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State of practice and emerging application of analytical techniques of nuclear forensic analysis: highlights from the 5th Collaborative Materials Exercise of the Nuclear Forensics International Technical Working Group (ITWG)

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Abstract
The Nuclear Forensics International Technical Working Group (ITWG), a community of nuclear forensic practitioners who respond to incidents involving nuclear and other radioactive material out of regulatory control, completed its fifth Collaborative Materials Exercise in 2017 (CMX-5). Forensic laboratories from 19 countries and one multinational organization aimed to advance nuclear forensic science and improve international cooperation in the event of a nuclear material security incident. In all, over 30 analytical techniques were utilized to investigate the samples, many techniques applying novel methods or offering improvements in turnaround time. An objective review of the state of practice and emerging application of analytical techniques of nuclear forensic analysis based upon this exercise is provided.

Keywords Nuclear Forensics International Technical Working Group (ITWG) · Collaborative Materials Exercise (CMX) · Nuclear forensic analysis · State of practice

Introduction

The Nuclear Forensics International Technical Working Group (ITWG) is an important forum for informal collaboration among nuclear forensics practitioners who share a common goal in preventing illicit trafficking of nuclear and radioactive materials out of regulatory control.

Nuclear forensics is multidisciplinary, bringing together a community of scientists, law enforcement personnel, and regulators that work to advance the best practices of nuclear forensics. This is achieved largely through the participation in a series of Collaborative Materials Exercises (CMXs) [1–6] and table top exercises (Galaxy Serpent Series) [7]. Each CMX helps advance the state of practice and art of nuclear forensic science by identifying analytical techniques ready for operational use and new laboratory methods worthy of ongoing development. This exercise represents the fourth paired-comparison exercise and the latest in a series of unique exercises that improve international cooperation and communication in the event of a nuclear material security incident.

The goals of nuclear forensic examinations span both legal and broader national security interests. With regards to the legal implications, nuclear forensic science supports law enforcement determinations in a criminal investigation and decisions regarding hazard management to first responders, law enforcement and the public. From a nation's security perspective, nuclear forensics can help authorities attribute material origins, aid in determining the 'when' and 'where' materials have escaped regulatory control and locate security vulnerabilities within nuclear facilities. For the purpose of CMX-5, this is achieved through group inclusion/exclusion analysis, in which the material in question is compared against an exemplar material and nuclear forensic library data.

The numerous illicit nuclear trafficking events that occurred in western and central Europe following the fall of the Former Soviet Union led to the need for a forum for nuclear forensic practitioners and international cooperation in nuclear forensics. The birth of this science eventually

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led to the formation of the Nuclear Forensics International Technical Working Group (ITWG). The group was formed in 1996 from the initiative of the "Group of 8" governments (G8), although the ITWG is an ad hoc group of official nuclear forensics practitioners [4, 6]. The work of the ITWG is supported by experts from some 40 countries (Fig. 1) and international partner organizations including the International Atomic Energy Agency (IAEA) [8] and INTERPOL. Besides providing a network of nuclear forensics laboratories that can assist law enforcement during a nuclear smuggling event, the ITWG is also committed to advancing the science of nuclear forensic analysis.

The stated goal of a CMX is to improve international technical nuclear forensics capabilities, cooperation, and communication between practitioners through the discovery, development and sharing of best practices. These exercises are designed to address investigatory questions of both "legal" and "national security" significance. Each exercise utilizes materials from the nuclear fuel cycle, rather than certified reference materials, and maintains anonymity of individual participant results to ensure these events are learning experiences for the community, not performance tests of any individual laboratory.

Exercise facilitators assumed that each participating laboratory maintains a functioning Quality Assurance and Quality Control program. Following recommendations by the IAEA [8], participating laboratories were required to submit preliminary reports to the exercise facilitator after the first 24 h and again after 1 week following the start of the exercise in all CMX exercises conducted since CMX-3. A final report is also collected 2 months after the start of the exercise. In the four previously conducted exercises the following analytical methodologies outlined in Table 1, have been employed and developed to support a nuclear forensic investigation.

The primary goal of CMX-5 was to improve international technical capabilities, cooperation, and communication in the event of a nuclear material security incident by identifying and sharing best practices concerning nuclear forensic protocols, procedures, analytical techniques, and data interpretation methods.

Objectives identified for the laboratories participating in CMX-5 comprised of:

- Exercise established and novel nuclear forensic methods to identify similarities and differences in exercise samples
- Perform basic nuclear forensics analyses to support legal investigations including Analytical Planning activities and documenting evidence Chain of Custody.
- Prioritize analytical techniques and methods used in the exercise
- Compare the materials using inclusion/exclusion determinations

Fig. 1 Map of the countries that have participated in the at least one of the materials exercises of the Nuclear Forensics International Technical Working Group (ITWG)

Table 1 Techniques and methods identified in the previous ITWG exercises

Techniques/methods	24-h	1-week	2-month
Classical forensics	e.g. Fingerprints		
Radiological	Dose rate (α, γ, neutron)		
	Surface contamination		
	Radiography		
Physical characterization	Visual inspection	SEM (EDX)	TEM (EDX)
	Photography	XRD	
	Weight and dimension	Optical microscopy	
	Optical microscopy		
	Density		
Isotope analysis	γ-Spectroscopy	MS (ICP-MS, MC-ICP-MS, SIMS, TIMS)	
	α-Spectroscopy	α-Spectroscopy	
Elemental/chemical	XRF	ICP-MS	Ion chromatography
		ICP-AES, IC	ICP-MS, ICP-AES
		XRF IDMS	IC, XRF, IDMS

- Utilize an ITWG developed, guideline Graded Decision Framework to accurately communicate results to the lead exercise coordinator
- Test the limitations of bulk isotopic analysis

CMX-5 was designed to test the resolving power of nuclear forensic techniques against visually dissimilar LEU samples that had identical bulk isotopic abundances and very similar bulk trace element signatures. This gave a unique challenge where novel methodologies were required in addition to the isotopic and trace elemental signatures. CMX-5 was the second exercise where participating laboratories were asked to characterise LEU materials. The materials were prepared exclusively for the exercise, which provided for a high level of detail regarding the sample processing histories. In addition, the supplier fully characterised samples prior to the exercise. Exercise samples (A and B) were derived from the same starting materials from enrichment and were blended to contain identical bulk isotopic abundances. Differences during the blending, crushing, mixing and pressing processes generated variations in appearance, morphology, and level of homogeneity of U isotopes. Consequently, unlike previous exercises, it was not until more advanced analyses had been undertaken that any chemical differences in the samples were identified, making CMX-5 different from the outset and creating an opportunity for emerging analytical techniques to be employed for sample analysis.

In this instance, accurate measurements of trace cobalt, chromium, iron, magnesium, manganese and nickel content within the uranium materials provided the participating laboratories potentially useful information about powder/pellet fabrication processes, such as pollution from forced fine sieving, grinding and high-pressure compaction, whose presence could ultimately could be linked to the origin of the materials. The heterogeneity of Material B coupled with the lack of potential signatures, added a level of complexity that challenged laboratories to explore novel techniques that could be used to more fully characterise and exploit features within this type of material. CMX-5 was also the first exercise where injected data was provided to enable the laboratories to establish any links and similarities between samples.

The science of employing nuclear forensics signatures to assess the material production process and facility of origin is developing. CMX-5 attempted to exercise this evolving science within a specified context by asking participants to attribute the origin of "unknown" materials to one of two potential facilities of interest by investigators. While decisively excluding or identifying one of these two facilities as the origin might not have been possible, the goal for CMX-5 was to encourage participants to explore the capabilities and, perhaps most importantly, limitations of the analytical results they generated. Through this process, CMX-5 endeavoured to generate discussion among experts regarding the scientific technologies that might be used to assess the process history and origin of unknown materials and assign levels of confidence to those assessments.

Thanks to efforts by the ITWG, the state of practice of nuclear forensic analysis is continually evolving. Improvements in the ability to process conventional forensics evidence, the toolkit of analytical methods available (over 30 employed in CMX-5) and methods which are continually improving from an emerging technology to state of practice are promising. In addition, the application of methods earlier in time has been a continuing trend; an example has been the reporting of SIMS results in the 1 week timescale in CMX-5. Figure 2 graphically summarizes the time horizons and

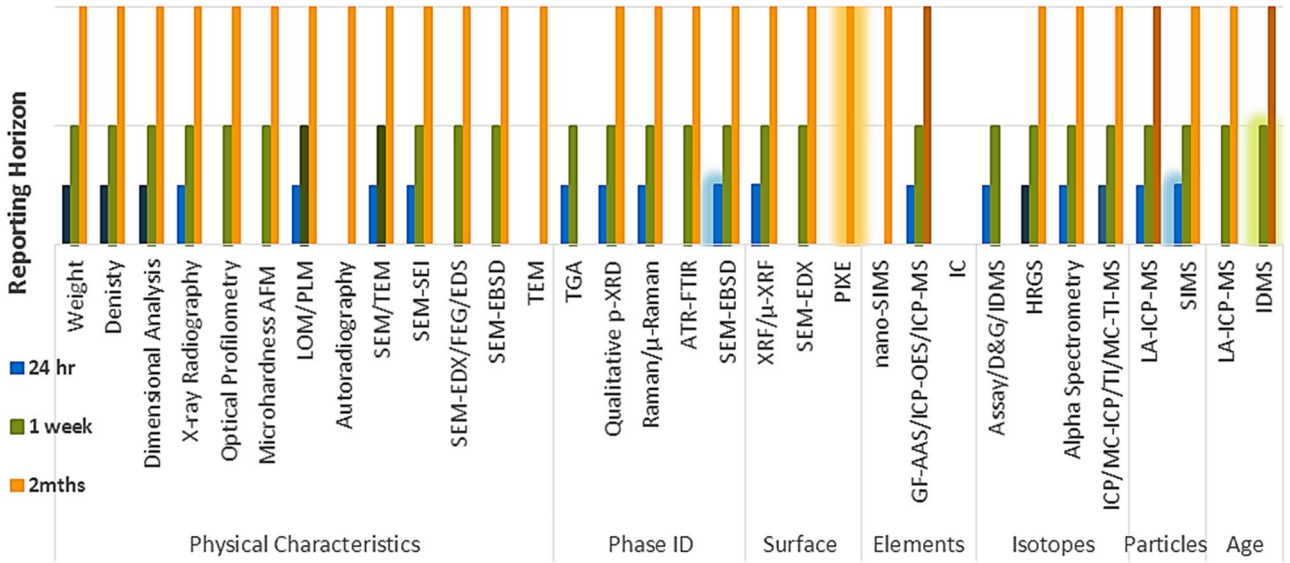

Fig. 2 Classification of state of practice where blue lines indicate analytical techniques used during CMX-5 used within 24 h, green lines 1 week and orange lines 2 months. Emerging technologies are the highlighted lines and a darker shade indicates analytical techniques used by most of the laboratories as a function of reporting time horizon (adapted from [4]). (Color figure online)

operational readiness of techniques used during CMX-5 as a representation of the state of practice.

The scenario

The fictional scenario was as follows:

"In February 2016, border authorities discovered a package in a 'Parcels International' van driven by John Smith at the border control check point between the countries Alpha and Beta. The contents of the package included a dense radioactive object that emitted radiation which has been quarantined by law enforcement (Sample A). The courier company lacked a certificate of a radiation inspection.

Previously in August 2015, a radiation monitor was set off as a vehicle carrying scrap metal entered a steel mill, located in the country Beta. The vehicle was owned by courier company, 'Packages International' and driven by Jack Smith. The scrap metal load was sent back to the scrap yard. Upon examination, a dense radioactive object was discovered and taken into evidence (Sample B). It was suspected to be a nuclear fuel pellet.

Law enforcement have identified that John and Jack Smith are brothers, working for the different courier companies. Additional enquiries interrogating the delivery schedules for 'Parcels International' have led investigators to a warehouse located in the country Alpha. Swipes taken from equipment stored at the back of the warehouse revealed traces of uranium oxide."

The exercise included written injects aligned with the reporting deadlines from the laboratories. The aim was to simulate the typical questions asked by law enforcement.

The exercise samples

Two materials (A and B) were provided by the French Commissariat à l'Energie Atomique (CEA) both of which consisted of high fired, low enriched, uranium oxide (UO_2) pellets. The pellets were manufactured specifically for the CMX-5 exercise in May 2014 in two batches from the same source materials, prepared using two different physical processes. The source materials were enriched UO_2, depleted UO_2 and alumina Al_2O_3. The UO_2 powders were manufactured by the integral dry route at AREVA FBFC-Romans.

$$UF_6 + 2H_2O \Rightarrow UO_2F_2 + 4HF \text{ (Hydrolysis)}$$
$$UO_2F_2 + H_2 \Rightarrow UO_2 + 2HF \text{ (Reduction)}$$

Material A was made using a process representative of AREVA manufacturing of pellets for PWR where the second compression cycle was at a higher pressure. For material B a process where the second compression cycle was used at a lower pressure than the first was performed. The later process had previously been used in the late 70 s, to test the thermal stability of pellets [9].

For each of the materials A and B, 30 pellets at ~ 6 g/pellet were prepared with both pellets containing the same bulk enrichments in ^{235}U relative to the weight percent of isotope. A 1% $^{235}U/U_{tot}$ was thus created by mixing a feed of

4.5% enriched with 0.3% depleted ^{235}U UO_2. However, two very different macrostructures were created, characteristic of each manufacturing process, with U-235 heterogeneity and morphological differences and greater ^{235}U heterogeneity in the macrostructure for material B. Globally traces of the original different powder/pellet fabrication processes, such as pollution from forced fine sieving, grinding and high-pressure compaction, were present in the materials with slightly higher levels in material A [9].

Experimental

In total, over thirty analytical techniques were applied by the 19 participant laboratories to the analytical challenge. The laboratory identities were anonymized for the exercise with a naming convention based on the names of common flowers. Therefore, results from specific laboratories discussed herein will refer to the naming convention employed. The analytical techniques are summarized in Fig. 2, grouped into analysis categories. These are summarized below and in the after-action report [4].

Physical characterization

Physical characterization techniques are used to determine measurands such as mass, density and sample dimensions. Measurement techniques such as X-ray radiography, surface roughness, micro-hardness, optical microscopy, and scanning electron microscopy (SEM), including secondary electron imaging (SEI) and electron back scatter diffraction (EBSD) have been employed during this exercise to physically characterise the samples.

The above techniques are well established in CMXs. These methods were typically used within the first 24 h to 1 week to confirm the material form. Emerging technologies for the community have included X-ray radiography, optical profilometry, atomic force microscopy (AFM), and transmission electron microscopy (TEM). In this exercise, EBSD, X-ray radiography and autoradiography showed valuable utility for the samples encountered in CMX-5.

Elemental analysis

Elemental analysis techniques were subdivided into either surface or bulk techniques. Surface techniques, such as X-ray fluorescence (XRF) and SEM energy dispersive X-ray spectroscopy (SEM–EDX), were utilized by less than half of the participating laboratories and are thus considered emerging technologies for nuclear forensics applications. The bulk methods used during CMX-5 included Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES), ICP-Mass Spectrometry (ICP-MS), isotope-dilution mass spectrometry (ID-MS) and uranium assay by ID-MS and Davies-Grey titration. These established techniques were useful in obtaining elemental data to discriminate between the two samples.

Isotopic analysis

The analytical techniques that were used to quantify U isotopes within exercise samples included three bulk analysis techniques (Alpha Spectrometry (AS), Gamma Spectrometry (GS) and Mass Spectrometry (MS)). In this exercise, a particle mass spectrometry technique was employed and shown to have utility for spatially resolved isotopic analysis (Secondary Ion Mass Spectrometry (SIMS)).

All participating laboratories utilized GS as an initial screening tool within the first 24 h to estimate isotope abundances and assay of ^{235}U and ^{238}U. Most participants measured isotopic composition using one of three bulk MS techniques (including single collector Inductively Coupled Plasma-Mass Spectrometry (ICP-MS), Multi Collector (MC-) ICP-MS, and Thermal Ionization Mass Spectrometry (TIMS)) or AS within 1 week of the start of the exercise to both to quantify U minor isotopes (e.g., ^{234}U and ^{236}U) not measurable by GS and to enhance the precision and accuracy of the initial ^{235}U and ^{238}U measurements initially made by GS. Due to the isotopic similarity on the bulk scale due to the starting materials. The results from spatial analysis were required to support inconsistent isotopic measurements in many cases reported by the participants. This highlights the utility of complementary trace and bulk analysis measurements to answer specific law enforcement questions.

Particle isotope analyses of exercise samples by SIMS were carried out by 7 laboratories, increasing from 2 in CMX-4. Both GS and bulk MS techniques were considered state of practice by the community within 24 h and 1 week, respectively, while AS and SIMS analyses were considered Emerging Technologies. Laser-ablation (LA)-ICP-MS was utilised by one laboratory for rapid 24 h isotopic and 1-week age dating analysis of the material and was particularly useful identifying the heterogeneity in Sample B. One laboratory also utilised accelerator mass spectrometry within the 2-month reporting window for high precision analysis of ^{236}U content. Both techniques are considered as emerging technologies for forensic analysis and were able to show utility this exercise.

Discussion

In The following section highlights the current state of practice and novel applications of analytical techniques to nuclear forensic analysis.

Physical characterization

All laboratories measured the mass of the samples which were consistent with the manufacture's declarations. The expanded uncertainties for mass measurement ranged from 0.0001 to 0.02 g, spanning more than two orders of magnitude and warrants discussion on approaches to quantifying uncertainty in weighing of the samples. Dimensional analysis was used by 17 laboratories to report the dimensions of the samples. In all instances, laboratories noted the dissimilar dimensions for pellets A and B, suggesting differences in the manufacturing of the pellets and the originating facility. In addition, all pellet dimensions for both height and diameter were consistent with manufacturer declarations. There were a variety of approaches using microscopy, magnified photography and digital callipers. The range of the expanded uncertainties were varied and values between 0.01 and 0.5 mm in resolution were reported, Fig. 3.

Density measurements were reported by fourteen of the laboratories and it is considered state of practice due to the utility of the information for modelling and phase determination. Sample B values were generally consistent with manufacturer's declarations, however, overall lower density values for Sample A were observed than those for Sample B and those reported by the originator. Since actinide materials have high densities, measurement of density with a small expanded uncertainty can be used in conjunction with other techniques such as XRF, to rapidly assign an initial actinide phase or to support modelling of sample geometry for radiometric measurements. Many laboratories identified the pellets as UO_2 based on the measured density within the 24-hour reporting window.

Since the CMX-4 exercise in 2014, X-ray radiography emerged as a tool to analyse sample integrity and homogeneity during sample receipt and was again demonstrated as an emerging non-destructive technique as part of the 24-h reporting window. The technique allows for high density objects to be imaged through the recipt packaging by using an ionising radiation source to produce a radiograph image. These images can then be used to estimate the initial quantity, integrity, homogeneity and dimensions of the samples prior to unpacking. The benefit of this technique is that it can allow for additional analysis planning and input data to non-destructive analysis techniques such as gamma spectrometry where dimensions of the sample may be of relevance to geometry modelling. During CMX-5, X-ray radiography allowed for the identification of two high-Z objects to be verified prior to analysis, Fig. 4.

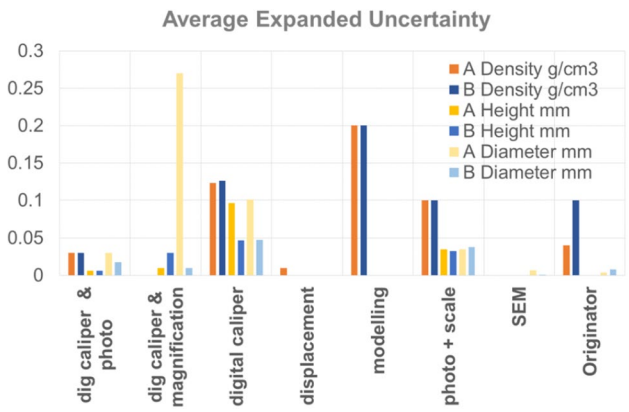

Fig. 3 Relative expanded uncertainties for measurements by technique

Autoradiography is also considered an emerging technology for nuclear forensics. Modern autoradiography techniques based on phosphorimaging technology using imaging plates (IPs) and digital scanning to produce quick and inexpensive spatially resolved images of the relative intensity of alpha and beta emissions from a two-dimensional surface.

The technique offers a relatively quick and inexpensive approach to nondestructively analyze the location of radioactive materials in a matrix or sample, and to map activity distribution in a material. The technique can therefore identify heterogeneities in activity distributions and reveal material properties, serving to inform subsequent analyses.

Such data are complementary to information gathered from radiochemical characterization via bulk counting techniques, and can guide the application of other spatially resolved techniques within a nuclear forensic investigation

The two samples were taken by participant Peony. Figure 5 shows the autoradiographs of the two samples A and B respectively, revealing size, shape, orientation, and distribution of isotopically distinct domains. Isotopically distinct domains were not evident for Sample A at resolution of method (0.0025 mm), whereas enriched Sample Angular domains were observed for Sample B, 0.000625–0.7 mm^2 (average = 0.058 mm^2), randomly distributed, and showed a faint horizontal orientation. Autoradiography was reported to be less labor intensive than microscopy and particle-based techniques and can be used inform the analytical planning of techniques to probe sample heterogeneity. In this case it was also shown to assist in the determination of different processing techniques in the manufacturing of the two samples.

Profilometry (surface roughness) was used as a rapid means for comparing process history. Dahlia reported using a KLA Tencor Alpha Step IQ surface profiler on the as-received pellets. The results confirmed the visual observation that Sample B had a greater surface roughness than Sample A. The surface profile plot (Fig. 6) is shown here to demonstrate this with a small height deviation profile which implies the sample lacked protrusions or features above the surface of the pellet. This is typically indicating a machined or polished surface in areas where the technique is routinely utilised, Fig. 6.

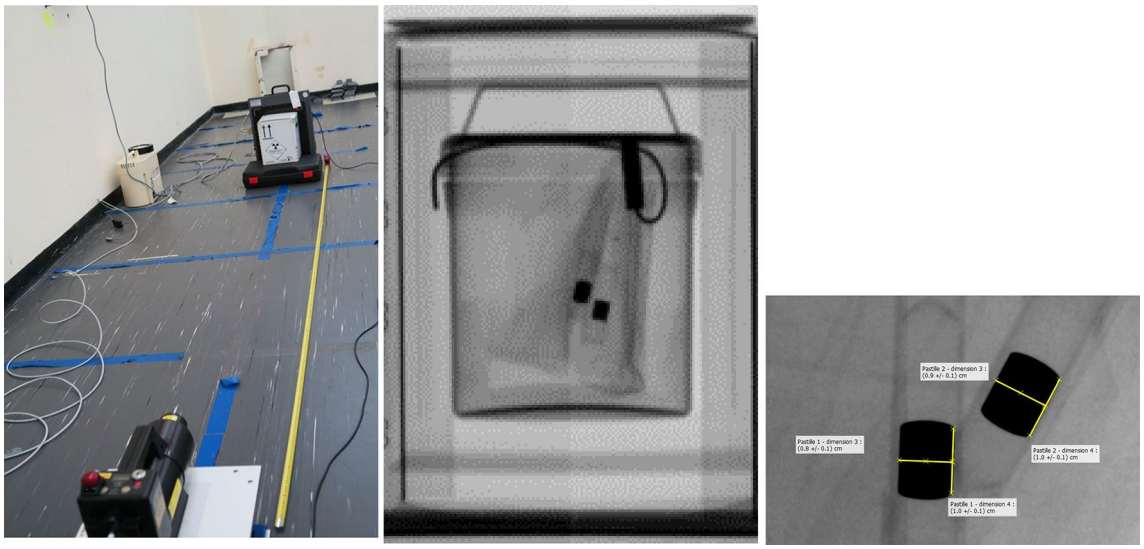

Fig. 4 Photographs from Poinsettia showing X-ray Radiography

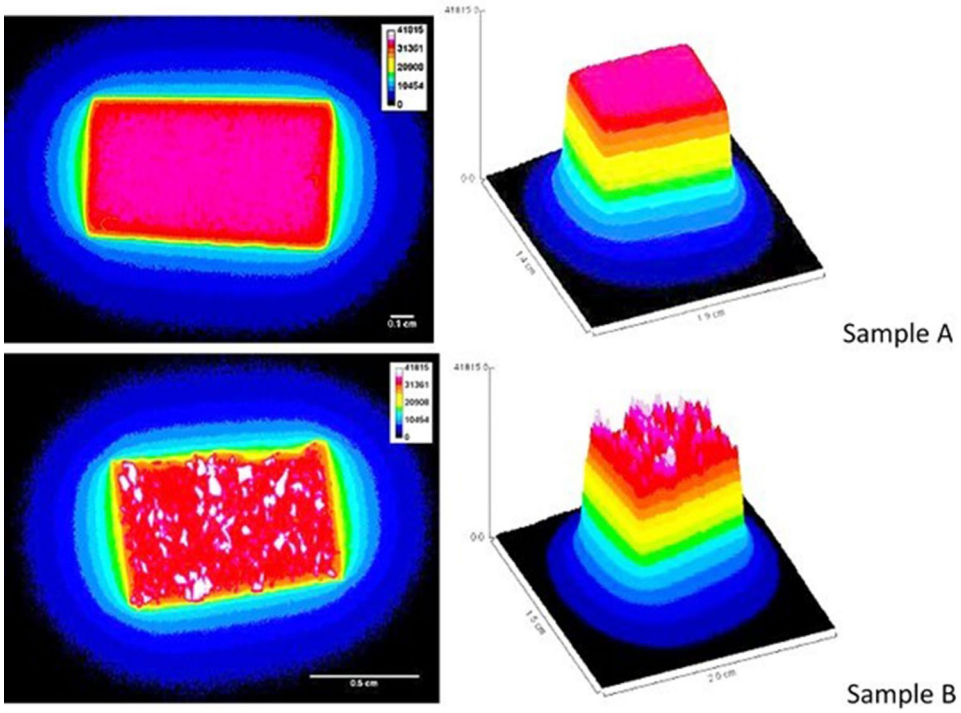

Fig. 5 Autoradiographs of Sample A (top) and B (bottom) provided by Peony revealing size, shape and orientation. The distribution of isotopically distinct enriched sample angular domains for sample B

Measurement of micro-hardness by atomic force microscopy for individual grains from samples A and B was performed by Snapdragon using the Vickers method. The microhardness for Sample A was reported to be 6.24 ± 0.32 GPa, while for Sample B, 5.79 ± 0.34 GPa was reported.

Optical Microscopy (OM) was successfully used to identify major differences and similarities between samples A and B, an example is shown in Fig. 7. Significant observations of microstructure and morphological features were reported by 17 laboratories. Reported differences in grain character, number of inclusions, the prevalence of cracks and pores and the finish and surface polish were considered process markers from sintering or pressing that suggested a different process history for each sample.

OM was complemented by scanning electron microscopy (SEM), 14 laboratories employed SEM for the analysis of samples. Where Secondary Electron Imaging was used it provided the same qualitative information that optical microscopy provided, but at a better resolution. The overall conclusions were that the pellets had a typical sintered

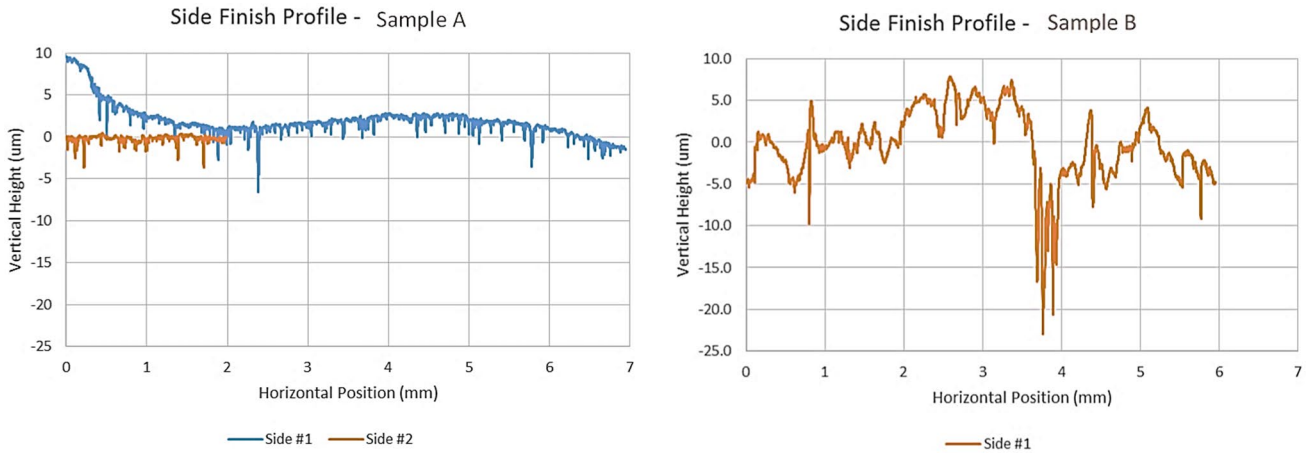

Fig. 6 Surface roughness measurements using a KLA Tencor Alpha Step IQ surface profiler by Dahlia on the as-received pellets, showing that Sample B had a greater surface roughness than Sample A. The presence of downward indentations only in the surface profile plot of Sample A and a lack of protrusions or features above the surface of the pellet suggests the surface machining or polishing

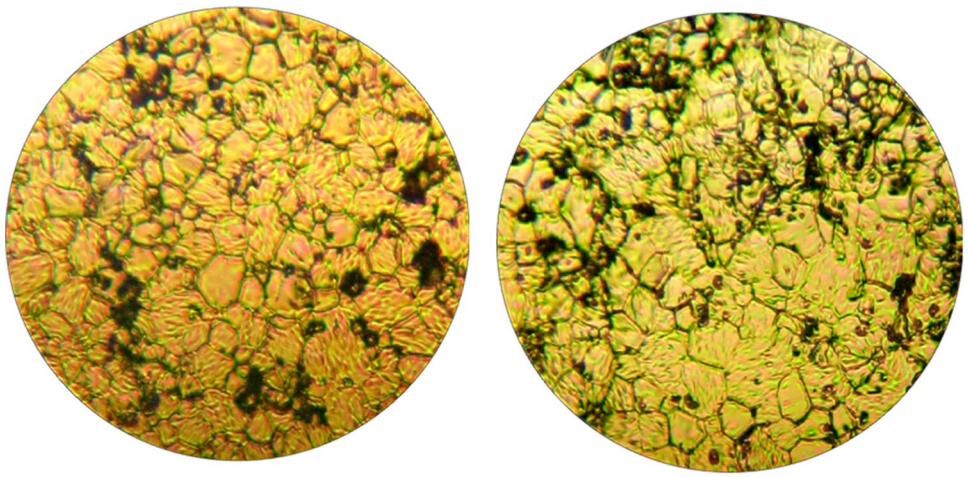

Fig. 7 Optical microphotography 320× Sample A left, Sample B right (Snapdragon)

grain structure with similar grain size but dissimilar grain structure. Both pellets exhibited indications of sintering. However, pellet A had a more solid structure indicative of machining/polishing, whereas B microstructure was dominated by cracks and a clearly visible grain feature suggesting it had been subjected to minimal machining/polishing following sintering. Most laboratories concluded the pellets had been manufactured using different processing. Some suggested differences with sintering temperature or pressure.

Porosity was found to be a distinguishing feature of the CMX-5 pellets and is an emerging technique. Sample A was found to have small and numerous characteristic pore spaces, while for Sample B, small pores and large and irregular cracks and voids that were clearly visible. Several laboratories reported pore size and distribution, relating small pore size with the final stage of the sintering process. Dahlia applied Image J software on 1000× SEI images of large fragments and sections of samples A and B that were chemically etched. Results from that analysis are shown in Fig. 8 and Table 2 and provide a potentially more quantitative indicator than grain size for discrimination of differences between Sample A and Sample B.

Seven laboratories applied EBSD to measure grain size within both A and B pellets. Most laboratories concluded that the range of grain size within Sample B µm was slightly larger than those within Sample A but reported that the pellets had similar average grain sizes. Figure 9 provided by Lily, Iris and Orchid show the slight difference in grain sizes ranges that were reported and the similar mean grain sizes of Sample A and Sample B. Tulip used SEM-EBSD within 24 h to identify that particles from both samples were UO_2.

Overall these emerging physical characterization techniques were shown to give a complementary body of evidence of processing difference between the two samples in a relatively non-destructive manner depending on the sample preparation employed (e.g. on an as received surface

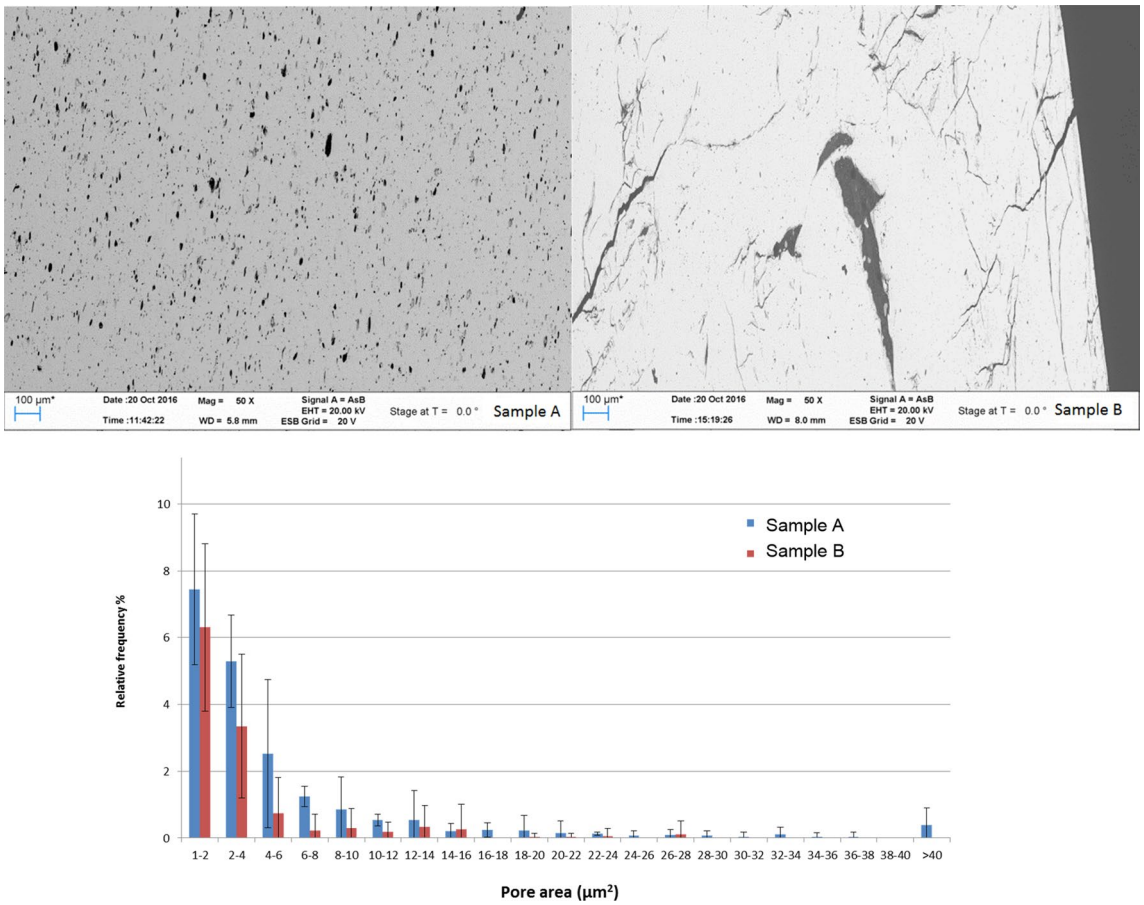

Fig. 8 Pore size images and tabulated data of frequency differences (Dahlia)

Table 2 Porosity data provided by Dahlia

Sample	0.2–1 µm² Relative frequency (%)	Uncertainty (2 S.D.)	> 1 µm² Relative frequency (%)	Uncertainty (2 S.D.)	% area porosity	Uncertainty (2 S.D.)
A	80	4	88	6	4.8	1.1
B	20	4	12	6	2.4	2.3

compared with a polished cross-section). Novel approaches and complementary techniques were shown to allow participants to identify signatures in the material to inform additional analytical planning to answer the exercise questions.

Phase identification

Seventeen Laboratories used Powder X-ray diffraction analysis on the CMX-5 exercise samples successfully identifying UO_2 as the major phase of both Sample A and Sample B within all reporting timescales. Five laboratories performed Raman spectroscopy to successfully identify spectra typical of pure UO_2 and this similar phase was identified in both samples A and B with no surface contaminants identified as being present.

One lab used near infra-red (NIR) reflectance spectroscopy which supported the presence of UO_2 in Sample A and B to complement the XRD analysis. Nine laboratories reported XRF measurements of microchemical analysis within 24-hours, 4 further laboratories within 1 week with two of these laboratories performing additional tests in 2 months. Most laboratories saw minor evidence of any trace constituents other than uranium with this technique.

SEM–EDX was used to identify and analyse inclusions within the pellets. The particpants confirmed metallic inclusions of tungsten, aluminium possibly as oxide, and titanium detected as discrete inclusions in the samples. SEM–EDX

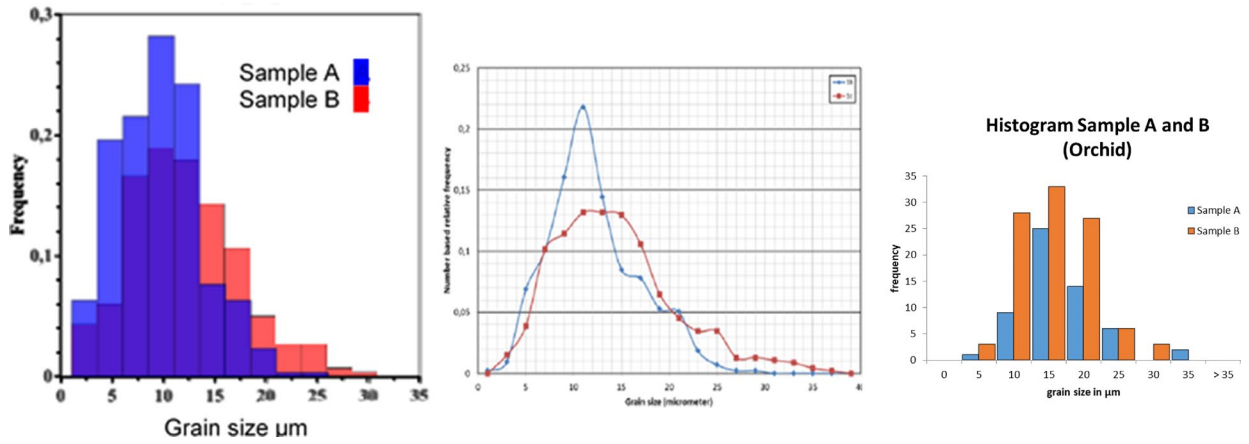

Fig. 9 Grain size and range of size reported by Lily (left), Iris (middle) and Orchid (right)

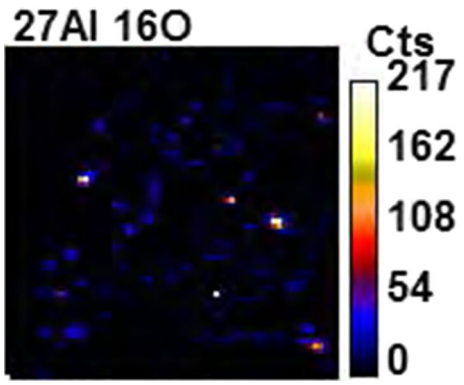

Fig. 10 Detection of discrete Al-oxide particles using nano-SIMS, Sample A (Peony)

was more sensitive for detecting discrete particle contaminants, while XRF provided a higher sensitivity for detecting homogeneously distributed contaminants. Another emerging technique was the use of a Cameca Nano SIMS 50 to survey loose discrete particles sampled using an adhesive carbon tab and processed using custom software. Particles of aluminium (Fig. 10), silicon, calcium, and iron were detected.

These spatial techniques were able to have additional benefits to phase identification, allowing for the the identification of inclusions and processing signatures from the samples. Emerging techniques such as EBSD and Nano SIMS also have the potential to complement isotopic analysis techniques and assist in the quantity of surface data collected from limited mass samples that require nuclear forensic analysis.

Bulk elemental analysis

After 1 week, trace element concentrations were reported by 8 laboratories. An additional 11 more laboratories reported trace element results in their 2-month reports. The results from these 19 laboratories showed small but consistent differences for: cobalt, chromium, iron (Fig. 11), magnesium, manganese, molybdenum and nickel content between Sample A and Sample B were consistent within the uncertainty of the measurement with the manufacturer specification. Overall, laboratories reported lower levels of these elements for Sample B which aligned with the levels injected for the artificial swipe Sample C (inject).

Upon post exercise investigation, some laboratories reported difficulties in fully dissolving samples or inconsistent trace elemental results between Sample Batches suggesting that sample preparation methods might have induced some variability in aluminium results. Consistent levels of alumina which were expected from the blending process were not evident, and consequently, aluminium could not be used as a discriminating identifier for inclusion/exclusion purposes in this exercise.

Isotopic characterization

CMX-5 could be considered a particularly challenging exercise because the pellets had been manufactured to contain the same bulk enrichments, roughly 1 weight percent. Bulk isotopic analysis is usually considered one of the most powerful discriminator techniques for radioactive materials but by design was, in this instance, of limited use for the purpose of comparing Sample A and Sample B.

All exercise participants measured the isotopic abundances of the major and minor isotopes of uranium using various analytical techniques HRGS, alpha spectrometry, and MS techniques, including ICP-MS, Multi-Collector-ICP-MS, TIMS, AMS and LA-ICP-MS. Most participants reported relatively consistent isotopic abundance for each mass that were also consistent within uncertainty that were also in agreement with the originator's analysis. Figure 12

shows the ^{235}U isotopic abundance determined by the participants of the exercise. In general, a greater variation of recorded isotopic abundance for each mass was observed in Sample B. This was also observed in the expanded uncertainties reported, they were larger for Sample B than A which would suggest greater heterogeneity in Sample B.

Tri-plots of $^{234}U/^{238}$ versus $^{235}U/^{238}U$, Fig. 13 below illustrate the conclusions that Sample A and B have indistinguishable bulk isotopic compositions that were

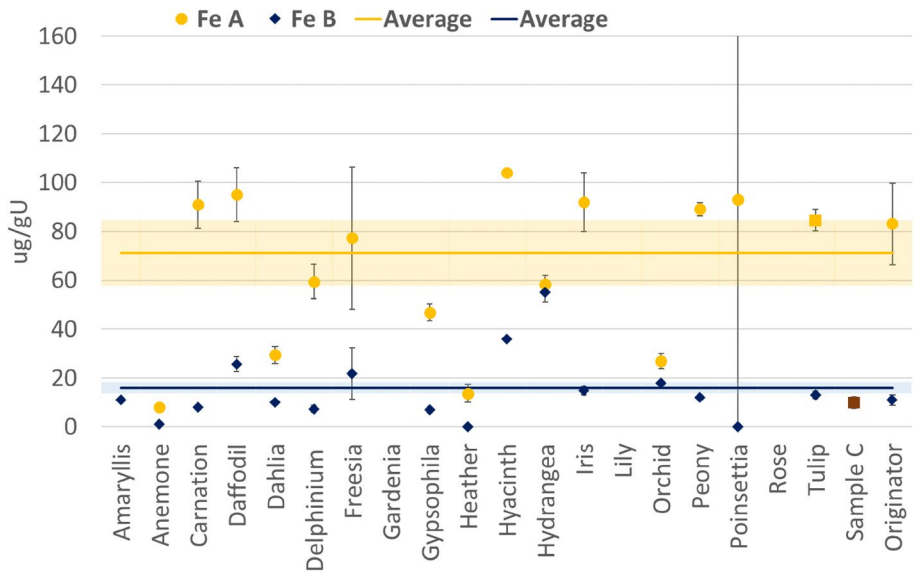

Fig. 11 Iron trace elemental results by exercise participants for determining different processing conditions between samples

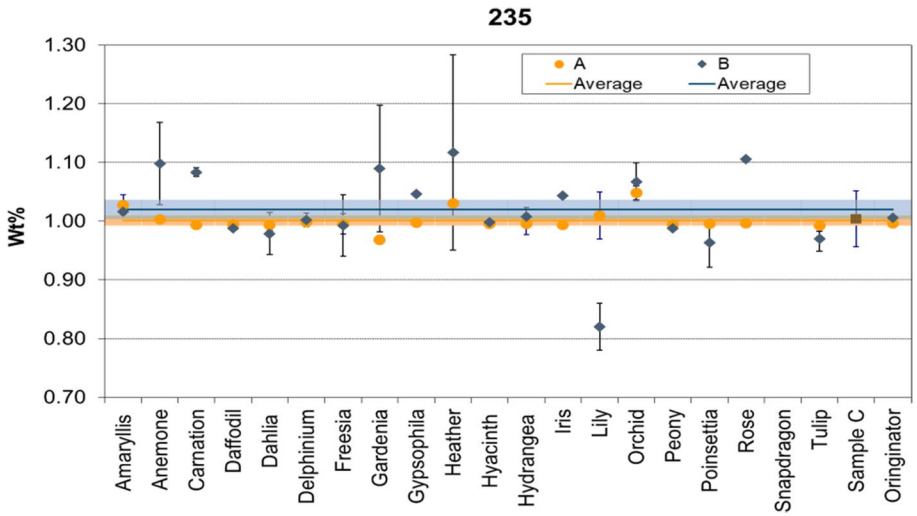

Fig. 12 ^{235}U isotopic abundance determined by the participants of the exercise

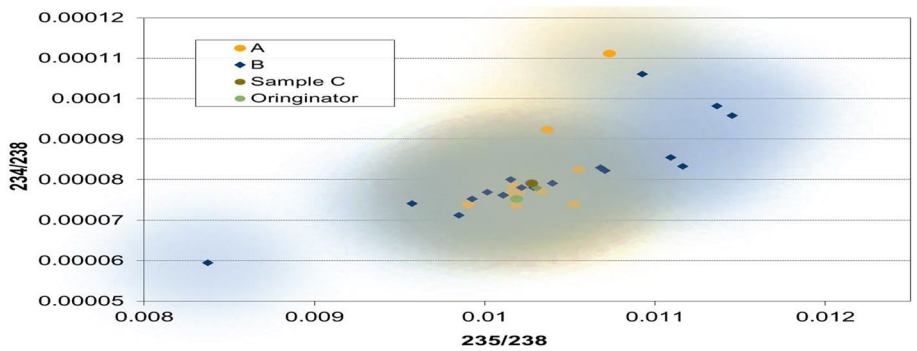

Fig. 13 Tri-plot Comparison $^{234}U/^{238}U$ versus $^{235}U/^{238}U$

consistent with Sample C (inject) and are consistent within the uncertainty of the measurement with the originators data. Any isotopic compositional differences would be shown as distinct cluster populations. The absence of distinct clusters in the tri-plot comparisons for A and B indicates that Sample A and B have indistinguishable isotopic compositions.

Multiple methods of varying complexity were used to detect heterogeneities in U isotopic abundances. Replicate bulk analysis is a simple, easy means for testing for heterogeneities, however resolution is limited to the minimum sample size collectable by the operator and is relatively tedious and time consuming to apply. Limited information may be provided due to restriction with the sample size and number of samples that can reasonably be processed and analysed in this manner.

Figure 14 provided by Peony shows the tri-plot of $^{235}U/^{238}U$ vs $^{234}U/^{238}U$ for three separate sample portions of each pellet. The analysed aliquots of Sample A (blue) are isotopically indistinguishable, whereas the three analysed aliquots of Sample B (orange) are isotopically distinct. All analyses of sample B fall within the uncertainty of a single linear regression.

An emerging technique in nuclear forensics is the use of alternate sample introduction techniques for state of practice techniques such as the use of a nano second laser to ablate the sample for ICP-MS. Small samples can be ablated at known positions of the samples to analyse for isotopic and elemental heterogeneity.

Hyacinth used laser ablation to answer questions posed by investigative authorities in CMX-5. They used a CETAC LSX-213 (213 nm) nanosecond LA-ICP-MS system equipped with a system microscope and coupled to an Agilent 8800 (QQQ) ICP-MS.

LA-ICP-MS can be used to detect heterogeneities in U isotopic abundances. The technique can sample a large number of spatially resolve replicate measurements with a good level of precision and accuracy relative to other spatially resolved techniques (e.g. SIMS). The laser ablation signal for ^{235}U for Sample B where the shaded area corresponds to the calculated enrichments, 0.39% and 4.6% respectively, in segments of the pellet, Figs. 15 and 16 respectively.

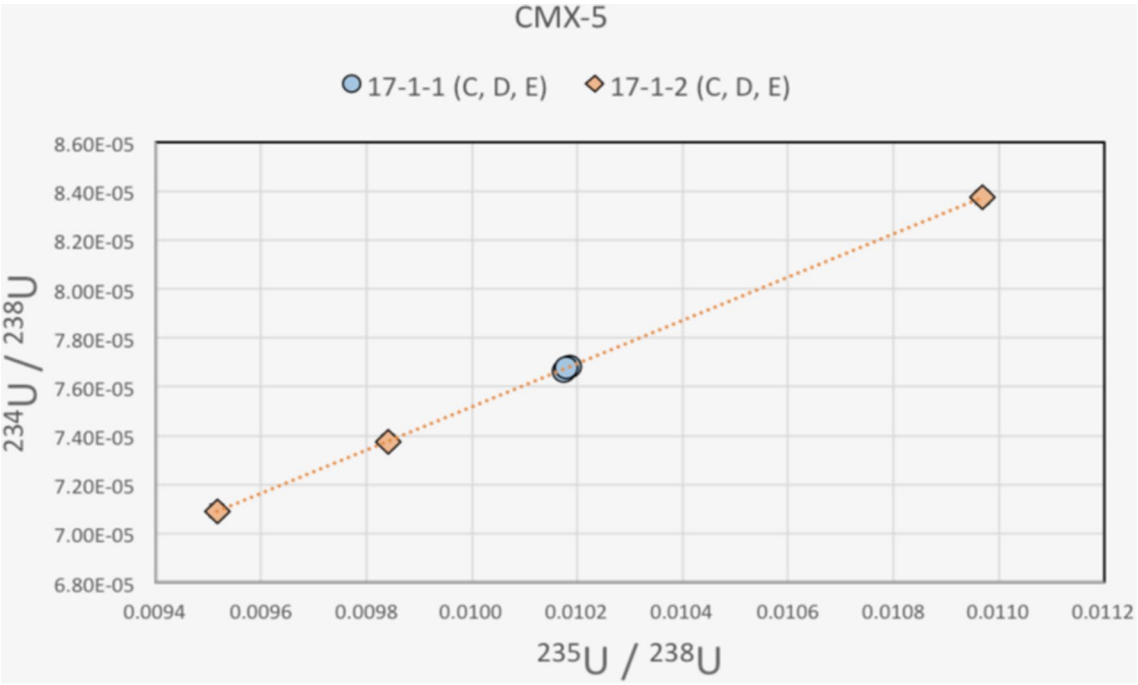

Fig. 14 Triplot of $^{235}U/^{238}U$ vs $^{234}U/^{238}U$ for three separate sample portions (Peony), Measurement uncertainties are smaller than plot symbols

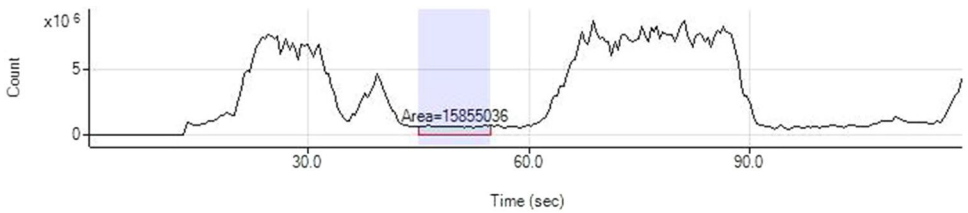

Fig. 15 Ablation signal corresponding to 0.39% 235U enrichment in Sample B, Hyacinth

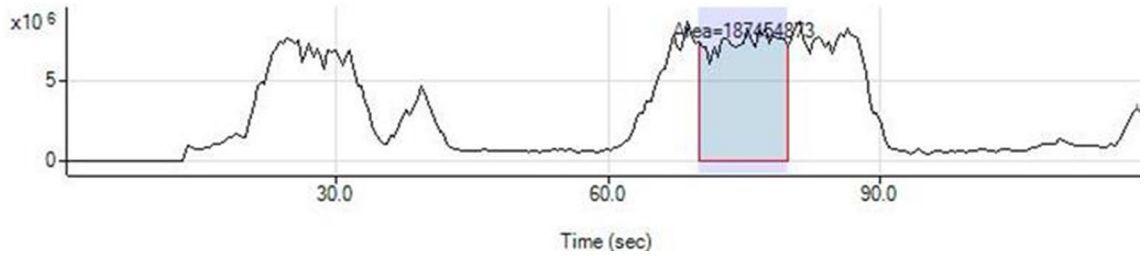

Fig. 16 Ablation signal corresponding to 4.6% 235U enrichment in Sample B, Hyacinth

Figure 17 graphically displays the use of LA-ICP-MS for the measurement of the isotopic abundance within each sample. The application of this emerging technique in this scenario shows the utility of the complementary spatial and isotopic data that can be obtained on a forensic sample, particularly for samples of limited mass.

Particle analysis

Six laboratories performed isotopic analysis on particles from Sample A and Sample B using SIMS. Different models of instruments were used, but, in general, the sample preparation and analysis were similar. Particles were collected by swipes or swabs followed by impaction of particles on to carbon planchets prior to analysis.

SIMS analyses measured isotopic abundances for individual particles within the samples. Generally, the six laboratories produced isotopic results for individual particles that were consistent with each other within the uncertainty of the technique, detecting greater variation in isotope abundances in particle to particle in Sample B relative to Sample A. Tulip analyzed particles using Large Geometry (LG)-SIMS, Fig. 18, and found that Sample A had average enrichment of 1% ^{235}U with no indication of blending. In Sample B, Tulip found that ~90% of the U particles were depleted to 0.3% and enriched and 10% were enriched to ~4.5%. Analysis of Sample B indicated blending of materials to deliver a bulk pellet enrichment at ~1%.

Radiochronometry

Radiochronometry has the potential to be a powerful nuclear forensics discriminator. CMX-5 results were consistent with the material processing and preparation history, well known since samples were prepared specifically for this exercise using the same source materials. Consequently, the time

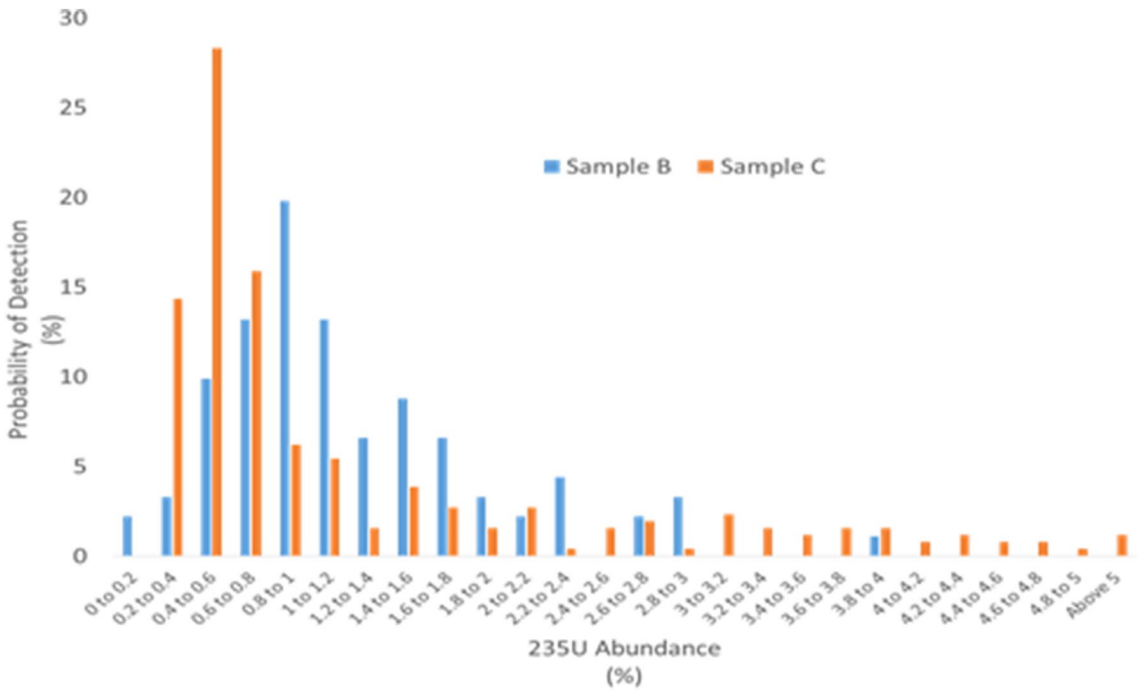

Fig. 17 LA-ICP-MS detection of 235U isotopic heterogeneity in samples (Hyacinth)

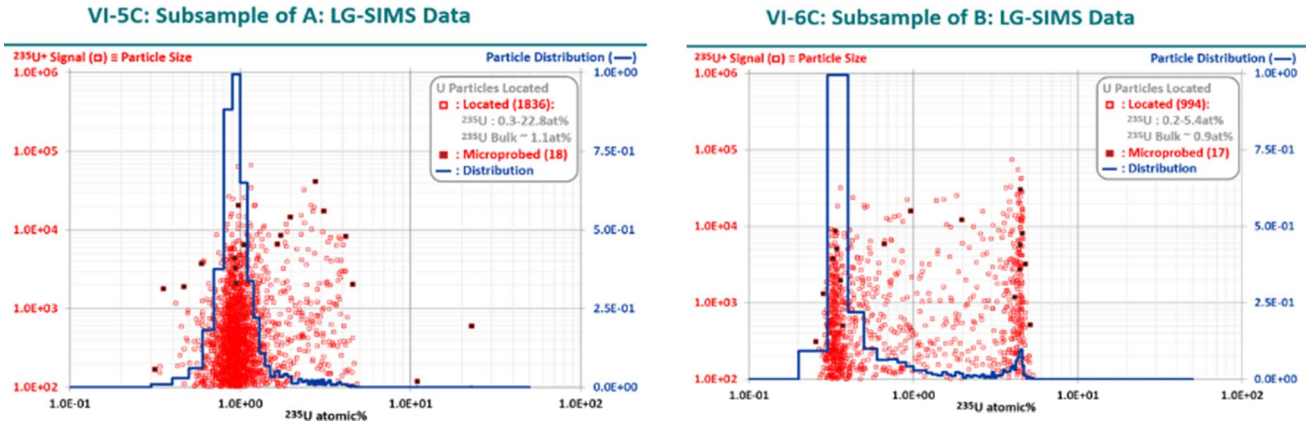

Fig. 18 LG-SIMS data showing particle distribution, size and enrichment (Tulip)

elapsed from material chemical processing when parent and daughter radioactive isotopes were last separated, was very similar. Most laboratories calculated apparent process age based upon the $^{230}Th/^{234}U$ decay relationship with assumptions that complete separation of parent/daughter isotopes occurred during processing; that there was known or zero concentration of the daughter at time zero and that no other system changes occurred following processing except radioactive decay. Results across laboratories were quantitatively and qualitatively consistent.

There was no evidence implying incomplete separation of Th that would cause laboratories to overestimate age. An underestimation of age may occur due to process loss during sample preparation or due to non-representative sampling of a heterogeneous material. 11 laboratories reported model ages for samples A and B, Fig. 19, that compare well with the originators known processing date for the oxide source materials, the 4.2% ^{235}U, 4.5% ^{235}U and 0.3% UO_2 powders blended to produce the feed materials of the pellets, March 2012. CMX-5 implies that radiochronometry can be used to accurately represent actual process age of a real-life unknown sample of similar process type and history and shows the continuing utility of this nuclear forensic signature.

The state of practice for nuclear forensic analysis

Timeliness of analyses are an important factor for nuclear forensic science in support of a law enforcement investigation. The IAEA's guidelines for nuclear forensics [8], recommend laboratories to submit preliminary reports after the first 24 h, after 1 week and a final report 2 months report to support a nuclear forensic investigation. Table 3 indicates typically what techniques could reasonably be used to produce good quality data for a given timeframe. From CMX-5, autoradiography, LA-ICP-MS and radiochronometry have all been added and alpha spectrometry has been identified as being used in the 1-week timeframe.

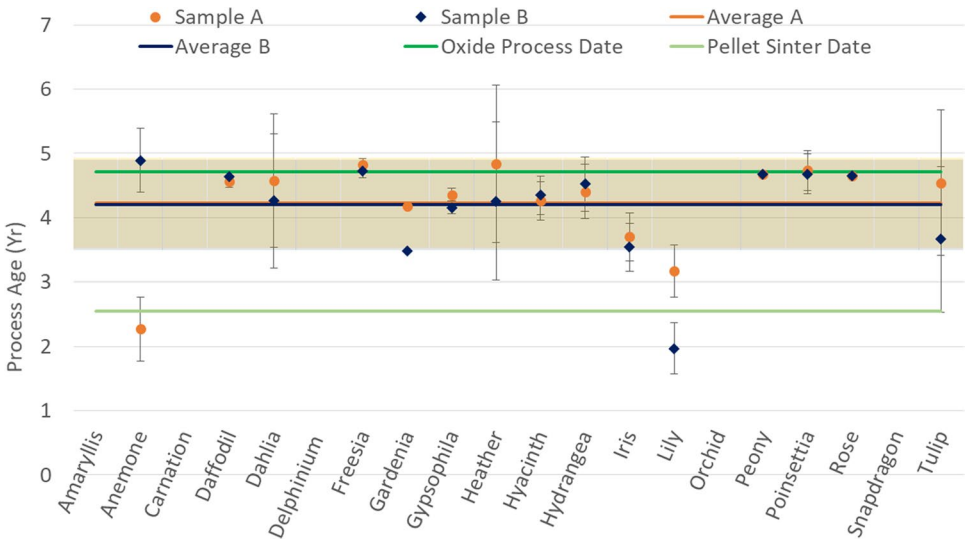

Fig. 19 Radiochronometry reported for CMX-5 samples A and B by 15 laboratories

Table 3 State of practice for nuclear forensic analysis updated following CMX-5

Techniques/methods	24-h	1-week	2-month
Classical forensics	Fingerprints	Toolmarks DNA	
Radiological	Dose rate (α,γ, neutron)	Autoradiography	
	Surface contamination		
	Radiography		
Physical characterization	Visual inspection	SEM (EDX, EBSD)	TEM (EDX)
	Photography	XRD	
	Weight and dimension	Optical microscopy	
	Optical microscopy		
	Density		
Isotope analysis	γ-Spectroscopy	MS (ICP-MS, MC-ICP-MS, SIMS, TIMS)	Radiochronometry
		α-Spectroscopy LA-ICPMS	
Elemental/chemical	XRF	ICP-MS	Ion chromatography
		ICP-AES, IC	ICP-MS, ICP-AES
		XRF IDMS	IC, XRF, IDMS

Table 4 Nuclear forensic laboratories participating in CMX-5

Australia, Australian Nuclear Science and Technology Organisation (ANSTO), New South Wales

Austria, Austrian Research Center, Seibersdorf GmbH, Austria

Brazil, Commissao Nacional de Energia Nuclear, Pocos de Caldas

Canada, Canadian Nuclear Safety Commission Laboratory, Ottawa, Canadian Nuclear Laboratories, Chalk River and Royal Military College, Kingston

China, Chemical Analysis and Test Center of China Institute of Atomic Energy (CIAE)

Czech Republic, Nuclear Research Institute, Rez.

European Commission, Joint Research Centre (JRC), Karlsruhe

France, Commissariat à l'Energie Atomique

Germany, Institut für Radiochemie, München

Hungary, Centre for Energy Research (EK), Budapest

Israel, Soreq NRC, Radiation Protection Division, Yavne

Japan, Japan Atomic Energy Agency (JAEA)

Lithuania, Lithuania Institute of Physics, Vilnius

Netherlands, Centre for Environmental Safety and Security, Bilthoven

Poland, Institute of Nuclear Chemistry and Technology, Warsaw

Republic of Kazakhstan, Center of Complex Environment Research, Institute of Physics, Almaty

Republic of Korea, KAERI, Nuclear Chem. Res. Div. Daejeon

Republic of Moldova, Laboratory of Radiology and Radiation Control, Chisinau

Romania, Horia Hulubei National Institute for R&D in Physics and Nuclear Engineering, Bucharest-Magurele

Russia, Laboratory for Microparticle Analysis, Moscow

Singapore, DSO National Laboratory

South Africa, NECSA-NOMS, Nuclear Forensics Lab

Sweden, FOI, CBRN Defence and Security

Turkey, Çekmece Nuclear Research and Training Center, Istanbul

United Kingdom, Atomic Weapons Establishment, Aldermaston

United States of America, Department of Energy, Lawrence Livermore and Los Alamos National Laboratories

Conclusions

The ITWG completed its fifth CMX in the 23 year history of the Group. CMX-5 was the largest materials exercise to date, with participating laboratories from 20 countries or multi-national organizations. Two fuel pellet samples of Low Enriched Uranium were shipped to these laboratories as part of a ''paired comparison'' exercise, simulating an illicit trafficking event, for which each laboratory was asked to conduct nuclear forensic analyses in support of a fictitious criminal investigation.

An objective review of the analytical techniques considered to be State-of-Practice and those finding emerging application for nuclear forensic analysis based upon the outcome of 2 month most recent exercise was conducted. In all, over 30 analytical techniques were applied to characterize exercise materials, 4 of those techniques were applied to ITWG exercises for the first time.

State-of-Practice isotopic techniques were not able to render conclusive evidence for group inclusion/exclusion evaluations of the samples due to the material isotopic similarity. This is contrary to previous sample investigations where this has been a key forensics signature. The exercise has therefore demonstrated that the characteristics useful for inclusion/exclusion assessments are case specific, and directly tied to the materials and questions being asked by investigators and the sample type under investigation. This further strengthens the case to continue these collaborative materials exchanges and evaluation of the state of practice, to ensure we can readily identify the techniques applicable to material type and investigator questions.

State-of-Practice techniques for physical characterization and elemental impurities were able to distinguish between the processing histories of the two samples to allow for determination of the production facility in a hypothetical scenario.

Emerging Technologies provided conclusive evidence for group inclusion/exclusion evaluations included l-hardness measurements using AFM, autoradiography, phase identification by microscopies (SEM-EBSD), and isotopic particle analysis using SIMS. In addition, isotopic heterogeneity was used to investigate the samples using SIMS and the emerging technique of LA-ICP-MS.

Analytical techniques deemed State-of-Practice that were able to provide suggestive evidence for group inclusion/exclusion evaluations were, SEM-SEI and bulk elemental analysis techniques (ICPMS, ICP-OES, GF–AAS).

Acknowledgements The exercise participants listed in Table 4 and the international technical working group on nuclear forensics are thanked for their patience and assistance in producing the manuscript and results presented herein.

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