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Radiochronometry in the CMX-4 Exercise-Draft

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The Application of Radiochronometry in the Nuclear Forensics International Technical Working Group's CMX-4 Exercise

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Radiochronometry in CMX-4

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Abstract

In a recent international exercise, 10 international nuclear forensics laboratories successfully performed radiochronometry on 3 low enriched uranium oxide samples, providing 12 analytical results using 3 different parent-daughter pairs serving as independent chronometers. The vast majority of the results were consistent with one another and consistent with the known processing history of the materials. In general, for these particular samples, mass spectrometry gave more accurate and more precise analytical results than decay counting measurements. In addition, the concordance of the ^{235}U-^{231}Pa and ^{234}U-^{230}Th chronometers confirmed the validity of the age dating assumption, increasing our confidence in the resulting conclusions.

Keywords

nuclear forensics, radiochronometry, uranium oxide, inductively coupled plasma mass spectrometry, thermal ionization mass spectrometry, gamma spectrometry, alpha spectrometry

Introduction

Nuclear Forensics

Over the past decade, nuclear forensics has developed into an integral part of a robust nuclear security program. It has been specifically identified in the Communiqués, Plans, and Joint Statements of the Nuclear Security Summits in 2010, 2012, 2014, and 2016 as an important focus area for research. The fundamental tenet underlying nuclear forensics is that identifying the origin of nuclear materials found outside of regulatory control can help identify gaps and weaknesses in the physical security and/or safeguards of a particular country or facility, which can then be strengthened in response. In addition, any country or organization that considers thwarting international law or practice by trafficking in such nuclear materials might be deterred by the knowledge that their complicity in such trafficking is likely to be identified [1]. The currently accepted definition of nuclear forensics is “the examination of nuclear or other radioactive materials or of evidence contaminated with radionuclides in the context of international or national law or nuclear security. The analysis of nuclear or other radioactive material seeks to identify what the materials are, how, when, and where the materials were made, and what were their intended uses [2]. ”

Radiochronometry

At the same time that the policy implications of nuclear forensics have become increasingly mature, laboratories around the world have continued to develop the underlying science, as well as the applications of that science to actual cases. The development of radiochronometry, or “age dating”, and its application to nuclear materials is one area of intense research [3-9]. Radiometric model ages are determined from measurements of parent and progeny isotopes (typically daughter, but also granddaughter) that accumulate in a material due to decay of the radioactive parent isotope. U- and Pu-series disequilibrium dating are most often used for nuclear forensic investigations. Calculated model ages are based on two fundamental assumptions: 1) the material was completely purified from decay products at the time it was produced, and 2) since the time that it was produced, the material has remained a closed system with neither gain nor loss of parent or progeny. The age of nuclear material is an important forensic signature because it can be used to constrain the time of purification or production (a predictive signature) and establish or eliminate potential genetic links among different samples of nuclear materials (a comparative signature). Ideally, the age inferred from the laboratory analysis of a sample (referred to as a “model age”) represents the actual production, processing, or purification age of the nuclear material of interest (referred to as a “sample age”). In practice, model ages may differ from sample ages because the sample production history is not necessarily consistent with the model assumptions on which the chronometry determinations are based. Understanding the physical and chemical causes of these inconsistencies and developing experimental and theoretical approaches to address them is an active focus area of nuclear forensics research. Increasing emphasis is being placed on using multiple chronometers to better understand the chemical or physical processes that might "reset" certain chronometers.

The Nuclear Forensics International Technical Working Group

The Nuclear Forensics International Technical Working Group (ITWG) is an organization of technical experts, law enforcement officials, policy makers, and diplomats from interested governments who cooperate to advance the field of nuclear forensics [10-11]. Since the first organizational meeting of the ITWG held at Lawrence Livermore National Laboratory (LLNL) in 1995, the ITWG has held twenty additional meetings, with participation from representatives of over 30 different countries and international agencies. Conducting inter-laboratory practical exercises has been one of the organization's key activities from the beginning. In 1999, ITWG conducted its first exercise involving the analysis of plutonium oxide powder from the European civil nuclear cycle. Its second exercise was held in 2003 and involved the analysis of highly enriched uranium (HEU) oxide powder [12-13]. The third ITWG round-robin exercise (RR-3) was completed in 2010 and was the first paired-comparison exercise conducted by the ITWG [14-15].

Collaborative Material Exercise 4 (CMX-4), the ITWG exercise featured in this paper, was designed to test the resolving power of isotope measurement techniques using low-enriched uranium (LEU) samples of very similar isotopic abundances. This was the first exercise where participating laboratories were asked to analyze LEU materials. This selection of material allowed the exercise participants to understand the viability of rapid, non-destructive assay (NDA) techniques to estimate enrichment levels of LEU materials. The use of bulk isotopic analyses, often considered the most powerful potential signature for the purpose of group inclusion/exclusion comparisons for the nuclear forensics community, was also highlighted during CMX-4. However, based upon the outcomes of the last ITWG materials exercise (Round Robin 3), information provided by material characteristics other than isotopic abundances were identified to be of growing interest to the nuclear forensics community. These characteristics include, but are not limited to, trace elemental content, solid phase composition, and morphological and microstructural character of materials. CMX-4 was designed to exercise analytical techniques that probe these characteristics. In keeping with ITWG practice, the identity of individual laboratories is obscured through the use of designators or code names. For this exercise, the laboratories were given the name of a famous artist.

Exercise Scenario

The fictional scenario provided as context for the nuclear forensic analyses was as follows:

> On a tip from a confidential informant, a passenger scheduled to fly out of Dallas International Airport to Frankfurt, Germany, has been stopped by the authorities at the airport for alleged "simple possession" of a radioactive substance without proper documentation. "Simple possession" means that possession alone is sufficient to demonstrate that a violation occurred. These laws also provide for exemptions for legitimate uses, to include research and industrial use, but require that a permit be issued for such uses. The authorities seized a small, flexible plastic container (commonly referred to as a "baggie") containing a black, powdery radioactive substance alleged by the confidential informant to contain uranium. In a separate search of the subject passenger's residence, Texas authorities located and took into evidence a second sample consisting of a dense radioactive object, suspected to be a nuclear fuel pellet that would be used for nuclear power generation. Similar uranium pellets have previously been seized by authorities two years prior at an abandoned warehouse outside of Frankfurt, Germany.

Experimental

Sample Materials

Two source materials (A and B) were used to create three CMX-4 exercise samples (ES-1, ES-2, and ES-3). These source materials were provided by the Australian Nuclear

Science and Technology Organisation (ANSTO) and consisted of high fired, LEU uranium oxide (UO_2) pellets of slightly different ^{235}U enrichments. These pellets were intended to be used as targets in the High Flux Australian Reactor (HIFAR) in the production of medical radioisotopes. They were originally produced by AREVA (FBFC, Framatome ANP) for ANSTO but were not used prior to retiring the HIFAR in 2007.

The pellets from source A were produced as part of a single batch in September 25, 2002, using UF_6 enriched on February 12, 2002. The pellets from source B were produced as part of a single batch in 2004 (the exact date is unknown), with the enrichment obviously having taken place before. Source A and B consist of 90 pellets each. The two source materials differed in enrichment of the isotope ^{235}U, ~ 2.19% and ~2.9%, respectively.

Three exercise samples were generated from Sources A and B and distributed to each laboratory participating in CMX-4 through a hub laboratory, the U.S. DOE Y-12 National Security Complex, which was capable of entering and removing source material into and out of International Atomic Energy Agency (IAEA) safeguards. ANSTO, with the help of a staff person from DOE’s Pacific Northwest National Laboratory (PNNL), prepared, characterized, and packaged samples prior to shipping them to Y-12. The preparation of each of these samples is described below.

> <u>Preparation of ES-1</u>: ES-1 was made up of Source B pellets that had been crushed to a powder and partially converted with heat to a higher oxide form. Specifically, a pellet from Source B material (taken from the same batch used to generate ES-3) was milled in a large Wig-L-BugTM for 2 minutes. The powder from this process was then heated to 325 °C at a ramp rate of 10 °C/minute. This temperature was held constant at 325 °C for 90 minutes.
>
> <u>Preparation of ES-2</u>: ES-2 consisted of a single, unadulterated, pellet taken from a single batch within source material A. The surface of each pellet was wiped clean prior to packaging for shipment.

> Preparation of ES-3: ES-3 consisted of a single, unadulterated, uranium pellet taken from a single batch within source material B. The surface of each pellet was wiped clean prior to packaging for shipment.

Radiochronometers

^{234}U-^{230}Th Chronometer

Because the half-life of ^{234}U is relatively short (2.45×10^{5} years) compared to the other naturally occurring uranium isotopes, ^{235}U and ^{238}U, the ^{234}U-^{230}Th chronometer is one of the most straightforward chronometers to measure and certainly the most widely applied [3,5,6,8,16]. The chronometer becomes increasingly easy to measure as the ^{234}U abundance, and hence the amount of its progeny, ^{230}Th, increases. Because the ^{234}U abundance tends to increase with ^{235}U enrichment for most enrichment technologies, its ease of application increases with increasing enrichment of the sample. Since the samples for CMX-4 were LEU, measuring the ^{234}U -^{230}Th chronometer should have been relatively straightforward, certainly easier than in natural uranium samples, although not as easy as with HEU samples.

The two most commonly applied techniques for quantifying the level of ^{234}U and ^{230}Th in uranium samples are mass spectrometry and alpha spectrometry. Due to the relatively long half-lives of ^{234}U and ^{230}Th, mass spectrometry, as an atom counting technique, normally provides lower detection limits and greater precision than alpha spectrometry, which is a decay counting technique. However, an alpha spectrometer is a relatively inexpensive instrument that can be found in many laboratories that do not have the necessary mass spectrometer. Note that both thermal ionization mass spectrometers (TIMS) and inductively coupled plasma mass spectrometers (ICP-MS), which may be equipped with either a single or multiple collector(s), can be used for age dating. The utilization of these techniques and instruments for age dating in CMX-4 are given in Table 1.

Table 1. List of Instruments Used for Age Dating in CMX-4

Technique/Instrument	**Th Analysis**	**U Analysis**
Alpha spectrometry	3	2
Multicollector ICP-MS	2	2
Sector field ICP-MS	3	2
Quadrupole ICP-MS	1	1
Multicollector TIMS	2	4

Regardless of technique, isotope dilution is typically used for quantification. With this method, quantification is achieved by measuring the isotope of interest (e.g. ^{234}U) relative to a spike or tracer isotope (e.g. ^{233}U). However, in CMX-4, 2 laboratories used unspiked isotopic analysis in combination with other assay techniques, delayed neutron counting (Cezanne) and external calibration using NIST SRM 4321C (Manet), to calculate the ^{234}U concentration necessary for age dating. For those labs that used isotope dilution for U quantification, 7 laboratories used ^{233}U spikes, one laboratory used a ^{232}U spike, and another used the NBL U930 standard as ^{235}U spike. For Th quantification, 8 laboratories used ^{229}Th, while the remaining 3 labs used ^{232}Th, as isotopic spikes for Th quantification.

All 3 laboratories that performed alpha spectrometry used chemical separation of the Th from the U, followed by fluoride microprecipitation to create plates for alpha counting. Both TIMS and ICP-MS also typically require chemical separation of Th from the U matrix prior to analysis. This is necessary to improve ionization efficiency (TIMS) and reduce matrix effects, low-mass tailing effects, and memory effects that may result from loading the instrument with high concentrations of U (ICP-MS). However, one of the laboratories used a procedure published by Varga et al [22] which offers an offline correction for the peak tailing effect and provides accurate Th results using ICP-MS. Purification of a bulk U sample prior to U analysis by TIMS or ICP-MS may not be necessary, depending on the purity of the sample. If the bulk sample is sufficiently pure, then molecular isobaric interferences in the U mass range, for example, ^{232}ThH^{+}, will be insignificant. In addition, tailing to nearby masses and hydride formation usually occur in the range of 10^{-5} – 10^{-6} [24], there will not be a need for correction due tailing or hydride formation from ^{232}Th on m/z=233.

For this exercise, all laboratories separated and purified the Th fraction prior to analysis by alpha spectrometry or mass spectrometry. However, only 3 laboratories purified the U fraction (2 from the bulk solution; 1 from the U fraction after separation from Th prior to analysis by alpha spectrometry). 7 laboratories used a TEVA column to separate the U and Th; 3 laboratories performed a subsequent purification using another TEVA column. 3 laboratories used a multi-step purification starting with an anion exchange column. Cezanne used an anion exchange column followed by a TRU-Spec column, and finished with a cation exchange column. Gauguin used an anion exchange column, followed by a TEVA column, and finished with another anion exchange column. Bondone used back-to-back anion exchange columns, the first of 120 µm particle size and the second of 25 µm particle size. Monet used a separation procedure based upon a macroporous Lewatit MP5080 ion exchange resin. All procedures used by the different participants for the ^{234}U-^{230}Th chronometer can be found in Table 2.

Table 2. Analytical Procedures Used by Each Participant

Participant	Analyte	Instrument	Purification prior to measurement	Separation	Spikes added	Reference if applicable
Rembrandt	^{230}Th	α spectrometry	Yes	TEVA® resin cartridge	^{229}Th	
	^{234}U	α spectrometry	Yes	Fe(OH)$_2$ precipitation; stacked TEVA®/TRU resin cartridges	^{232}U	
Cezanne	^{230}Th	α spectrometry	Yes	anion exchange resin column; TRU resin column	^{229}Th	
	^{234}U	α spectrometry	Yes	TRU resin column; cation exchange resin column	N/A	
Pollock	^{230}Th	α spectrometry	Yes	TEVA® resin cartridge	^{229}Th	
	^{234}U	MC-TIMS	No		NBS930 (^{235}U)	
Picasso	^{230}Th	SF-ICP-MS	Yes	TEVA® resin column	^{229}Th	16
	^{234}U	SF-ICP-MS	No		^{233}U	16
Vermeer	^{230}Th	SF-ICP-MS	Yes	TEVA® resin column (two times)	^{229}Th	16
	^{234}U	SF-ICP-MS	No		^{233}U	16
Bounarotti	^{230}Th	SF-ICP-MS	Yes	TEVA® resin column	^{232}Th	16
	^{234}U	MC-TIMS	No		^{233}U	16
Monet	^{230}Th	MC-TIMS	Yes	anion exchange resin column	^{229}Th	
	^{234}U	MC-TIMS	Yes	anion exchange resin column	^{233}U	
Gauguin	^{230}Th	MC-ICP-MS	Yes	anion exchange resin column; TEVA® resin column; anion exchange resin column	^{229}Th	6
	^{234}U	MC-ICP-MS	No		^{233}U	6
Caravaggio	^{230}Th	MC-ICPMS	Yes	TEVA® resin column	^{232}Th	
	^{234}U	MC-ICPMS	No		^{233}U	
Bondone	^{230}Th	MC-TIMS	Yes	anion exchange resin column (two times)	^{229}Th	
	^{234}U	MC-TIMS	No		^{233}U	
Manet	^{230}Th	Q-ICP-MS	Yes	TEVA® resin column	^{232}Th	
	^{234}U	Q-ICP-MS	No		N/A	

TEVA® and TRU resins are products of Eichrom® Technologies

^{235}U-^{231}Pa Chronometer

Even though ^{235}U is much more abundant than ^{234}U in almost all uranium materials, the much longer half-life of ^{235}U (7.04×10^8 years) and the absence of a long-lived spike isotope for Pa has limited routine application of this chronometer until relatively recently. Although radiometric techniques (gamma spectrometry, alpha spectrometry) have been used to quantify ^{231}Pa for age dating in the past [17], the only participant in CMX-4 to apply the ^{235}U-^{231}Pa chronometer (Gauguin) used mass spectrometry, according to the procedure developed by Eppich et al. [4]. The key feature of the method is the use of a ^{233}Pa spike for quantifying ^{231}Pa. Due to the short half-life of ^{233}Pa (26.97 days), no certified ^{233}Pa reference material exists; neither does a certified ^{231}Pa reference material that may be used for a newly-prepared ^{233}Pa spike. Rather, the spike must be prepared immediately prior to use and calibrated for ^{233}Pa concentration (atoms of ^{233}Pa g^{-1}), typically using a geologic material as a secular equilibrium standard, for its working-lifetime of approximately 3 – 4 months.

^{234}U-^{214}Bi Chronometer

Age dating U samples using high resolution gamma spectrometry (HRGS) [18-22] has the advantage of being non-destructive, hence no sample preparation is required. Analogous to the ^{234}U-^{230}Th chronometer the progenies of ^{234}U are used, however nuclides detectable by gamma-spectrometry must be chosen. For practical reasons ^{214}Bi-^{234}U ratio is used based on the secular equilibrium between ^{214}Bi ↔ ^{226}Ra. The method does not require the use of reference materials of known ages. It is most suitable for measuring U samples of higher enrichments and older ages (higher ^{214}Bi levels).

Results and discussion

The age dating results for CMX-4 are presented in Table 3 and Figure 1 (Sample ES-1), Table 4 and Figure 2 (Sample ES-2), and Table 5 and Figure 3 (Sample ES-3). All uncertainties are expanded combined standard uncertainties with k=2. For ES-1 and ES-3, the material processing date is encompassed by a 1-year range (2004), delineated by dashed red lines on the figures, during which the samples were reported to have been manufactured. For ES-2, the material processing date is encompassed by a range extending from the known enrichment date (February 12, 2002) to the known manufacturing date (September 24, 2002), which is the pelletization process. We expect the actual sample material processing date to be the date of conversion from enriched UF_6 to UO_2, since neither Th nor Pa form volatile fluorides and would, therefore, be expected to deposit out and remain in the cylinder during UF_6 release. The conversion date for these samples is unknown, but must have occurred sometime between enrichment and manufacturing of the fuel pellets. For the ^{234}U-^{214}Bi chronometer, an upper limit of ≈ 11 years was estimated uniformly for the 3 samples from the ^{214}Bi activity corresponding to the detection limit, because of the low enrichment and age of the samples.

Table 3. Age dating results for ES-1

Designator	Technique	Ref Date	Model Age (years)	EU (years)	Model Date	EU (days)
Picasso	Gamma Spec		<11	N/A	Jan-04	N/A
Rembrandt	Alpha Spec	16-Dec-14	12.0	2.7	28-Dec-02	1000
Cezanne	Alpha Spec	Mar-15	7.3	2.1	Jan-08	780
Pollock	Alpha Spec (Th) MC-TIMS (U)	15-Oct-14	7.62	0.50	6-Mar-07	180
Picasso	SF-ICP-MS	25-Mar-15	10.90	0.86	24-Mar-04	310
Vermeer	SF-ICP-MS	6-Oct-14	10.19	0.37	30-Jul-04	140
Buonarotti	SF-ICP-MS (Th) MC-TIMS (U)	3-Nov-14	10.20	0.20	Aug-04	73
Monet	MC-TIMS	1-Nov-14	10.23	0.46	10-Aug-04	170
Gauguin (Th-230)	MC-ICP-MS	23-Oct-14	10.356	0.075	14-Jun-04	27
Gauguin (Pa-231)	MC-ICP-MS	23-Oct-14	10.14	0.25	30-Aug-04	92
Caravaggio	MC-ICP-MS	13-Nov-14	9.80	0.40	4-Feb-05	150
Bondone	MC-TIMS	2-Dec-14	9.90	0.21	9-Jan-05	78
Manet	MC-ICP-MS	25-Nov-14	11.00	0.90	25-Nov-03	330

EU = expanded uncertainty (k=2)

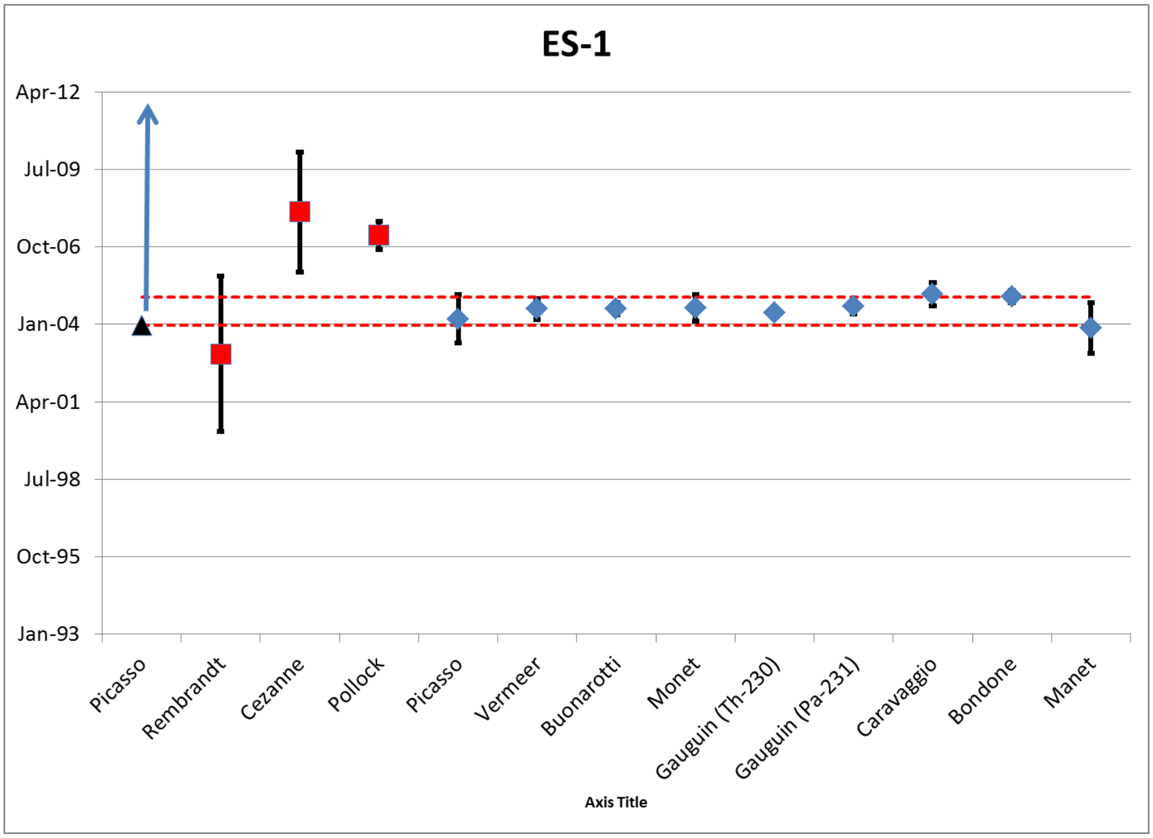

Figure 1. Age dating results for ES-1 compared against known sample processing history. The dashed red lines (----) indicate the range of probable processing dates according to the known history of the samples (see text). Results using gamma spectrometry are indicated by black triangles (▲). Alpha spectrometry results are indicated by red squares (■). Mass spectrometry results are indicated by blue diamonds (♦).

Table 4. Age Dating Results for ES-2

Designator	Technique	Ref Date	Model Age (years)	EU (years)	Model Date	EU (days)
Picasso	Gamma Spec		<11	N/A	Jan-04	N/A
Rembrandt	Alpha Spec	16-Dec-14	14.5	0.52	10-Jun-00	190
Cezanne	Alpha Spec	Mar-15	5.5	2.2	Sep-09	820
Pollock	Alpha Spec (Th) MC-TIMS (U)	15-Oct-14	10.65	0.50	24-Feb-04	180
Picasso	SF-ICP-MS	25-Mar-15	11.00	0.71	23-Sep-01	260
Vermeer	SF-ICP-MS	7-Oct-14	11.22	0.79	21-Jul-03	290
Buonarotti	SF-ICP-MS (Th) MC-TIMS (U)	3-Nov-14	12.51	0.30	Apr-02	110
Monet	MC-TIMS	1-Nov-14	12.53	0.53	23-Apr-02	190
Gauguin (Th-230)	MC-ICP-MS	23-Oct-14	12.677	0.092	17-Feb-02	34
Gauguin (Pa-231)	MC-ICP-MS	23-Oct-14	12.50	0.31	22-Apr-02	110
Caravaggio	MC-ICP-MS	13-Nov-14	11.90	0.20	5-Jan-03	73
Bondone	MC-TIMS	2-Dec-14	12.10	0.19	29-Oct-02	69
Manet	MC-ICP-MS	24-Nov-14	12.10	0.60	18-Oct-02	220

EU = expanded uncertainty (k=2)

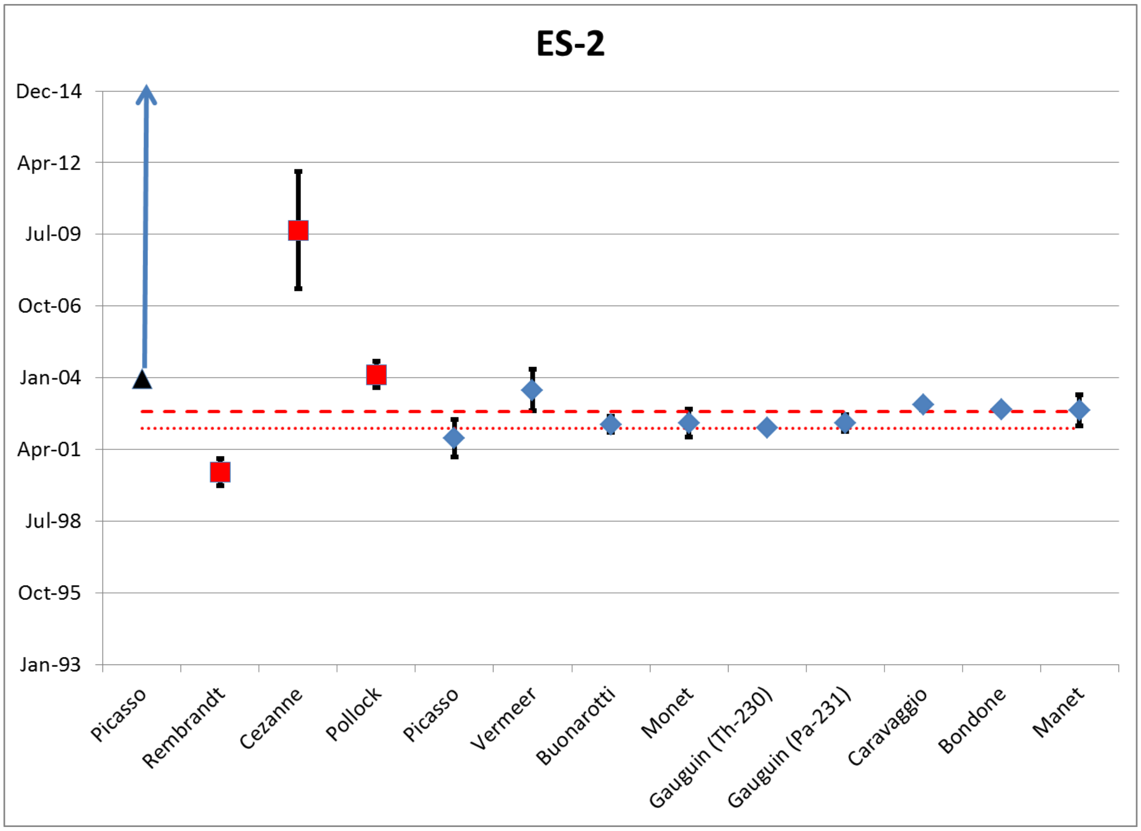

Figure 2. Age dating results for ES-2 compared against known sample processing history. The dashed red lines (----) indicate the range of probable processing dates according to the known history of the samples (see text). Results using gamma spectrometry are indicated by black triangles (▲). Alpha spectrometry results are indicated by red squares (■). Mass spectrometry results are indicated by blue diamonds (♦).

Table 5. Age dating results for ES-3

Designator	**Technique**	**Ref Date**	**Model Age (years)**	**EU (years)**	**Model Date**	**EU (days)**
Picasso	Gamma Spec		<11	N/A	Jan-04	N/A
Rembrandt	Alpha Spec	16-Dec-14	12.20	0.64	19-Sep-02	230
Cezanne	Alpha Spec	Mar-15	11.5	3.6	Sep-03	1300
Pollock	Alpha Spec (Th) MC-TIMS (U)	15-Oct-14	7.25	0.50	16-Jul-07	180
Picasso	SF-ICP-MS	25-Mar-15	13.5	0.61	29-Apr-04	220
Vermeer	SF-ICP-MS	15-Oct-14	9.94	0.65	7-Nov-04	240
Buonarotti	SF-ICP-MS (Th) MC-TIMS (U)	3-Nov-14	10.22	0.18	Aug-04	66
Monet	MC-TIMS	1-Nov-14	10.19	0.46	23-Aug-04	170
Gauguin (Th-230)	MC-ICP-MS	23-Oct-14	10.380	0.076	5-Jun-04	28
Gauguin (Pa-231)	MC-ICP-MS	23-Oct-14	10.22	0.25	5-Aug-04	93
Caravaggio	MC-ICP-MS	13-Nov-14	9.80	0.20	8-Feb-05	73
Bondone	MC-TIMS	2-Dec-14	9.72	0.51	16-Mar-05	190
Manet	MC-ICP-MS	25-Nov-14	10.80	0.60	6-Feb-04	220

EU = expanded uncertainty (k=2)

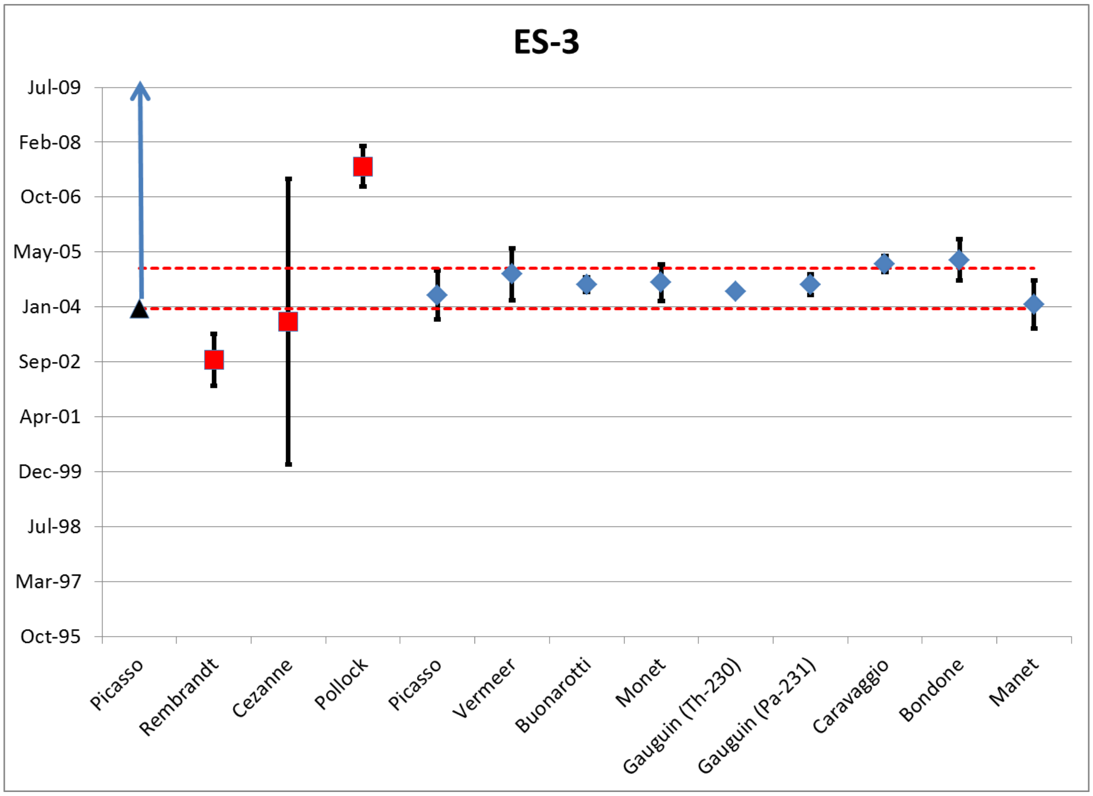

Figure 3. Age dating results for ES-3 compared against known sample processing history. The dashed red lines (----) indicate the range of probable processing dates according to the known history of the samples (see text). Results using gamma spectrometry are indicated by black triangles (▲). Alpha spectrometry results are indicated by red squares (■). Mass spectrometry results are indicated by blue diamonds (♦).

Interpretation of Results

The first conclusion upon looking at the results is that most of the laboratories measured ages consistent with one another and consistent with the known history of the material. For ES-1 and ES-3, only 2 results out of 12 did not overlap the known history of the material within their stated analytical uncertainty. For ES-2, only 3 results out of 12 did not overlap the known history of the material within their stated analytical uncertainty.

The second conclusion is that these age-dating results were useful in comparing the 3 samples (ES-1, ES-2, and ES-3) with one another, one of the key points of the exercise. When combined with other signatures, including the similarity of the U isotopic composition between ES-1 and ES-3, these age-dating results supported the conclusion that ES-1 and ES-3 might have had a similar processing history. Again, when combined with other signatures, these age-dating results also supported the conclusion that ES-2 was a different material from ES-1 and ES-3, sharing neither isotopic similarity nor processing history.

The third conclusion is that mass spectrometric methods of measuring these chronometers provided more accurate and precise results than counting methods offered for these samples. Picasso reported that the level of enrichment in these samples was too low to measure more than an upper limit on the age using gamma spectrometry and the ^{214}Bi-^{234}U chronometer. In addition, those laboratories that used alpha spectrometry to perform chronometry provided results that tended to be either less accurate or less precise than results provided by laboratories that used mass spectrometry. In particular, for ES-2, none of the alpha spectrometry results agree with the stated sample history or with one another. Following the conclusion of the exercise, Rembrandt (who conducted only a single U/Th column separation to generate their Th alpha sources) further purified their Th alpha sources. The repurified sources yielded comparable ages to mass spectrometry. This finding clearly demonstrates the need for multiple U/Th separation steps to adequately remove ^{234}U from the ^{230}Th spectral region.

The final conclusion, drawn from Gauguin's results, is that the consistency of the ^{234}U-^{230}Th and ^{235}U-^{231}Pa results validated the age-dating assumption, namely that there was a real purification event that removed Th and Pa from the U quantitatively. It is highly unlikely that there would be a process that would partially purify both Th and Pa, but in a proportion that retained the concordancy of the two chronometers. This is a different conclusion than that of ITWG round robin #3, in which, due to the complex production history of the HEU metal samples, these two chronometers differed remarkably from one another (7, 15, 23). Knowing the true material processing date (assumed to be the conversion date) would be helpful in a real investigation in identifying potential material sources and excluding others.

Conclusions

In the CMX-4 exercise, 10 international nuclear forensics laboratories successfully performed radiochronometry on the 3 CMX-4 samples (ES-1, ES-2, and ES-3), providing 12 analytical results using 3 different parent-daughter pairs serving as independent chronometers (^{234}U-^{230}Th, ^{235}U-^{231}Pa, ^{234}U-^{214}Bi). The vast majority of the results were consistent with one another and consistent with the known processing history of the materials. In general, for these particular samples, mass spectrometry gave more accurate and more precise analytical results than decay counting measurements. In addition, the concordancy of the ^{235}U-^{231}Pa chronometer with the ^{234}U-^{230}Th confirmed the validity of the age dating assumption, increasing our confidence in the nuclear forensic conclusions and in the model age in particular. When combined with other analytical results, age dating helped confirm a relationship between ES-1 and ES-3 and a lack of relationship between ES-2 and ES-1 and ES-3

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