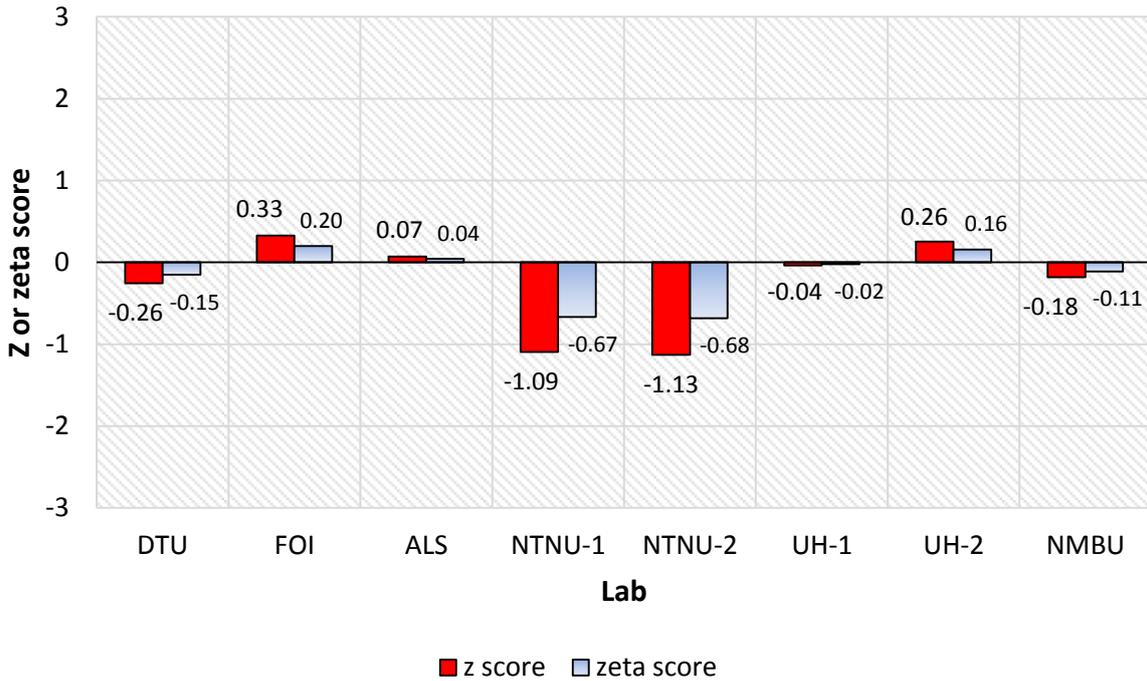
Figure 6 *Z*-score and *zeta*-score calculated for $^{234}U/^{238}U$ atomic ratios from the measurement of the reference material NBL CRM 103-A.

$^{234}U/^{235}U$ atomic ratio: As depicted in Figs 1-2, it can be seen that all the $^{234}U/^{235}U$ atomic ratios obtained in this inter-comparison are within the range of natural variation of natural uranium. The absolute values of *z*-score and *zeta*-score obtained for all results are less than 2, indicating the reported values and uncertainties are acceptable.

$^{235}U/^{238}U$ atomic ratio: the recommended range of natural uranium is relatively narrow, some of the reported results (ALS, NTNU-1 and UH-2) deviated from that range (Fig. 3). Except *z*-score for NTNU-1 is 2.01, all the other values are within ± 2 (Fig. 4), indicating that nearly all results meet the quantitative requirement (σ_t) set for this inter-comparison. However, in the *zeta*-score test, one value of |*zeta*| is in between of 2 and 3 (ALS=2.68), while two values are above 3 (NTNU=11.4 and UH=3.59). This may be due to the reference material being in-homogenous, or that some bias was not taken into consideration when calculating the isotope ratio or the uncertainty.

$^{234}U/^{238}U$ atomic ratio: Results from all the laboratories in this inter-comparison are within the range of natural variation of natural uranium (Figs. 5). The absolute values of *z*-score and

zeta-score obtained for all results are less than 2, indicating the reported values and uncertainties are acceptable.

Plutonium measurement

Five labs reported the plutonium isotopes results for both the pre-purified IAEA-384 material and the raw material (Table 3). In the purification of plutonium from IAEA-384 for direct measurement by ICP-MS by participating labs, removal of uranium was deliberately retained insufficient, in order to evaluate the performance of each lab in calibrating the polyatomic ions and tailing effect of ^{238}U at m/z=239 and 240.

Among the five labs, radiochemical methods used for the determination of plutonium in the raw IAEA-384 material were based on sample pre-treatment followed by extraction chromatographic separation and ICP-MS measurement. DTU and FOI used a single TEVA column, UH used tandem UTEVA + TRU columns for the extraction chromatographic separation and ALS used a single UTEVA column, as described earlier.
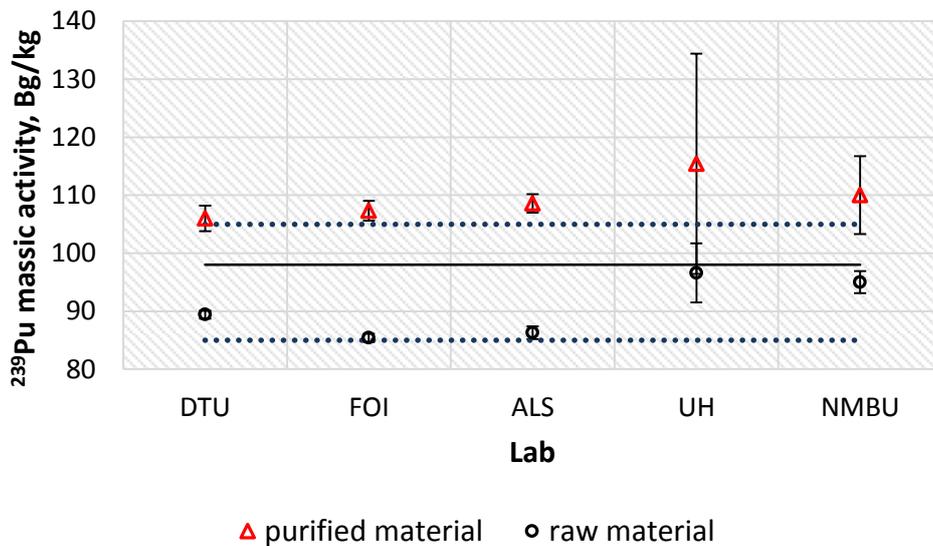
Figure 7 ^{239}Pu massic activities from the measurement of the reference material IAEA-384. The solid line represents the reference value and dotted lines represent the 95% confidential interval [11]. The error bars of the results represent the expanded uncertainty with a coverage factor, *k*=1.
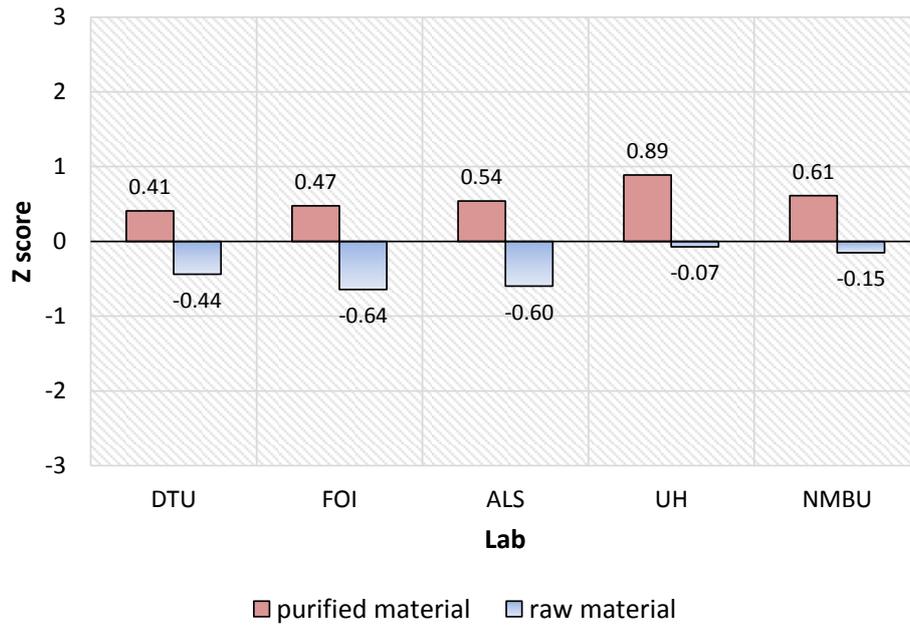
Figure 8 *Z*-score calculated for ^{239}Pu massic activity from the measurement of the reference material IAEA-384.
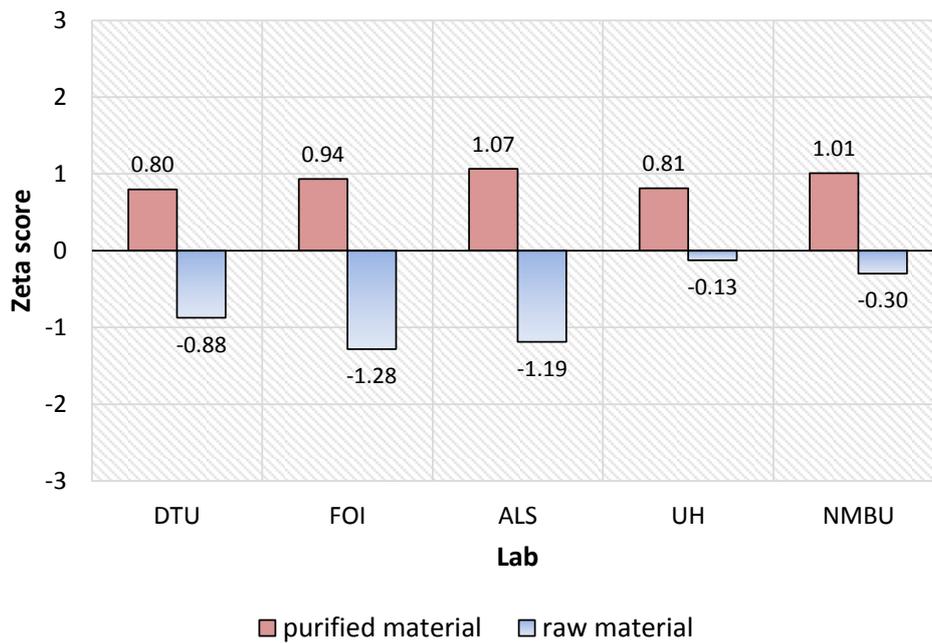
Figure 9 *Zeta*-score calculated for ^{239}Pu massic activity from the measurement of the reference material IAEA-384.
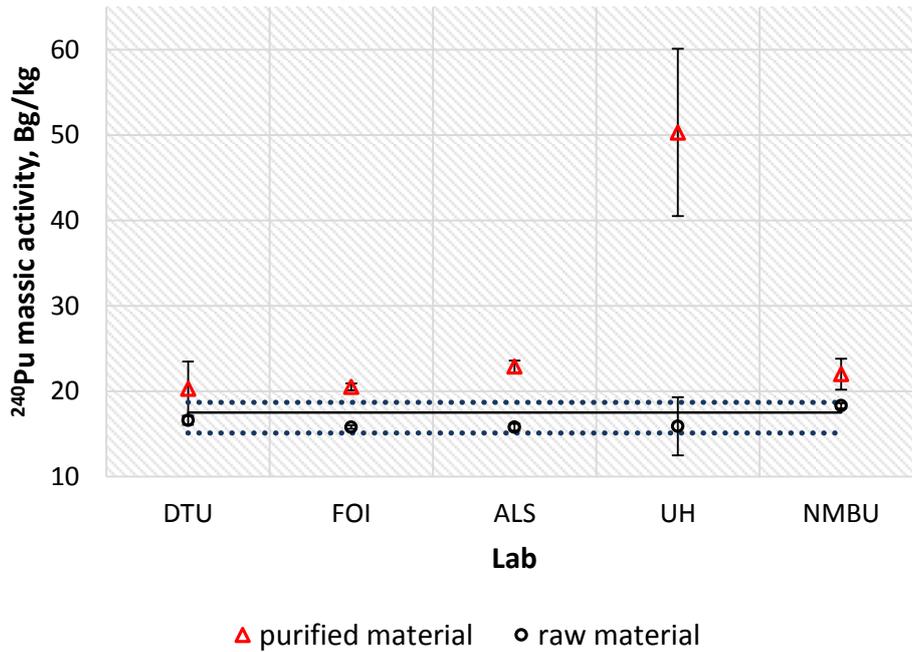
Figure 10 ^{240}Pu massic activities from the measurement of the reference material IAEA-384. The solid line represents the reference value and dotted lines represent the 95% confidential interval [11]. The error bars of the results represent the expanded uncertainty with a coverage factor, $k=1$.
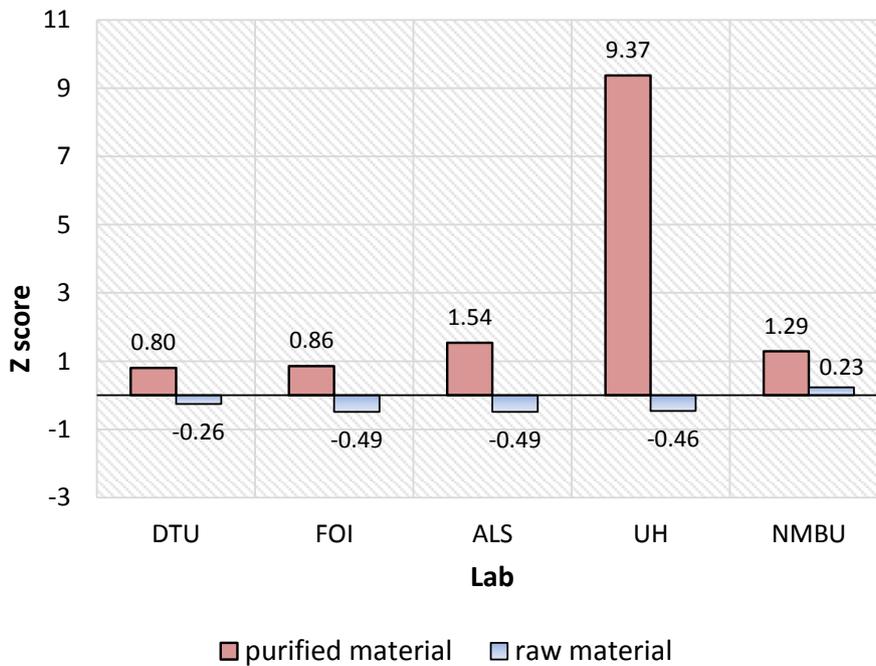
Figure 11 Z-score calculated for ^{240}Pu massic activity from the measurement of the reference material IAEA-384.
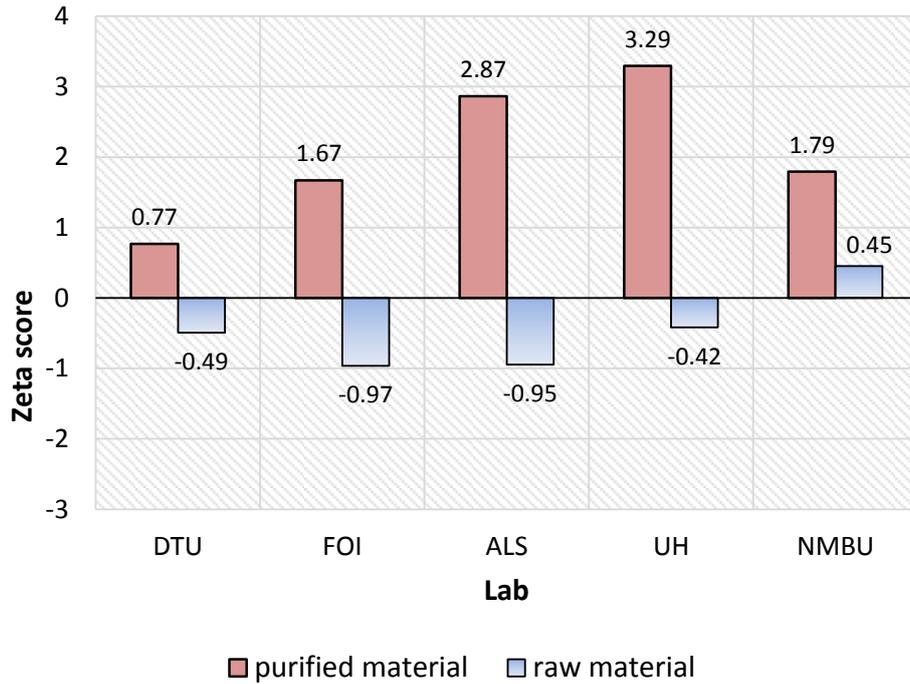
Figure 12 *Zeta*-score calculated for ^{240}Pu massic activity from the measurement of the reference material IAEA-384.
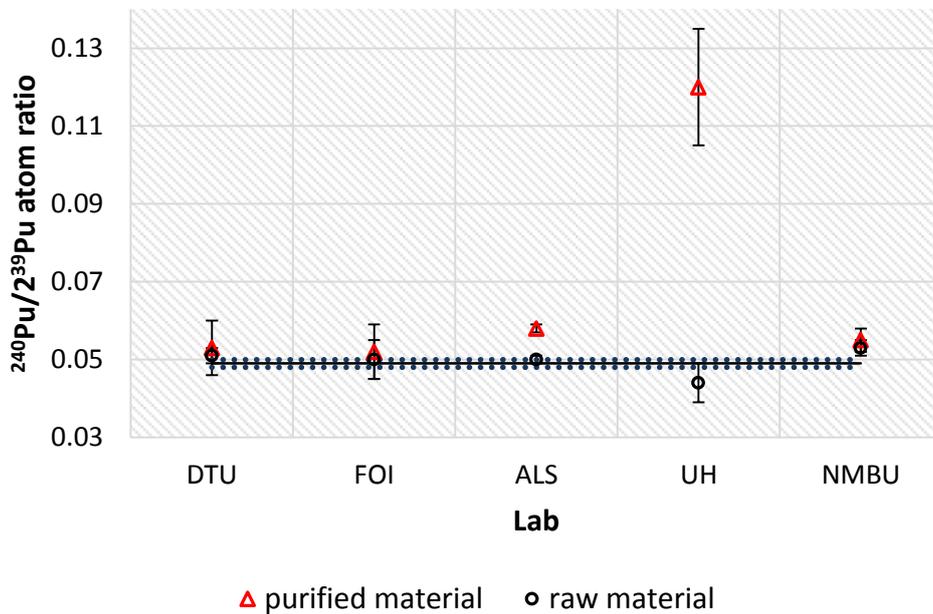
Figure 13 ^{240}Pu/^{239}Pu atomic ratio from the measurement of the reference material IAEA-384. The solid line represents the reference value and dotted lines represent the 95% confidential interval (Povinec et al, 2007). The error bars of the results represent the expanded uncertainty with a coverage factor, $k=1$.
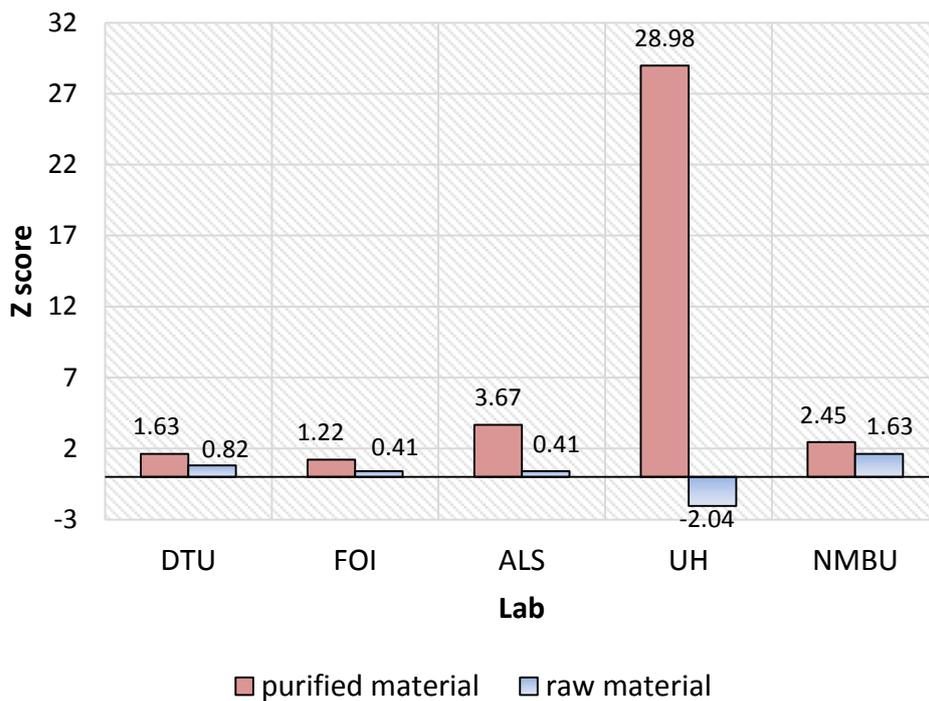
Figure 14 *Z*-score calculated for $^{240}Pu/^{239}Pu$ atomic ratios from the measurement of the reference material NBL IAEA-384.
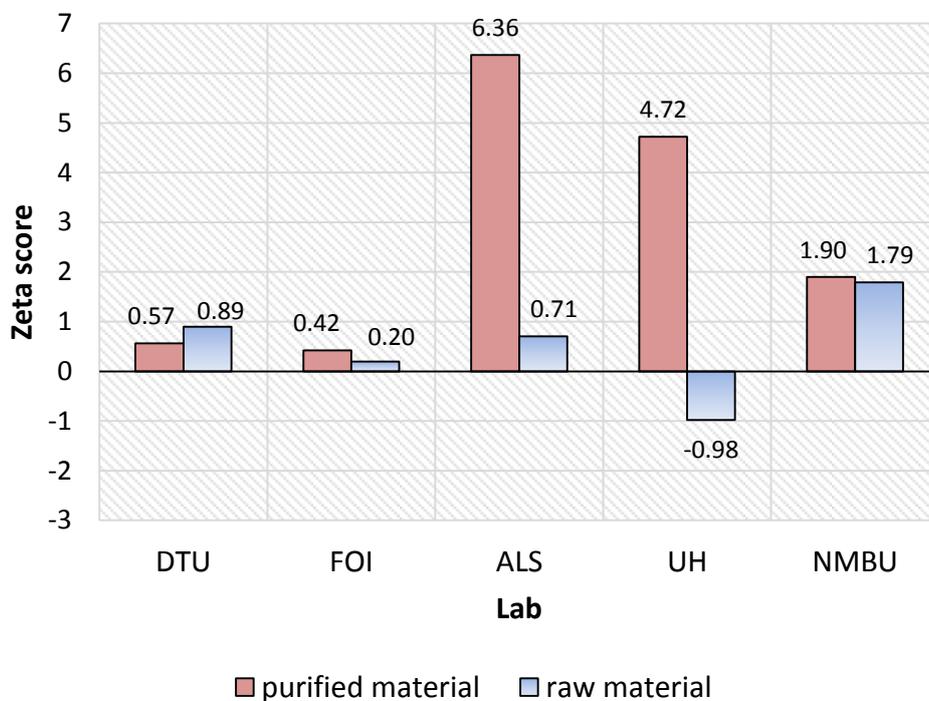
Figure 15 *Zeta*-score calculated for $^{240}Pu/^{239}Pu$ atomic ratios from the measurement of the reference material NBL IAEA-384.

^{239}Pu massic activity: All the ^{239}Pu values obtained for the pre-purified material in this inter-comparison are higher than the reference value and most of them are even above the upper limit of the 95% confidential interval (Fig. 7). All the ^{239}Pu results obtained for the raw material are lower than the reference value but well within the 95% confidential interval. However, it must be kept in mind that the reference values for IAEA-384 for separate ^{239}Pu and ^{240}Pu are information only values, and as such they cannot be regarded as a certified reference value. From the results presented, it is expected that *z*-score and *zeta*-score tests (Figs. 8-9) would result in positive values for the purified material, while tests for the raw material would result in negative values. All the results passed the *z*-score and *zeta*-score tests, indicating acceptable values and uncertainty for ^{239}Pu massic activity. A possible explanation to the positive bias of the results for the pre-purified plutonium samples could be that there might be lanthanides present in the solution, which in turn form lanthanide phosphates. These species interfere at m/z 235 and above, and thus all plutonium nuclides are interfered [12]. As described by Nygren *et al*. (2005), the presence of lanthanide phosphates can be avoided by assuring that plutonium is present as Pu(IV) during the separation and thus the lanthanides, which are trivalent, are removed from the sample.

^{240}Pu massic activity: Similar to ^{239}Pu, and possibly due to the same reason [12], all the ^{240}Pu values obtained for the pre-purified material are above the upper limit of the 95% confidential interval (Fig. 10). The ^{240}Pu values obtained for the raw material are lower than the reference value, but well within the 95% confidential interval. It can be seen from Fig. 11 that, except the UH result (9.37) for the purified material fails in the *z*-score test, all the other *z*-score values for ^{240}Pu are distributed within the acceptance criteria. In the *zeta*-score test, the *zeta*-score for the ALS result in purified material is 2.87, indicating the ^{240}Pu value obtained is of questionable quality. This might be a consequence of relatively low uncertainty for the reported results. The *zeta*-score of the result of ^{240}Pu in purified material reported by UH is above 3.29, indicating that the analysis is considered to be out of control.

^{240}Pu/^{239}Pu atom ratio: The reference value for the ^{240}Pu/^{239}Pu atomic ratio for IAEA-384 is 0.049±0.001 [11]. For the raw material, except UH that obtained a *z*-score of -2.04, all the other *z*-score and *zeta*-score values obtained by each individual lab meet the criteria of the acceptable performance. However, for the purified material, results indicate some deviation: in the *z*-score test, one value (NMBU=2.45) is questionable and two values (ALS=3.67 and UH=28.98) are unacceptable; in the *zeta*-score test, the ALS and UH results (6.36 and 4.72, respectively) could be considered to be out of control. The high *zeta*-score obtained by ALS

for purified material might be related to the relative lower uncertainty in the reported results. The UH result of the ^{240}Pu/^{239}Pu atomic ratio for the purified material that was out control might be due to unexpectedly high tailing in the spectra from ^{238}U. The positive deviation from the reference value may be a result from not having control of the correction of the tailing at m/z=240 from ^{238}U. In this work, UH used a linear regression model for explaining the tailing from ^{238}U on the masses above. However, this model might not explain the tailing properly, thus under-correction of the spectral interference is plausible.

Character of different ICP mass spectrometric instruments

In this inter-comparison exercise, three ICP-SFMS, two ICP-QQQ and one MC-ICPMS instrument were used for the uranium isotopic ratio measurement. For the plutonium concentration and isotopic ratio measurement, four ICP-SFMS and two ICP-QQQ were used for the inter-comparison exercise.

In general, ICP-SFMS enables measurements with the highest resolution but in this work all analysis using ICP-SFMS were done at low-resolution with maximum transmission and flat topped peaks to allow the best peak jumping conditions. The MC-ICPMS enables flat-topped peaks even at higher resolution but drops in sensitivity, hence the analysis was done at low resolution mode. The MC-ICP-MS is superior to the other instruments used with respect to isotope ratio measurements, provided that contributions from counting statistics is negligible. Sensitivity (cps/ppq) for the different instruments used is approximately the same although ICP-SFMS instruments (single or multi-collector) usually show better transmission due to higher extraction voltage. Instruments equipped with improved interface design have yet an order of magnitude better transmission due to both geometry factors and the increased pumping rate. The quadrupole instruments have their main advantage in superior abundance sensitivity, which in particular is valid for the ICP-QQQ instrument using two quadrupoles thus enabling abundance sensitivities in the order of 10^{-14}. The ICP-QQQ further has a gas reaction cell enabling active removal of polyatomic interferences but at a cost in ion-transmission. For example, in the case of ^{239}Pu measurement, with the use of oxygen gas in the reaction cell, ^{238}U could be separated from ^{239}Pu.

Practical observation during the inter-comparison exercise

During this inter-comparison exercise, it was observed that some problems were encountered when performing the ICP-MS measurements. For example, it was noticed that some mathematical corrections of spectral interference were not under control. Also worthy to note is that some laboratories lack experience and availability of instrumentation. When shared

ICP-MS instruments were used for the measurements, the planned measurements were delayed due to other demands of the instruments. Project schedule may be hard to maintain if one has to apply for measurement time from an external institution. In that situation altering the measurement time may imply waiting for another slot at the shared instrument, thus not being able to keep the deadline of a project. In addition, there might be a knowledge gap between radiochemical analysis of the samples and ICP-MS method used for these samples. It is essential for both parties to be aware of interfering impurities in the sample before the measurements by ICP-MS, as well as the requirements for the samples set by the ICP-MS. Both separation method and ICP-MS-method should be planned, keeping in mind the expected quality and quantity of both impurities and analytes. This requires a functioning dialogue between radiochemical and MS laboratories, preferably even before the radiochemical separations. On the other hand, long experience and comprehensive skills of the ICP-MS-experts is a great benefit for the quality of the analysis results.

Conclusions

It is concluded that inter-laboratory comparison for the determination of radionuclides using ICP-MS techniques are much needed within the Nordic society. Experience can be shared between the laboratories by performing inter-comparison exercises and by having user meetings with the intention to discuss radionuclides measurements using ICP-MS. For the coming years, inter-comparison exercises and ICP-MS user meetings, activities similar to those within the NKS projects, are desired within the ICP-MS community.

Acknowledgements

Table 2. Results of uranium isotopic ratios for NBL CRM 103-A from each institute for the inter-comparison exercise (u is the expand uncertainty with a coverage factor of k=1)

Atom ratio		DTU	FOI	ALS	NTNU		UH		NMBU	Ref. value
					Sub-1	Sub-2	Sub-1	Sub-2		
^{234}U/^{235}U	**Average**	0.007530	0.007672	0.007630	0.007085	0.007152	0.007547	0.007627	0.007490	
		(n=10)	(n=6)	(n=6)	(n=3)	(n=3)	(n=1)	(n=1)	(n=10)	
	***u* (*k*=1)**	0.000123	0.000049	0.000015	0.000043	0.000048	0.000017	0.000017	0.000035	
^{235}U/^{238}U	**Average**	0.007193	0.007268	0.007225	0.007328	0.007247	0.007263	0.007292	0.00727	0.007255
		(n=10)	(n=6)	(n=6)	(n=3)	(n=3)	(n=1)	(n=1)	(n=10)	
	***u* (*k*=1)**	0.000098	0.000022	0.000010	0.000004	0.000048	0.000009	0.000009	0.000027	0.000005
^{234}U/^{238}U	**Average**	0.0000542	0.0000558	0.0000551	0.0000519	0.0000518	0.0000548	0.0000556	0.0000544	0.0000549
		(n=10)	(n=6)	(n=6)	(n=3)	(n=3)	(n=1)	(n=1)	(n=1)	
	***u* (*k*=1)**	0.0000012	0.0000004	0.0000001	0.0000003	0.0000007	0.00000018	0.00000016	0.0000003	0.0000045

Table 3. Results of plutonium isotopes for IAEA-384 from each institute for the inter-comparison exercise (u is the expanded uncertainty with a coverage factor of $k=1$)

Institute		DTU		FOI		ALS		UH		NMBU		Ref. value
Sample name		Pre-purified Pu (n=5)	Raw material (n=2)	Pre-purified Pu (n=1)	Raw material (n=3)	Pre-purified Pu (n=5)	Raw material (n=2)	Pre-purified Pu (n=1)	Raw material (n=1)	Pre-purified Pu (n=3)	Raw material (n=2)	Raw material
^{239}Pu, Bq/kg	Average	106.0	89.4	107.3	85.4	108.6	86.3	115.4	96.6	110.0	95.0	98 (85-105)
	u ($k=1$)	2.2	0.7	1.7	0.7	1.6	1.1	19.0	5.1	6.7	1.9	
^{240}Pu, Bq/kg	Average	20.3	16.6	20.5	15.8	22.9	15.8	50.3	15.9	22.0	18.3	17.5 (15.1-18.7)
	u ($k=1$)	3.2	0.5	0.4	0.2	0.7	0.4	9.8	3.4	1.8	0.3	
^{240}Pu/^{239}Pu atom ratio	Average	0.053	0.051	0.052	0.050	0.058	0.050	0.120	0.044	0.055	0.053	0.049
	u ($k=1$)	0.007	0.002	0.007	0.004	0.001	0.001	0.015	0.005	0.003	0.002	0.001

References

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Title	An inter-comparison exercise on the application of ICP-MS techniques for measurement of long-lived radionuclides
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Abstract max. 2000 characters	Inductively coupled plasma (ICP) spectrometry techniques are widely used in the fields related to environmental monitoring, nuclear waste disposal and management, radioecology and tracer studies, as well as nuclear forensics and nuclear emergency preparedness. Especially ICP mass spectrometry (ICP-MS) is playing an important role for determination of low-level long-lived radionuclides and their isotopic ratios. ICP optical emission spectrometry (ICP-OES) is commonly used for determining stable elements (Al, Fe, Ca, etc.) and cannot perform isotopic ratio

measurement with desirable precision and at low analyte concentrations. Therefore ICP-OES is often used as a supplementary technique to ICP-MS in the analysis, for instance, to screen the matrix composition of a sample, or to determine Sr and Y chemical yield in the Sr-90 analysis, etc.

Among the Nordic countries, there are probably less than 20 ICP-MS instruments which are currently applied in the nuclear field for the measurement of radionuclides and their isotopic ratios. Due to different application purposes and technical background of the analysts, each ICP lab has different set-ups and experiences in running these instruments. More efficient application of ICP-MS will be achieved when these experiences are well shared among these labs. Also, for newly established ICP labs or scientists/students in the Nordic countries to quickly build up the competence in operating their instruments in practice, hands-on experience is very valuable. Therefore, within the Nordic-ICP project, an inter-comparison exercise was performed during 2016, which was focused on the measurement of uranium and plutonium isotopes in certified reference material by ICP-MS in combination with radiochemical separation. This report summarizes the results and conclusions obtained base on this inter-comparison exercise.