

High Precision Isotopic Analysis of Actinide Bearing Materials: Performance of a New Generation of Purpose Built Actinide Multi- Collector ICPMS Instruments

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Abstract. Recently, a new class of multi-collector inductively coupled plasma mass spectrometers (MC-ICPMS) has been introduced commercially that includes detector arrays purpose-built for actinide measurements. These detector arrays significantly enhance the data quality possible for applications encountered in nuclear forensics. Two such instruments are described in this paper, the Neptune*Plus*TM, developed by Thermo-Fisher (Bremen, Germany), and the NuPlasma2, developed by Nu Instruments (Wrexham, UK). Research results are presented that have been obtained by the authors using the first commercial Neptune*Plus*TM. This paper also presents performance characteristics and results for traditional liquid introduction, including a means for ultra-trace detection *via* electrochemical separation prior to solution nebulization, as well as solid sample introduction with femtosecond-laser ablation. We also discuss the advantages and limitations of the current systems for detection of the transient signals associated with these two methods for introducing sample into the plasma.

1. Introduction and Instrument Descriptions

Multicollector ICPMS instruments have been on the commercial market since the early 1990s. The first instruments developed by VG Isotech and VG Elemental combined the ICP ion source developed for the early high resolution magnetic sector ICP-MS instruments with a multi-collector mass analyzer that had been developed for Thermal Ionization Mass Spectrometry (TIMS). This first instrument, the “Plasma 54”, quickly demonstrated that high precision isotope ratio measurements could be performed despite the “noisy” ICP ion source. The enhanced ionization capabilities of the ICP allowed measurements to be made on a wide range of elements that had hitherto been impossible to measure by thermal ionization. In addition, the more robust ICP ion source offered the promise of allowing somewhat more relaxed sample preparation requirements that greatly shortened the analysis time compared to TIMS. Sample introduction of liquids and the use of laser ablation for direct solid sampling also extended the range of isotopic measurements that could be made for the first time. The early MC-ICP-MS instruments were not particularly sensitive ~10 V/ppm and mass bias effects were generally larger than those observed for TIMS. As the technique developed, isotope ratio precision and accuracy began to rival that of TIMS with precision better than 10 ppm achieved for elements like Sr. As a result, the sales of MC-ICP-MS instruments have grown rapidly in the two decades since its inception, displacing TIMS in many applications, although TIMS is still regarded as the “gold” standard in terms of precision and accuracy in many isotope ratio measurements.

Table 1: Comparison of MC-ICPMS Instrument Features.

**NeptunePlus values listed are for the first commercial “Plus” instrument; delivered to PNNL in 2009.

Instrument Feature	Nu Plasma 2	NeptunePlus
Sector Configuration	E-B	E-B
High voltage section	Ion Source	Mass Spectrometer
Response: Li-Sr-U	40-700-1000 V/ppm	300-800-1250 V/ppm
Detectors - Total	22	16 (up to 19)
Faraday cups**	16	11
Full Size EM**	Up to 6	3
Compact EM**	0	2
Abundance Sens. Filters	Up to 5	2

In 2008, we began thinking about new possibilities for a detector array specific for uranium measurements. In particular, we wanted an instrument that had the ideal detector available for each isotope (^{233}U , ^{234}U , ^{235}U , ^{236}U , and ^{238}U) and for uranium enrichment ranging from depleted to highly enriched. ThermoFisher was the successful bidder and working further with Thermo’s staff in Bremen, Germany, we completed a conceptual design of the detector array. Other innovations in the prototype instrument included new cone designs in the ICP-to-vacuum interface and the use of all dry pumping during development, testing, and installation. The first NeptunePlus was delivered to PNNL in 2009. Since then Thermo has sold many additional “Plus configuration” instruments and extended this detector array design to their thermal ionization product, the “Triton”, now “TritonPlus”. Nu Instruments has also produced an advanced detector array version of their “NuPlasma”, the NuPlasma2. Together, these new instruments have dramatically changed the actinide isotope ratio measurement capability available. Some key features of these two instruments are listed in Table 1.

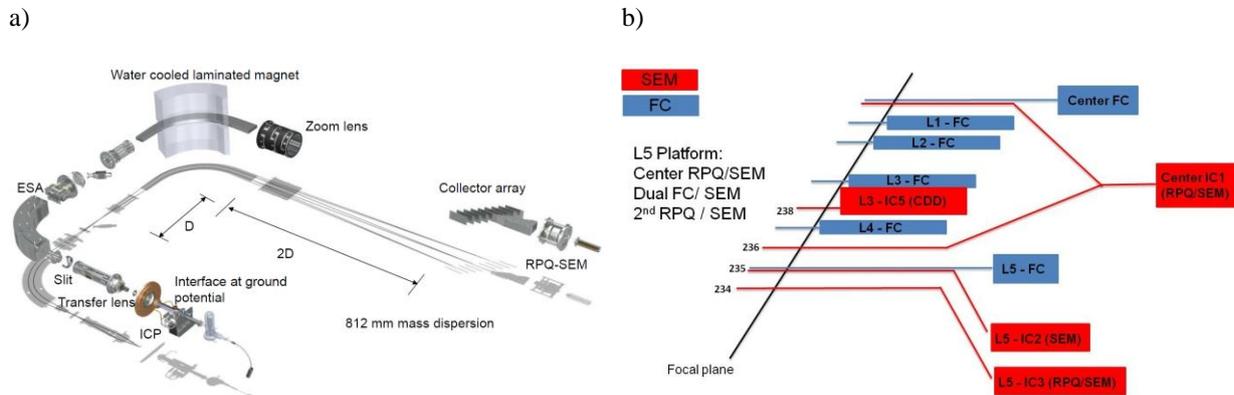


Figure 1. a) Schematic overview of the Neptune instrument. b) Schematic of the “L5” uranium detector array incorporated on the low mass side of the Neptune detector array.

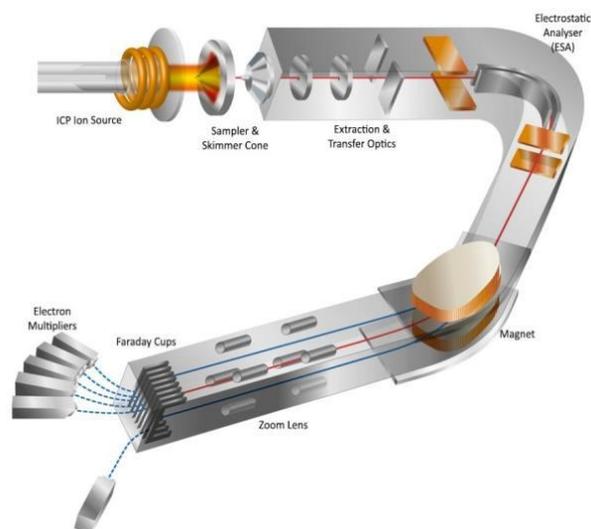


Figure 2. Schematic overview of the Nu Plasma2 layout.

2. NeptunePlus Performance Characteristics

2.1. Solution Introduction

These instruments can be characterized by several performance metrics, but most of these metrics are the same as are relevant to predecessor MC-ICPMS instruments having multiple Faraday cups and a single pulse counting detector. We thus focus on just a few performance metrics unique to the new detector formats. These metrics include SEM gain stability and the precision of isotope ratio measurements made using combinations of full size SEM detectors and so-called “compact discrete dynode” detectors, and for uranium measurements, the ability to perform internal corrections for UH^+ interferences, e.g., $^{235}\text{UH}^+$ interference with $^{236}\text{U}^+$.

The sensitivity of the NeptunePlus for uranium is approximately 80 V/ppm with an aqueous sample flow rate of $50 \mu\text{L min}^{-1}$ and high performance cones. This can be increased dramatically to 1250 V/ppm with a desolvating nebulizer for sample introduction and the use of Thermo’s “Jet/X” cones. The instrument blank signal on the faraday cups is usually less than 0.01 mV with a 4 s integration time. The uncertainty for measurement of an isotopically natural $^{235}\text{U}/^{238}\text{U}$ ratio for a 20 pg U/mL solution is typically 0.1 – 0.2% with the desolvator-Jet-X cones configuration, a flow rate of $50 \mu\text{L min}^{-1}$, a 4 s integration time per observation and 50 or more observations.

Figure 3 shows the stability of the NeptunePlus based on measurement of the $^{238}\text{U}/^{235}\text{U}$ ratio in a uranium standard (NBL U030, ~3% ^{235}U). The measured ratio is stable over a period of 1 hour to 0.011% (1-sigma). Uranium measurements on the SEM/CDD detectors is impressive even for very small signals, e.g., the precision measured for NBL U015 $^{235}\text{U}/^{238}\text{U}$ ratio was 0.1% at a ^{235}U signal level of 10K cps.

Cross-talk between the electron multiplier detectors was a potential concern, but has been shown to be less than 0.1ppm (that is, less than 0.1 cps registered on adjacent SEMs or CDDs when a beam of $\sim 1\text{E}6$ cps impinges on a given EM detector). Abundance sensitivity is another key metric to characterize how well very small isotopic abundances can be measured. The “Plus” array has two retarding potential quadrupole (RPQ) equipped SEM detectors which enhance the abundance sensitivity for those two SEM detection channels by a factor of 10, from $\sim 5\text{ppm}$ without the RPQ to $\sim 0.5\text{ppm}$ with the RPQ operating, both measured as the 237/238 ratio in isotopically natural uranium.

The new “jet” cones used in the NeptunePlus™ instrument yield sensitivity in the range of 2% for uranium, i.e., 2 counts are registered for every 100 atoms removed from the solution.

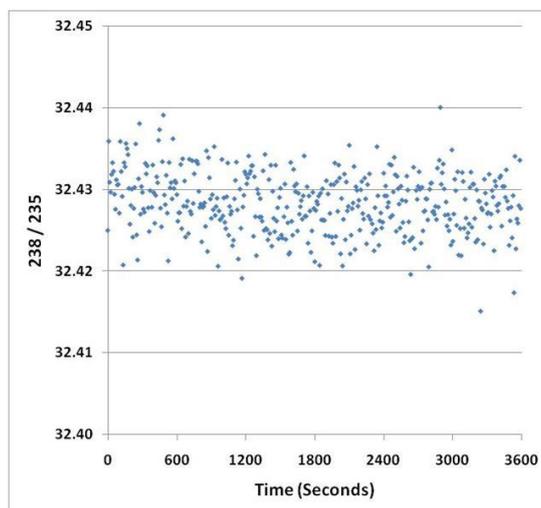


Figure 3. Uranium isotope ratio stability test. Measure U030 on Faradays for one hour, 8 sec integrations, ~7 Volts $^{238}\text{U}^+$; measured stability is 0.0114% (1-sigma).

2.2. Electrochemically Modulated Separations (EMS)

The new detector arrays and greater sample utilization efficiency of these instruments allow for ultra-trace measurements that were not practical with other instruments. With the aid of online electrochemical separations, we have used the NeptunePlus to make ultra-trace plutonium measurements.

Isolating U from Pu is generally regarded as essential for low level Pu analysis by mass spectrometry, either because of abundance sensitivity issues since U concentration is much greater than Pu in most samples, or for ICP-MS the formation of the $^{238}\text{U}^1\text{H}^+$ ion hinders the detection of $^{239}\text{Pu}^+$. The conventional laboratory approach to the separation and isolation of these two elements from a sample matrix is usually based on ion exchange chromatography. Several different methods have been summarized in review articles.[1-4] In general ion exchange separation is usually a complex, multistep, time consuming process taking hours or even days, requiring samples to be prepared off-line prior to analysis hindering sample throughput.

EMS exploits the potential dependent and opposite affinities that U and Pu ions display in weak (0.1-5 %) nitric acid solutions towards the anodized surface of a glassy carbon electrode.. U accumulates on the electrode when the applied potential is -0.2 V (relative to an Ag/AgCl reference electrode), while Pu is either stripped from the electrode or displays no tendency to co-accumulate with U. When a positive potential +1.0 V is applied, U and Pu display the opposite behavior, U strips from the electrode while Pu accumulates on the surface. The whole process takes place in weak nitric acid, without the addition of any other chemicals, in a matrix that is ideally suited for direct ICP-MS sample introduction. The accumulation and stripping process is easily controlled, relatively fast and selective. In addition as EMS accumulates the target analyte from the sample solution the method offers the benefits of analyte pre-concentration that enhances low-level detection capabilities. Employing a single working electrode allows only one analyte to be accumulated from a sample per injection, but with dual working electrodes both U and Pu can be simultaneously isolated and then sequential stripped, simply by changing the voltages applied to the cell electrodes.

Figure 4 illustrates U and Pu behavior in a dual working electrode cell operated to selectively isolate both elements from a sample and then strip each selectively for analysis.

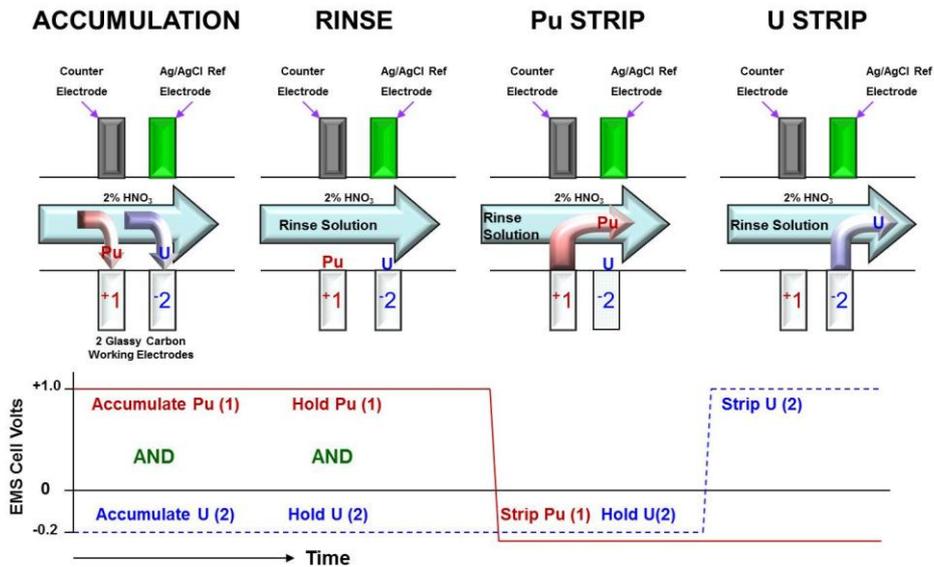


Figure 4. Simultaneous U and Pu isolation followed by sequential stripping from a dual working-electrode EMS cell.

The design of the flow-through EMS cell used for U-Pu ICP-MS analysis is based on a modified commercial design.[5] The main modifications involved replacing the stainless steel components contacting the sample solution with the inert polymer PolyEther Ether Ketone (PEEK) and the platinum counter electrode with rhodium to eliminate the possible formation of platinum-argides in ICP-MS that overlap with uranium isotopes. Figure 5 highlights the layout of the system with the EMS cell operating in line to the ICP-MS for fixed volume, sequential sample introduction using a 6-port injection valve. The analysis steps include:

1. Set cell electrode potential to strip the target analyte, U or Pu.
2. Load the sample into the fixed volume injection loop.
3. Set the electrode potential to accumulate the target analyte, U or Pu.
4. Switch the injection valve in-line to the EMS cell.
5. Push the sample through the EMS cell using 2% HNO₃ acid carrier.
6. Once the entire sample has been passed through the cell, switch the injection valve back to load.
7. This allows the EMS cell to be rinsed clean of the sample using the carrier.
8. Change the cell potential to strip the target analyte, U or Pu, for analysis.
9. Repeat steps 1-8 for the next sample.

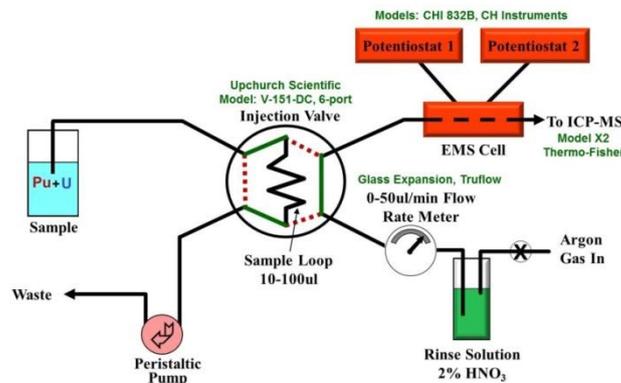


Figure 5. Flow-through EMS system layout.

In the configuration highlighted in Figure 5 the ICP-MS is always on-line to the EMS cell. This allows for constant monitoring of the separation-isolation process, although the sample could be directed to waste once processed if ICP-MS contamination was an issue. Coupled to a sensitive ICP-MS this approach requires very small samples, e.g., 25-50 μl , to make U or Pu detection or isotopic measurements at femtogram or attogram levels. Typical analysis times are 15 minutes for analyte accumulation, 10 minutes for the cell rinse, while the sample strip takes 1-2 seconds. By employing the shortest length possible of micro-bore tubing between the EMS cell and the sample introduction system of the ICP-MS the delay between analyte stripping and ICP-MS detection is <10 seconds. As both U and Pu are stripped rapidly back into a small carrier solution volume $\sim 1 \mu\text{l}$, the analyte pre-concentration factor is large and the precise timing of the transient strip peak ensures reliable detection, even when analyte concentrations are very low.

The EMS separation technique has been applied directly to solutions (leached or total HF dissolution) prepared from ashed swipes. The only preparation step required is to dilute the HNO_3 acid concentration to $\sim 2\%$. Both U and Pu could be isolated and analyzed in this matrix in less than 60 minutes using a single working electrode cell, with the potential for the dual working electrode cell to reduce isolation and analysis time for both U and Pu even further to <40 minutes. This short isolation and analysis time allows EMS to greatly improve the thru-put of swipe analysis without sacrificing sensitive detection. Figure 6a illustrates the low level Pu detection capabilities of EMS when coupled to a NeptunePlus, where 2.6 attograms or just 6600 atoms ^{239}Pu produced a readily detectable strip peak in an ashed swipe matrix. The volume of sample injected was just 25 μl , while Figure 6b illustrates the corresponding behavior of the un-spiked ashed swipe blank, illustrating no discernible response for ^{239}Pu . Even the presence of very high levels of U does not prevent reliable ^{239}Pu measurement as the accumulation process is very selective as illustrated in Figure 7, where 26 attograms of ^{239}Pu was readily detected in the presence of 1.25ng of U. A tiny amount of U appears to co-strip with the Pu but the equivalent UH^+ contribution based on the hydride formation rate is <2cps. The entire separation and detection was accomplished in just 25 minutes.

EMS offers a rapid separation of U and Pu for ICP-MS analysis, much faster than ion exchange methods. It is readily operated in-line to an ICP-MS as the whole separation process takes place in 2% HNO_3 and is well suited to small samples 25-50 μl volume without compromising detection limits. Ion detection efficiencies for EMS-ICP-MS have been estimated to be $\sim 1\%$ for U and $\sim 0.5\%$ for Pu, where the slower washout of Pu is the main cause of its lower efficiency. Even shorter separation times could be accomplished using the dual working electrode EMS cell has been operationally proven, but requires some further development to reach the efficiency and selectively displayed by single working electrode cell.

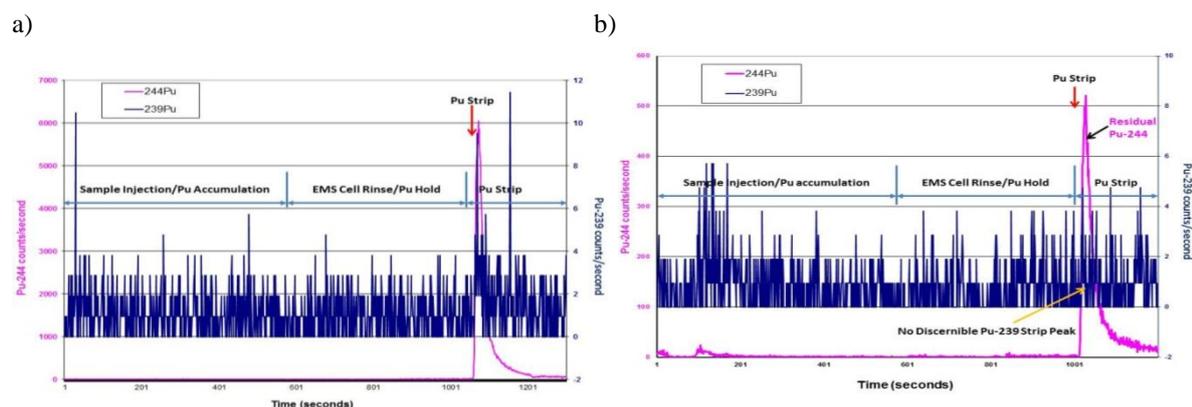


Figure 6. a) EMS MC-ICP-MS detection of 2.6 attograms (~ 6600 atoms) of ^{239}Pu and 7.5 femtograms of ^{244}Pu spiked into a leached ashed swipe matrix. b) ^{239}Pu background obtained by EMS MC-ICP-MS from a blank leached ashed swipe solution matrix.

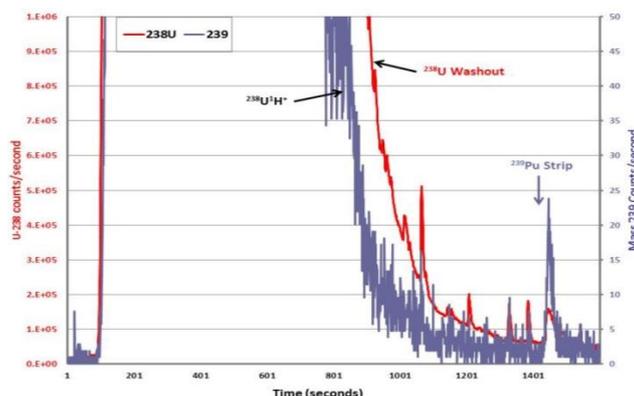


Figure 7. Detection of 26 attograms of ^{239}Pu ($\sim 6.5 \times 10^4$ atoms) in the presence of 1.25 nanograms of ^{238}U by in-line EMS U-Pu separation.

2.3. Laser Ablation Sampling

While modern MC-ICPMS instruments were designed for traditional nebulized liquid sample introduction, laser ablation sample introduction adds significant capability to these instruments, namely, direct solid sample introduction. For example, Lloyd et. al. used laser ablation to measure uranium isotope ratios of particulates collected around a uranium processing facility.[6] More recently, Bellucci et. al. laser sampled “Trinitite”, post-detonation debris from the first nuclear explosion, to measure uranium[7] and lead[8] isotope ratios. Kaiyun et. al. also used laser ablation to determine lead isotope ratios in a wide range of glass reference materials.[9] Schuessler et. al. employed fs-laser ablation to measure silicon isotope ratios in geologic samples[10] and Cagno et. al. used laser ablation to look at plutonium isotope ratios in environmental samples.[11] Finally, Resano et. al. coupled fs-laser ablation with MC-ICPMS to research disease identification via copper isotope ratios in dried urine.[12] These reports listed above are only a small sample of the application space made available by coupling a laser ablation system to a multicollector mass spectrometer.

Our own research group has employed fs-laser ablation coupled to the uranium detector array of a NeptunePlus ICPMS to extensively examine the uranium isotope values for NIST 61x ($x=0, 2, 4, 6$) glasses. Uranium isotopic ratios were collected by rastering the laser across the surface of the NIST glass wafers for ca. 60 seconds. The integrated signal for each raster is corrected against isotopic standards that were introduced as nebulized solutions before and after the glass analysis. Details of the experimental parameters are published elsewhere.[13, 14] The results of this research make an excellent case study to illustrate the advantages and limitations of laser ablation coupled to MC-ICPMS instruments.

The NIST 61x series of glasses are widely used as elemental standards for laser ablation. These glasses were made by diluting a spike of 61 elements in bulk glass material to make four glasses ranging in nominal concentration from 500 to 0.05 $\mu\text{g/g}$, respectively for NIST 610 to NIST 616. Most of the elements in these glasses are isotopically natural,[15] with uranium as the clear exception.[13] The uranium spike was isotopically depleted and thus, when mixed with the natural uranium in the matrix glass, resulted in each NIST glass having a unique isotopic content. Figure 8 shows this isotope mixing on a three-isotope plot ($^{236}\text{U}/^{238}\text{U}$ plotted against $^{235}\text{U}/^{238}\text{U}$). It is clear from the Figure that NIST 610 has the highest ^{236}U content and as the spike becomes more dilute in the matrix glass, the ^{236}U content moves towards the expected value of zero for natural uranium.

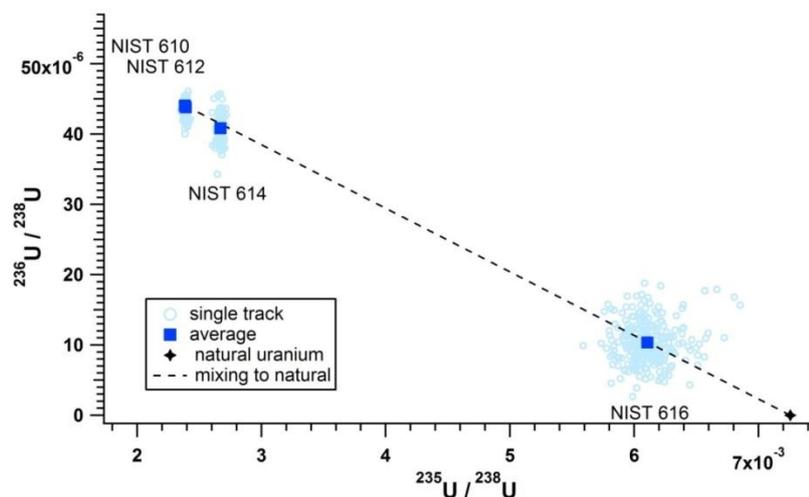


Figure 8. Three isotope plot of uranium ($^{236}\text{U}/^{238}\text{U}$ vs $^{235}\text{U}/^{238}\text{U}$) in NIST 61x glasses showing two component mixing between the depleted uranium spike and isotopically natural uranium in the matrix glass.

What is not visualized in the data in Figure 8 is the impact of PtAr^+ on uranium isotope ratio measurements. Since the NIST glasses were prepared in platinum melting crucibles[16] each glass has Pt contamination that is remarkably inhomogeneous and mixes with the argon in the ICP to interfere with the uranium signals. For the minor isotopes of lowest concentration glass, this interference produces a signal ca. 10 times larger than expected for uranium alone. The reason the minor isotopes ratios still fall on the expected mixing line, i.e. no evidence of PtAr^+ interference, is the high resolving power of the NeptunePlus instrument. Using the medium resolution slits, providing a resolving power of ca. 4000 ($M/\Delta M$), is sufficient to mass resolve the polyatomic interference from the actual atomic U^+ signal. Using the platinum inhomogeneity, it is possible to make a correction and measure the uranium in low resolution, but the accuracy and precision is dramatically improved with the interference removed. For example, the $^{234}\text{U}/^{238}\text{U}$ ratio for NIST 616 was measured at 49 ± 2 ppm in low resolution and 44.3 ± 0.6 ppm in medium resolution both compared with a value of 43.1 ± 1.4 ppm obtained from dissolving NIST 616 glass, separating the uranium, and measuring ratios with thermal ionization mass spectroscopy. The lower uncertainty for the laser ablation value compared with the TIMS value is likely an artifact of the number of analyses. Hundreds of individual ablation tracks were averaged over multiple days to get the LA value whereas the TIMS value was based on a single solution loaded filament.

While medium resolution allows for the partial mass resolution of platinum argides from uranium, it also reduces the sensitivity due to significantly lower transmission of ions by the narrower slits required. Given the low concentration of uranium in NIST 616 and the signal loss due to the requirement of medium resolution, the isotopic ratios for this glass are only measureable because of the excellent beginning sensitivity of the NeptunePlus ICPMS. For solution introduction into the NeptunePlus the sample utilization efficiency (SUE), atoms in the nebulized solution compared to ions detected, has been measured at ca. 2%. [17] Typical quadrupole SUE is one to two orders of magnitude lower. The uranium concentration in NIST 616 is certified at 0.0721 ppm putting the ^{236}U content at 0.7 ppt. At this concentration, each minute long raster would return tens of counts of ^{236}U , well above the ca. 1 cpm dark noise of the detector. With typical “quadrupole sensitivity”, the ^{236}U would have been unquantifiable above the noise.

The other major advantages to coupling fs-LA with MC-ICPMS for isotopic analysis are rapid analysis and high spatial resolution. Depending on the number of replicates, repeatedly rastering (10-30 lines) across each glass wafer with bracketing standards requires 4-6 hours or analysis time. Dissolving the glasses followed by chemical separation of uranium took a couple of days followed by a similar analysis time. In addition, the uranium chemical separation we employed was inadequate to

completely separate the platinum, thus still requiring medium resolution for ICPMS analysis (although this was not a problem for TIMS). The high spatial resolution for fs-LA-MC-ICPMS comes from the small laser spot size. The diameter or width of the ablated features in our fs-LA system can be as small as 10 microns providing the ability to isotopically map sample surfaces. Figure 9 shows the results of rastering the laser across the surface of a NIST 616 wafer onto which six 20-30 micron NIST 610 particles were placed. These isotope intensity maps clearly show the location of each uranium particle. The apparent elongation of the images is due to washout of the LA gas cell.

For samples such as NIST glass, where the analyte of interest is only a fraction of a percent by mass, the transient signals that result from ablation result in transient signals that are easily measured on the proper detectors. However, when more concentrated samples are ablated the ablation aerosol can present an unruly transient signal that poses a problem for mass spectrometer detectors.

Figure 10 plots ^{234}U and ^{235}U signals measured on secondary electron multiplier (SEM) detectors following ablation of a concentrated uranium sample (“Schoepite” mineral particle). The ^{234}U signal is scaled by the isotopic abundance to match the ^{235}U signal. For most of the transient signal the two isotopes scale together, however at the large spike at ca. 380 s the ^{235}U signal does not track the ^{234}U . This spike is an example of an unruly transient signal that cannot be accurately measured with an SEM detector. The suspected cause of the unruly transient signals is that a larger aerosol particle traveling through the ICP results in a high count rate over a very short time window. Consequently, even though the expected count rate was about 100,000 cps the ^{235}U ions arrived too close together to be properly counted with the SEM. This phenomenon has also been observed by researchers studying single particle detection via ICPMS. “Even small aerosol particles (1000 total counts) can produce transient signals with peak count rates of 10^7 – outside the typical operating range of SEM detectors.”[18] These unruly transient signals are a major weakness for LA-MC-ICPMS analysis and alternate detection strategies need to be developed to handle these types of signals.

In spite of drawback of occasional unruly transient signals, fs-LA-MC-ICPMS has proven to be a powerful tool for spatially resolved isotopic analysis.

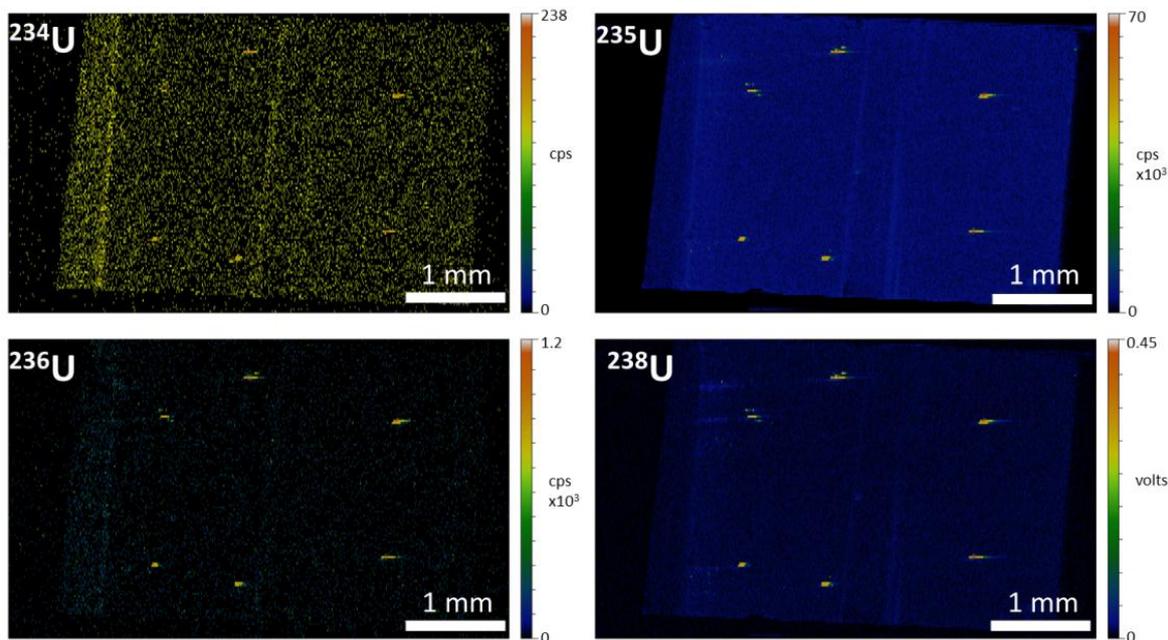


Figure 9. Uranium intensity maps for uranium isotopes showing the location of six 20-20 micron NIST 610 particles on top of a NIST 616 background.

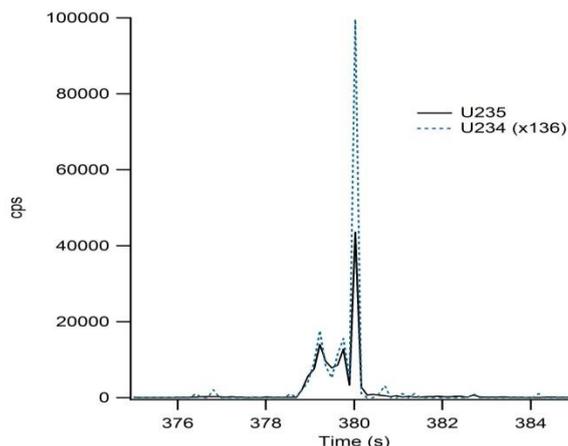


Figure 10. ^{235}U and ^{234}U (scaled by isotope abundance to match ^{235}U) signals as a function of time. The ^{235}U does not track the ^{234}U signal across the largest transient spike.

3. Conclusion

A brief description was provided for two instruments in a new class of MC-ICPMS, instruments with custom, complex detector arrays purpose built for specialized analyses such as isotopic characterization of low level actinides. These instruments mark an important new step in the development of ICPMS, namely, the design of detector arrays where every isotope of interest is “collected” simultaneously, using the best available detector (and abundance filtering). With future improvements in SUE and Faraday Cup sensitivity, further combinations of Faradays, CDDs, and full size SEMs will likely occur. More work is needed to fully characterize the performance of these instruments, e.g., to measure precision and overall uncertainty as functions of uranium isotopic composition and sample amount available for analysis.

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Invited Paper

IAEA Coordinated Research Project: Application of Nuclear Forensics in Combating Illicit Trafficking of Nuclear and Other Radioactive Material

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Abstract. Nuclear forensics, as a sub discipline of forensic science, utilizes measurements of physical characteristics, chemical and elemental composition, and isotopic ratios of nuclear and other radioactive material, together with associated traditional evidence to provide information about material origin and history. Data is interpreted to produce findings that may identify associations between people, places and events to deter and respond to a nuclear security event as well as strengthen a nuclear security infrastructure. Research and development is a means to foster innovation applicable to nuclear forensic examinations as well as demonstrate the validity of nuclear forensic methodologies. The challenges posed by a response to nuclear security events to include the illicit trafficking of nuclear and other radioactive materials demands scientific innovation to ensure state of practice methods and techniques are being developed and implemented as a component of national response to nuclear or other radioactive material out of regulatory control.

1. Introduction

By analyzing inherent signatures that are intrinsic or imparted during manufacturing and use, materials may be linked to people, places, and events important to a law enforcement investigation, a criminal prosecution as well as assessments of nuclear security vulnerabilities [1]. Because nuclear forensic examinations may involve analysis and interpretation of a range of nuclear and other radioactive material, appropriate methodologies together with high confidence measurements are essential. In addition, the ability to examine traditional evidence (e.g., DNA, fingerprints, hair, and fibers) contaminated with radionuclides may be required as part of an investigation of a nuclear security event. Nuclear forensic analysis and interpretation, presented as nuclear forensics findings, can provide information that may be applied to law enforcement investigations, regulatory inquiries, policy making and assist other relevant stakeholders to make informed decisions to improve nuclear security and prevent future nuclear security events [1]. The integrity of nuclear forensic findings relies upon existing, proven analytical techniques together with the development and validation of novel techniques and applications for nuclear forensic methodologies.

The IAEA promotes research and development *inter alia* to support effective nuclear security through Coordinated Research Activities (CRAs) and in this instance through Coordinated Research Projects (CRPs). Research project proposals are submitted to the IAEA and once the proposal has been positively evaluated, the IAEA may offer institutes in developing countries a research, technical or doctoral contract and institutes in developed countries a research agreement or technical contract. The CRP approach gives an opportunity for a broad range of experts and institutions of a broad range of States to participate at periodic Research Coordination Meetings (RCMs) to report the developments of their research project. Research is completed in the institutes' countries, with the chief scientific investigator for each project invited to attend the periodic RCMs for face to face discussions,

exchanges of information and to facilitate the building of professional bonds that will outlast the lifetime of the CRP.

Nuclear forensic science CRPs are a component of nuclear security capacity building and capability development that contributes to the credibility of findings as well as complements training, education, awareness and exercises. The importance of the science should not be diminished. The use of nuclear forensic science and attribution to identify the source of nuclear and other radioactive material out of regulatory control and to increase the likelihood of assigning responsibility for such acts is discussed in the IAEA Nuclear Security Series Technical Guidance No. 6 on Combating Illicit Trafficking in Nuclear and other Radioactive Material [2]. Tracing seized material via interpretation of nuclear forensics data is increasingly valued and it is recognized that there is a requirement for quality assurance of results to provide confidence in findings. Confidence in analytical results depends upon three factors: 1) validated methods; 2) certified reference materials; and 3) demonstrated competencies.

Nuclear forensics has emerged as an important discipline of forensic science. Research and development is essential to build confidence in nuclear forensic findings and evaluate the reliability of nuclear forensic signatures as a basis to determine origin and history. In particular, research should focus on areas such as improving procedures and analytical techniques for the identification and characterization of nuclear and other radioactive materials, identification of nuclear forensic signatures to aid in determinations of material origins and history, understanding how signatures are created, persist and are modified throughout the nuclear fuel cycle, and how signatures can be accurately measured [3].

Extracting relevant information from material seized in a criminal context, together with information about the perpetrators of criminal or unauthorized acts, may also help contribute to an analysis of the flow of radioactive material into and through illegal markets. High confidence measurements of nuclear and other radioactive material and their resulting interpretation may allow for patterns in activities such as perpetrators of criminal or unauthorized acts and the movement of radioactive material through illegal markets to become evident. Consequently, nuclear forensics is an increasingly important tool in determining the source of contraband radioactive material [2].

The goal of CRPs, to include those in nuclear forensics, is to promote improvements in current technology, encourage international best practice, stimulate confidence building via peer-to-peer networking and increase competence among nuclear security practitioners. In this regard the IAEA has organized two CRPs in nuclear forensics. The first CRP was implemented from 2008 to 2012 and focused on the requirements of state of practice measurements of seized materials, techniques to collect and preserve evidence, and improvements to interpretative capacities for law enforcement and nuclear security purposes. The second CRP commenced in 2013 and will continue for three years. The CRP is titled 'Identification of high confidence nuclear forensic signatures for the development of a national nuclear forensics library'. Through its contractual conditions, the IAEA ensures that the research results are freely available worldwide for use of its Member States, with the IAEA publicising widely on the research.

2. Coordinated Research Project: Application of Nuclear Forensics in Combating Illicit Trafficking of Nuclear and Other Radioactive Material

The first CRP ran from 2008 to 2012 and focused on the requirements of state of practice measurements of seized materials, techniques to collect and preserve evidence, and improvements to interpretative capacities for law enforcement and nuclear security purposes. Conclusions of the first CRP focused on the areas of 1) instrumentation and field collections, 2) laboratory methods and techniques and 3) modeling and interpretation and demonstrated that the CRP provided a forum for sharing improved techniques and procedures (to include radiation detection and mass spectrometry techniques), the importance of a staged nuclear forensics analytical plan with nondestructive analysis preceding destructive analysis, the value of predictive signatures in the analysis of irradiated materials, the considerations to preserve evidence contaminated with radionuclides, and the necessity for research activities to be commensurate with State's requirements for nuclear forensics.

The following seven projects were undertaken as part of this CRP and are summarized in Table I together with the principal research topic.

Table I. Participating research institutions of Coordinated Research Project: Application of Nuclear Forensics in Combating Illicit Trafficking on Nuclear and Other Radioactive Material.

Research institution	Title	Research topic
Australian Nuclear Science and Technology Organisation, Australia	Exploiting critical evidence contaminated with alpha emitting radionuclides	Laboratory methods
Instituto de Pesquisas Energéticas e Nucleares, Brazil	Establishment of procedures and techniques for nuclear forensic investigations Part II – workshop on nuclear forensics	Laboratory methods; modeling and interpretation
IDEA System GmbH, Germany	Identification, localization, and categorization of RDD	Instrumentation and field work
Democritus University of Thrace, Greece	Determination of the origin of unknown nuclear material through an isotopic fingerprinting method	Modeling and interpretation
Centre for Energy Research, Hungarian Academy of Sciences, Hungary	Development of nuclear forensics methods and techniques for combating illicit trafficking of nuclear and other radioactive material	Laboratory methods
Korea Institute of Nuclear Safety, Republic of Korea	The development of IT-based in-situ mobile response supporting system for deterring illicit trafficking of nuclear and radioactive materials	Instrumentation and field work
Institute for Transuranium Elements, European Commission	Procedures and techniques for nuclear forensic investigations	Laboratory methods; modeling and interpretation

3. Coordinated Research Project: Identification of High Confidence Nuclear Forensic Signatures for the Development of a National Nuclear Forensics Library

The second CRP entitled ‘Identification of high confidence nuclear forensic signatures for the development of a national nuclear forensics library’ commenced in 2013. This project recognizes a national nuclear forensics library as one possible tool to aid in nuclear forensics interpretation through enabling the comparison of material characteristics and signatures with materials used, produced or stored within a State.

Within the context of nuclear forensics, signatures are the characteristics of a given sample of nuclear or other radioactive material that distinguishes that material from other nuclear or radioactive material. Analysis of these signatures may aid in the identification of the origin and processing history of the material. The project also recognizes that the comparison of material characteristics and signatures would benefit from the identification of peer reviewed and validated signatures across the nuclear fuel cycle and the manufacture of radioactive sources.

The objectives of this CRP seek to address the data requirements of a national nuclear forensics library for stages of the nuclear fuel cycle and for the manufacture of radioactive sources, as well as promote research into novel signatures that are indicative of nuclear processing and important to high confidence interpretation and nuclear forensics findings. Of interest, for example are resolving intrinsic signatures of natural uranium from those that are introduced as a result of production and manufacturing processes during milling, isotopic enrichment, fuel manufacture and reactor operations.

A fundamental question to be considered by this CRP is how signatures are imparted and how they persist. The outcomes of this project will be used to provide technical guidance to States for the development of a national nuclear forensics library and the measurement of material characteristics and signatures. Table II summarizes the following ten projects included in this CRP together with the principal research topic.

Table II. Participating research institutions of Coordinated Research Project: Identification of High Confidence Nuclear Forensic Signatures for the Development of a National Nuclear Forensics Library.

Research institution	Title	Research topic
Australian Nuclear Science and Technology Organisation, Australia	Investigation of various signatures and their application to the provenancing of material at the front end of the nuclear fuel cycle	Laboratory methods; modeling and interpretation
Instituto de Pesquisas Energéticas e Nucleares, Brazil	Identification of nuclear forensic signatures in environmental samples	Laboratory methods; modeling and interpretation
Chalk River Laboratories; Atomic Energy of Canada Limited, Canada	Nuclear forensics signatures of irradiated CANDU fuel	Modeling and interpretation
Democritus University of Thrace, Greece	Parametrisation of unknown spent nuclear fuel from nuclear reactors in view of identifying its origin	Modeling and interpretation
Centre for Energy Research, Hungarian Academy of Sciences, Hungary	Establishment of a national library for nuclear forensics purposes in Hungary	Laboratory methods; modeling and interpretation

Bhabha Atomic Research Centre, India	Mass spectrometry, radiometry and other analytical techniques for nuclear forensics	Laboratory methods
Center for Nuclear Science and Technology, National Nuclear Energy Agency, Indonesia	Identification of high confidence nuclear forensic signatures for mining, milling and conversion process	Laboratory methods; modeling and interpretation
Swedish Defence Research Agency, Sweden	Measurement of lanthanides in uranium matrices	Laboratory methods;
Institute for Transuranium Elements, Joint Research Centre, European Commission	Propagation of nuclear forensics signatures at the front-end fuel cycle	Laboratory methods; modeling and interpretation

4. Communication of Research Outcomes

The premise of IAEA coordinated research projects, to include those in nuclear forensics, is to promote improvements in current technology, encourage international best practice, stimulate confidence building via peer-to-peer networking and increase competence among nuclear security practitioners. The CRP ensures that technical advancements in nuclear forensics are shared for maximum benefit for all States [3]. The IAEA, through a programme of developing technical guidance and provision of outreach and training, assists States to promote the awareness and understanding of nuclear forensics as well as their development of technical capability. The IAEA's programme of CRPs offers a mechanism for collaborative international scientific research and confidence building.

REFERENCES

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