Nuclear Forensic Science: Analysis of Nuclear Material Out of Regulatory Control*

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Abstract

Nuclear forensic science seeks to identify the origin of nuclear materials found outside regulatory control. It is increasingly recognized as an integral part of a robust nuclear security program. This review highlights areas of active, evolving research in nuclear forensics, with a focus on analytical techniques commonly employed in Earth and planetary sciences. Applications of nuclear forensics to uranium ore concentrates (UOCs) are discussed first. UOCs have become an attractive target for nuclear forensic researchers because of the richness in impurities compared to materials produced later in the fuel cycle. The development of chronometric methods for age dating nuclear materials is then discussed, with an emphasis on improvements in accuracy that have been gained from measurements of multiple radioisotopic systems. Finally, papers that report on casework are reviewed, to provide a window into current scientific practice.

Ian Hutcheon, our friend, colleague, and mentor, passed away on March 26, 2015, during the writing of this review paper. Ian (PhD, Physics, University of California, Berkeley, 1974) was Group Leader of the Chemical and Isotopic Signatures Group in the Nuclear and Chemical Sciences Division and Deputy Director of the Glenn T. Seaborg Institute, Physical and Life Sciences Directorate, at Lawrence Livermore National Laboratory. Ian came to Lawrence Livermore National Laboratory in 1993, after 20 years as senior research associate at the University of Chicago and the California Institute of Technology, where he established his reputation as a pioneer in secondary ion mass spectrometry and its application to the field of cosmochemistry. Ian was a key developer of nuclear forensics both as a field of scientific investigation and as a scientific discipline with significant applications to national security and cowrote the definitive nuclear forensics book, Nuclear Forensic Analysis. *Ian also made numerous contributions to the study of the isotopic composition of meteorites, in particular the characterization of isotopic anomalies in refractory inclusions in meteorites and what they reveal about the evolution of the early Solar System. He conducted groundbreaking work in the formation mechanisms of planets and meteorites, and diffusion transport processes in terrestrial and planetary melts, glasses, and minerals. He authored more than 200 papers and book chapters. His awards in recent years included being named a Distinguished Member of Technical Staff at the Laboratory; receiving the Lawrence Livermore National Laboratory Outstanding Postdoc Mentor award in 2010; and having a newly discovered mineral, Hutcheonite, named in his honor. In recent years Ian and members of his group were involved in establishing collaborations with colleagues around the world to help encourage their nuclear forensics efforts. To honor Ian's contributions, both the Department of Homeland Security Domestic Nuclear Detection Office's National Nuclear Forensics Expertise Development Program and the Office of Defense Nuclear Nonproliferation have established separate fellowships to support nuclear forensics and international collaborations. The Defense Nuclear Nonproliferation fellowship announcement stated, "To the nuclear nonproliferation world, Hutcheon brought not only a passion for science, but an ability to reach out to partners around the world, engaging them in the science that supports our nuclear security efforts. Because of his innate ability to engage, teach and inspire, Hutcheon was one of our very finest scientist-diplomats, with a unique ability to grow and inspire young talent."*

INTRODUCTION

Nuclear forensic science, or nuclear forensics, is increasingly recognized by the international community as an integral part of a robust nuclear security program. It was specifically identified in the Communiqués and Work Plans of the last three Nuclear Security Summits (in 2010, 2012, and 2014; see **http://www.state.gov/t/isn/nuclearsecuritysummit/index.htm**) as an important focus area for research. The fundamental tenet underlying nuclear forensics is that identifying the origin of nuclear materials found outside 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.[1] 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 (Allison 2008).

The use of the term nuclear forensics first began in the mid-1990s, as laboratories grappled with the analysis of nuclear material from an increasing number of seizures in support of law enforcement investigations. However, the term has been refined over time. The definition adopted in the International Atomic Energy Agency (IAEA) publication *Nuclear Forensics in Support of*

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[1]Note that technical conclusions from nuclear forensic analysis are combined with information from law enforcement and intelligence in a process known as attribution, or the assignment of responsibility. Although the source of nuclear material cannot be uniquely determined in all cases, the elimination of certain facilities from consideration as the source of the material can be important. See also the report *Nuclear Forensics: Role, State of the Art, and Program Needs* (Nuclear Forensics Working Group 2008).

Investigations is as follows: "Nuclear forensics is the examination of nuclear or other radioactive material, or of evidence that is contaminated with radionuclides, in the context of legal proceedings under international or national law related to 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 their intended uses were" (IAEA 2015, p. 1).

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. It is difficult to overstate the importance of geochemistry in the development of nuclear forensics. Geochemical analysis methods form the basis for investigations not only of materials produced at the front end of the fuel cycle by processes such as mining, milling, and conversion, where the influences of the geologic origin of the nuclear material are of prime importance, but also of materials from the back end of the fuel cycle, where techniques like radiochronometry, developed originally for geochemical applications, are routinely applied.

This review highlights areas of active research in nuclear forensics that are underlain by geochemical principles, focusing on forensics relevant to interdicted materials, sometimes known as predetonation nuclear forensics or nonproliferation nuclear forensics, and does not cover areas such as forensics applicable after a nuclear detonation (postdetonation nuclear forensics) or after a major nuclear power plant accident, such as Chernobyl or Fukushima. First, literature applying nuclear forensics to materials from the front end of the nuclear fuel cycle, such as uranium ore concentrates (UOCs), is reviewed. UOCs have become particularly attractive for nuclear forensic researchers because of the richness in impurities compared to materials produced later in the fuel cycle, and because the materials themselves are not generally considered as sensitive as materials from the back end of the fuel cycle, such as highly enriched uranium or plutonium. Second, the development of radiochronometry, or age dating, and its application to nuclear materials are discussed. Emphasis is placed on the increasing interest in using multiple chronometers to better understand the chemical or physical processes that might reset certain chronometers. Finally, although the application of nuclear forensics to actual cases is often sensitive or classified, there have been a number of papers that have reported on such casework. We review these papers and discuss how these investigations help provide a window into how current scientific practice influences the conclusions that can be reached in actual scenarios.

NUCLEAR FORENSICS OF URANIUM ORE CONCENTRATES

Uranium ore is mined and milled to produce UOC, also referred to as yellowcake, prior to conversion to uranium hexafluoride (UF_6) for enrichment (**Figure 1**). The high uranium concentration (>60%) and relative ease of transport of UOCs have made them a commonly traded commodity on the worldwide market (Kristo & Tumey 2013). As a result, UOCs are attractive materials for diversion from civilian power purposes to possible weapons production. Modern UOCs consist of approximately 60–80% uranium and can be composed of many different chemical compounds, including ammonium diuranate, sodium diuranate, uranyl hydroxide, uranyl peroxide, or uranium oxide (U_3O_8). Various trace element and organic impurities are associated with UOCs. The high concentration of elemental impurities in UOCs has triggered a number of studies aimed at defining impurity signatures, with the expectation that these signatures could be used to trace a UOC to the mine or mill of origin.

The first formal nuclear forensic study of impurities in UOCs was associated with the "Great Yellowcake Caper," the 1978 theft of five barrels of UOC from the Standard Oil Company of Ohio (Sohio) uranium mill in New Mexico (Budinger et al. 1980). The Federal Bureau of Investigation
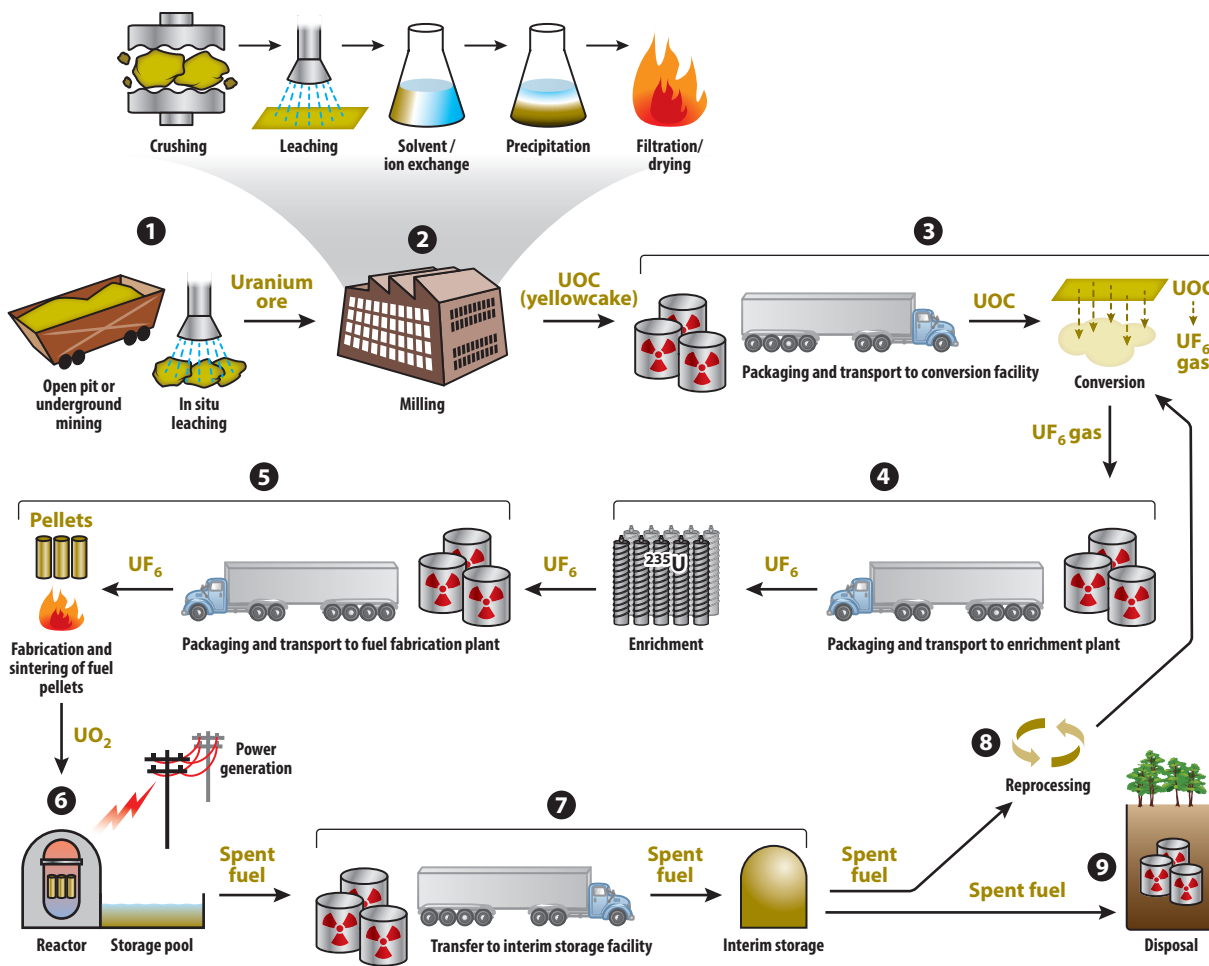
Figure 1

Activities associated with the production of electricity from nuclear reactors are referred to as the nuclear fuel cycle. (❶) The cycle begins with recovering uranium from ore deposits through open pit mining, underground mining, or in situ leaching. (❷) Milling is typically carried out close to a uranium mine. The ore is typically crushed and leached, and then the leachate undergoes solvent extraction, ion exchange chromatography, or both to separate the uranium from the rest of the ore material. The uranium is then precipitated as uranium ore concentrate (UOC, also known as yellowcake) and is filtered and dried. (❸) The UOC is then packaged and shipped to a conversion facility. Enrichment from natural ^{235}U abundance to the levels needed for most nuclear power plants requires conversion of the UOC material to gaseous form, wherein UOCs are converted to UF_6. (❹) From there the material is loaded into cylinders for transport to an enrichment plant, where the uranium is enriched in ^{235}U by spinning the UF_6 gas in fast-spinning centrifuges. Following enrichment, the enriched UF_6 gas is reconverted to uranium oxide (UO_2). (❺) Next it goes to the fuel fabrication plant, where the UO_2 is pressed into fuel pellets and sintered at temperatures of over 1,400°C to achieve high density and stability. The fuel pellets are then packed in long metal tubes to form fuel rods; these are then grouped in fuel assemblies for introduction into a reactor. (❻) The fuel assemblies are used in the reactor to generate electricity for 3–6 years; 25–30% of the fuel is replaced each year. Spent fuel assemblies are first stored in spent fuel pools and ultimately can be (❼) transferred to an interim storage facility prior to being either (❽) reprocessed or (❾) queued for long-term disposal. Fuel that is reprocessed must be converted, enriched, and fabricated into new fuel prior to use in a reactor. Plutonium recovered from the spent fuel can be mixed with uranium to fabricate mixed oxide fuel.

eventually arrested three suspects in the theft and recovered the five barrels of UOC. Following the recovery of the stolen material, the research department at Sohio was requested to determine to whom the UOC belonged. The Sohio lab collected samples of UOCs from the Sohio mill as well as from neighboring mills in the area. The researchers then employed trace metals analysis and organic analysis to develop signatures for each of the UOCs. Ultimately, the Sohio researchers were able to confirm that the stolen UOC did appear to be sourced from the Sohio mill, rather than from surrounding mills. Although the impurity signatures were never used as evidence in court, the data were used to develop a case against the suspects and to extract a confession. This early work in UOC forensics helped to launch a productive branch of research into the elemental impurities in UOCs.

To date, research on UOC signatures has included studies of uranium isotopic composition, trace elemental impurities, and organic impurities; the use of Raman, infrared, and near-infrared reflectance spectroscopy; investigations of stable and radiogenic isotopic composition and morphology; and the use of age dating and chemometrics. In this section, we address how the techniques have been applied to constrain the geologic provenance, the processing history, and perhaps the age of UOCs.

Uranium Isotope Ratios

Although it had long been assumed that the $^{235}U/^{238}U$ ratio of terrestrial materials was invariant, recent work has shown that the terrestrial $^{235}U/^{238}U$ ratio varies over a range of 1.3‰ in different geologic materials (e.g., Weyer et al. 2008). Early work by Cowan & Adler (1976) on the $^{235}U/^{238}U$ ratio in uranium ore samples concluded that there was a bimodal distribution of uranium ores with a 0.3‰ difference between sandstone-hosted and magmatic deposits. More recent work by Richter et al. (1999) observed isotopic variations in $^{234}U/^{238}U$, $^{235}U/^{238}U$, and even $^{236}U/^{238}U$ in natural uranium ores and proposed the use of U isotopic variation as a possible forensic signature for nuclear materials. Although the possibility of distinguishing between most samples with only one set of U isotope ratios is quite limited, they suggested some promise for a combined approach using multiple U isotopes. Based on a small study of six uranium ore samples, Richter et al. (1999) found that no two samples have the same isotopic composition when all three isotopic ratios are considered. Brennecka et al. (2010) investigated the $^{235}U/^{238}U$ of UOC samples with the goal of relating the $^{235}U/^{238}U$ variations observed to the mechanisms of U mineralization in the ore body. These authors noted that when $^{234}U/^{238}U$ and $^{235}U/^{238}U$ ratios are considered together, it is possible to distinguish UOCs from different geologic environments, thus potentially restricting the range of deposits from which an unknown UOC might be derived. Specifically, Brennecka et al. (2010) found that, at low temperatures, the redox transition from U(VI) to U(IV) causes a discernable $^{235}U/^{238}U$ ratio fractionation during deposition. As a result, UOCs produced from low-temperature redox-type deposits have characteristically distinctive $^{235}U/^{238}U$ ratios. Although ^{236}U is generally considered to be anthropogenically produced, it is also naturally produced at very low levels as a result of neutron capture on ^{235}U. Because $^{236}U/^{238}U$ ratios in U ores can range from 10^{-13} to 10^{-9} (Richter et al. 1999; Wilcken et al. 2008 and references therein; Murphy et al. 2015), the $^{236}U/^{238}U$ ratio has been proposed as a potentially strong complement to the existing isotopic signatures from UOCs. Work by Srncik et al. (2011) compared the $^{236}U/^{238}U$ measured in U ores and UOCs and found that, with limited exceptions, $^{236}U/^{238}U$ ratios do not correlate in paired ore/UOC samples. The conclusion from this work is that UOC samples rather than U ores should be the starting materials for investigation.

Trace Elements

The study of trace element variation in UOCs has been an active field of research since the mid-2000s. Work by Švedkauskaitė-LeGore et al. (2008) identified the utility of elemental impurity data in conjunction with Pb isotope data in identifying the origin of uranium ore samples. In a comprehensive study of Australian UOCs, Keegan et al. (2008) analyzed uranium and lead isotopes and 23 trace elements in samples from three active mines in Australia. They found that UOCs from the three operational U mines could readily be distinguished on the basis of Pb isotopes, $^{234}U/^{238}U$, and trace elements using a multivariate statistical approach. Keegan et al. (2008) also observed significant variability in rare earth element (REE) ratios between the three samples. In a study focusing on UOC from several different countries, clear differences in anion ratios and concentrations were observed between UOCs from different sources (Badaut et al. 2009). One limitation of the anion signatures is that substantial variation in anion concentrations occurs in different samples from the same deposit, although this effect is smaller than the variability between samples from different mines. UOCs from a number of deposits have distinctive anion signatures, and these appear to be related to processing history. A significant conclusion from this work is that the ratios of anion concentrations provide a more robust signature than the concentrations of individual anions. Further work by Keegan et al. (2012) confirmed that anionic impurities do appear to provide evidence of UOC processing steps. For example, high Cl^-/SO_4^{2-} ratios are observed in UOCs from mills that use $NaCl/H_2SO_4$ as an eluent and NaCl strip solutions during processing. Like the other elemental and isotopic signatures, however, they cannot be used as a single unambiguous indicator of UOC origin. This is because, as in the example above, many U processing mills use (or have used) $NaCl/H_2SO_4$ and NaCl strip solutions; therefore, the finding that a UOC appears to have been processed in this way does not provide a unique fingerprint to a specific facility.

Uranium-bearing minerals (uraninite, coffinite, etc.) have distinctive REE signatures (Fryer & Taylor 1987, Mercadier et al. 2011, Eglinger et al. 2013). It has been hypothesized that REE would be unlikely to be fractionated during processing and therefore might make a robust UOC signature (Varga et al. 2010a). In order to more accurately determine low-level REE concentrations in samples with a high concentration of U, Varga et al. (2010b) developed a selective extraction chromatographic separation using TRU resin (Eichrom Technologies, Inc.) to preconcentrate the REE prior to analysis. In this study, they analyzed the REE patterns of 38 UOCs from a variety of U deposit types and mills. Like studies of U ore minerals, this study showed that REE patterns may be used to distinguish UOCs from U mines hosted in different geologic environments in some specific cases (e.g., phosphorite deposits, quartz-pebble conglomerates). The study also compared the REE signatures in UOCs and U ores from the same deposits, and the authors surmised that the REE ratios were minimally affected by processing.

Although REE patterns were found to be distinctive forensic signatures for UOCs, the consensus is that in isolation REE patterns are not sufficient to distinguish UOCs of differing origins, and they must instead be used in conjunction with other trace elemental and isotopic impurity signatures (i.e., Badaut et al. 2009, Varga et al. 2010b, Keegan et al. 2012). REE patterns are more likely to indicate deposit type than to indicate a specific deposit, and in many cases (i.e., sandstone-hosted deposits, intrusive deposits), the pattern is insufficiently distinct to be diagnostic. It seems plausible, however, that if the origin of a UOC is constrained to a specific region (perhaps through other evidence), REE could possibly be useful for distinguishing the likely source. For example, the REE patterns of uranium ores from the Pan-African Lufilian belt differ depending on location (Eglinger et al. 2013). It is possible that UOCs from this region could be distinguished from one another on the basis of REE patterns. Because the deposits occur on two sides of an international

border, it might be possible to attribute a UOC to a specific country on the basis of REE patterns in this case.[2]

Lead, Strontium, and Neodymium Isotopes

The variability of Pb isotope ratios is related to the age of a uranium ore body as well as its U/Pb and Th/Pb ratios and therefore forms the basis for a potentially robust isotopic signature in natural materials (Švedkauskaitė-LeGore et al. 2007). The radiogenic Pb component, which results from radioactive decay of U and Th, can be calculated from the measured Pb isotope ratios by subtracting the common Pb component (i.e., Stacey & Kramers 1975) determined from the abundance of ^{204}Pb, a nonradiogenic isotope. Švedkauskaitė-LeGore (2007) found that radiogenic Pb isotope abundance ratios vary significantly between different U mines. Subsequent work revealed that Pb isotope ratios could be used in conjunction with trace elemental impurities to distinguish between UOC samples of differing origins (Švedkauskaitė-LeGore 2008), although Varga et al. (2009) urged caution in the use of Pb isotope ratios as a signature for UOCs because of substantial within-mine variability. These authors also observed dilution of the intrinsic radiogenic lead signature of the ore by common lead during processing, in some samples to the extent that no radiogenic lead signature remained after processing. Varga et al. (2009) applied a common lead subtraction to constrain the radiogenic Pb isotopic composition of the ore. Using this radiogenic Pb isotopic composition, it is possible to calculate an age of the U ore deposit, although this approach is viable only if the radiogenic Pb signal is strong relative to the common lead signature. Like the other potential signatures of UOC origin, Pb isotopes cannot be used in isolation for origin assessment because the Pb isotopic compositions are not unique to specific UOC sources.

The measured ^{87}Sr/^{86}Sr of UOCs varies over a wide range [0.7034 to 0.7606 and higher (e.g., Varga et al. 2009)]. As a result, the ^{87}Sr/^{86}Sr ratio is useful for distinguishing samples of different origins as well as comparing with known samples. Unlike Pb isotopes, which can exhibit significant within-mine variability, Sr isotopes are typically constant in samples from a single mine or mill (i.e., Varga et al. 2009). Although a few UOCs have distinctively high ^{87}Sr/^{86}Sr ratios, in general there is considerable overlap between mines/mills, and the technique, like the others discussed in this review, must be used in conjunction with other signatures in order to uniquely identify UOCs from different sources.

Nd isotope ratios provide yet another promising forensic signature that could potentially be used to identify the U deposit from which a particular sample was derived. The ^{143}Nd/^{144}Nd ratio in UOCs varies over an extremely wide range [from 0.510 to 0.515, $\pm \sim$40 epsilon units (Krajkó et al. 2014)]. In addition, the ^{143}Nd/^{144}Nd ratio and Sm/Nd can be used as combined signatures to distinguish UOCs of different origins (Krajkó et al. 2014). Although neodymium isotopic ratios vary on the order of 10–20 epsilon units between paired U ores and UOCs, the ^{143}Nd/^{144}Nd ratio for a series of samples from a given mine remains more consistent than other isotope ratios [e.g., Pb, Sr (Krajkó et al. 2014)]. The consistency of neodymium isotopic signatures appears to make them one of the most promising signatures for UOC provenance yet developed.

Sulfur Isotopes

Sulfur isotopes can be used to distinguish between UOCs produced with or without sulfuric acid. δ^{34}S values (deviation of ^{34}S/^{32}S relative to the Canyon Diablo Troilite standard) have been found

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[2]These deposits have not yet been exploited for UOC production.

to range from $-20‰$ to $+20‰$ in UOCs (Han et al. 2013). This range is smaller than the total range of sulfur isotope variation in the different types of uranium ore deposits but is still sufficient to distinguish between UOCs of different origins. Both sulfate concentration and sulfur isotope concentrations vary among different UOC samples, and together these analytes appear to form the basis of a predictive signature. Low sulfate concentrations ($<1,000$ μg/g) in conjunction with low sulfur isotope ratios ($\delta^{34}S < -10‰$) appear to be associated with UOCs produced by in situ leaching from sedimentary sandstone-type deposits (Han et al. 2013). Because UOCs can have either an enriched or depleted $\delta^{34}S$ relative to the host rocks, additional research will be required to determine the broad applicability of sulfur isotopes as a predictive signature. It is also worth noting that for reasons of economics, metallurgical favorability, and environmental regulation, sulfuric acid is not always used in processing uranium ores. Sulfur isotope ratios may ultimately be most useful for distinguishing between ores produced in the presence or absence of sulfuric acid. Such information could potentially help to distinguish UOCs from locations with similar geology but differing processing approaches.

Spectrometric Techniques

Applications of Raman, infrared, and near-infrared reflectance spectroscopy to UOC samples have also been reported (Hausen 1998, Varga et al. 2011a, Lin et al. 2013, Klunder et al. 2013, Plaue et al. 2013). These techniques yield a set of parameters that are characteristic of the material and its history. Fourier-transform infrared spectroscopy has been found to be an effective tool for identifying the chemical compound(s) of U present in UOCs (i.e., uranyl peroxide, ammonium diuranate, etc.). In one of the earliest studies, samples were analyzed in a KBr press and were classified into several categories of U compounds using soft independent modeling of class analogy based on libraries of spectra of known materials (Varga et al. 2011a). The technique was found to be sensitive to a number of anionic impurities that could provide indications of production methods (Varga et al. 2011a). Subsequent work on near-infrared reflectance spectroscopy focused on distinguishing between common UOC compounds precipitated from a variety of reagents (Plaue et al. 2013, Klunder et al. 2013). Uranium ore processing schemes can employ a wide variety of reagents and unit operations, making the near-infrared/visible spectra particularly useful indicators of processing scheme. Understanding how a UOC was processed has important forensic implications for understanding where a particular UOC was produced. Because NIR is a nondestructive technique, it appears especially promising for nuclear forensics applications in which the quantity of the sample is limited. Raman spectroscopy yields information similar to that derived from the other spectroscopic techniques, but because it can be achieved with handheld and field-deployable instrumentation, it could potentially be a highly useful nuclear forensics tool for rapid process identification (Lin et al. 2013).

Organic Impurities

Although a number of organic compounds have historically been used in UOC production, to date only two studies have attempted to assess the applicability of organic signatures to UOC forensics. One major reason why organics analysis is so difficult is that many UOCs are subjected to a high-temperature calcination step to reduce the water content, which volatilizes many organic compounds. In their paper about the "Great Yellowcake Caper," Budinger et al. (1980) attempted to extract organic compounds from the seized UOC and sought a match for tridecanol, an additive that was distinctive to the Sohio U processing facility. Although they were successful in extracting some organic compounds, they did not detect tridecanol. This is likely because the final product was

calcined at 1,200°C, significantly above the boiling point of tridecanol. Although the identification of key organic compounds was not achieved, the authors were able to detect compounds associated with the silicone/ethylene glycol polymeric antifoam surface active agents in use at the Sohio plant. In a more recent study, Kennedy et al. (2013) used sorptive extraction in conjunction with gas chromatography mass spectrometry to assess the applicability of organic compounds as forensic signatures. Kennedy et al. (2013) used the variation in abundances of specific organic compounds to distinguish between two unknown UOC samples submitted for forensic investigation. The authors concluded that the samples were likely derived from two different purification processes based on the presence of Alamine 336 and decanol in one sample and the absence of these compounds in the second sample. These studies indicate that abundance of organic compounds in UOCs may be a promising signature of processing.

RADIOCHRONOMETRY FOR NUCLEAR FORENSICS

The age of nuclear material is an important forensic signature because it can be used to constrain the time of purification or production of nuclear material (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 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 are an active focus area of nuclear forensics research. In this section, we present a summary of analytical methods used for radiochronometry in nuclear forensics and discuss examples that illustrate how a sample's history can be revealed through the analysis of multiple chronometers.

Analytical Methods

Radiometric model ages are determined from measurements of parent isotopes and the progeny isotopes (typically daughter, but also granddaughter) that accumulate in a material due to decay of the radioactive parent isotope. U-series and Pu-series disequilibrium dating methods are the radiochronometry methods that are most often used for nuclear forensic investigations. U-series disequilibrium chronometry was developed in the late 1950s and 1960s for dating carbonate formed in geologic environments (e.g., Kaufman & Broecker 1965, Szabo & Rosholt 1969, and references therein). These methods have since been applied to myriad geologic materials. U-series and Pu-series radiochronometry methods were developed for use in nuclear forensic and safeguards applications in the late 1990s and 2000s (**Table 1**).

Decay products may be present in samples in concentrations ranging from parts per billion up to fractions of a percent or higher. Therefore, the analytical approaches that have been used vary widely from sample to sample. In devising an analytical approach for actinide decay chain measurements, a number of factors are typically considered. These include the isotopic composition of the bulk material, the presumed age, the desired chronometer, the expected concentration or activity level of the analyte, the amount of sample available for analysis, and the desired precision for the end use of the result. Another important point that must be evaluated is whether sample material may be consumed during analysis; if not, nondestructive analysis will be required. Decay counting methods, as well as mass spectrometry, are commonly used in radiochronometry for

Table 1 Uranium-series and plutonium-series radiochronometry methods for use in nuclear forensic and safeguards applications

Radiochronometer	Analytical method	Method validation studies
Analytical methods for radiochronometry of bulk uranium		
^{230}Th-^{234}U	TIMS	Wallenius et al. 2002, Pointurier et al. 2013
	(MC/HR)-ICP-MS	Varga & Surányi 2007, Williams & Gaffney 2011, Pointurier et al. 2013, Gaffney et al. 2015
	ICP-MS	Wallenius et al. 2002, Varga et al. 2010
	AS	Wallenius et al. 2002
^{231}Pa-^{235}U	MC-ICP-MS	Eppich et al. 2013
	AS	Morgenstern et al. 2002
	GS/AS	Moorthy & Kato 1997
^{229}Th-^{233}U	HR-ICP-MS	Ramebäck et al. 2008
^{226}Ra-^{230}Th-^{234}U	MC-ICP-MS	Kayzar & Williams 2016
^{227}Ac-^{231}Pa-^{235}U	MC-ICP-MS	Kayzar & Williams 2016
^{214}Bi-^{234}U	HRGS	Nguyen 2005; Nguyen & Zsigrai 2006a,b
Analytical methods for radiochronometry of bulk plutonium		
^{234}U-^{238}Pu	TIMS	Wallenius & Mayer 2000, Spencer et al. 2009, Sturm et al. 2014
	SIMS	Wallenius et al. 2001
^{235}U-^{239}Pu	TIMS	Wallenius & Mayer 2000, Spencer et al. 2009, Sturm et al. 2014
	SIMS	Wallenius et al. 2001
^{236}U-^{240}Pu	TIMS	Wallenius & Mayer 2000, Spencer et al. 2009, Sturm et al. 2014
	SIMS	Wallenius et al. 2001
	(MC/HR)-ICP-MS	Nygren et al. 2007, Chen et al. 2009
	AS	Chen et al. 2009
^{241}Am-^{241}Pu	WDX/TIMS	Shinonaga et al. 2009
	HR-ICP-MS	Nygren et al. 2007
	GS	Wallenius & Mayer 2000, Nguyen 2006
^{233}Pa-^{237}Np-^{241}Am-^{241}Pu	GS	Keegan & Gehrke 2003

Abbreviations: AS, alpha spectrometry; GS, gamma spectrometry; HR-ICP-MS, high-resolution (sector field) inductively coupled plasma mass spectrometry; ICP-MS, quadrupole inductively coupled plasma mass spectrometry; MC-ICP-MS, multicollector inductively coupled plasma mass spectrometry; TIMS, thermal ionization mass spectrometry; WDX, wavelength dispersive X-ray spectrometry.

nuclear forensics. This section provides a very brief overview of these analytical methods; a detailed and comprehensive review is given by Mayer et al. (2013).

The two decay counting methods commonly used for radiochronometry analyses are gamma spectrometry and alpha spectrometry. The primary advantage of gamma spectrometry is that it is nondestructive, requires minimal or no sample preparation, and is relatively inexpensive. Thus, a gamma spectrometry analysis can be performed quickly (<24 h) while preserving the sample for subsequent analyses. Gamma spectrometry requires large sample masses, however,

and is best suited for high-activity samples; the method generally is less precise than mass spectrometry or alpha spectrometry methods. Gamma spectrometry can be used with bulk uranium materials (Moorthy & Kato 1997; Nguyen 2005; Nguyen & Zsigrai 2006a,b; Ramebäck et al. 2008) as well as bulk plutonium materials (West & Sherwood 1981, Wallenius & Mayer 2000, Keegan & Gehrke 2003, Nguyen 2006). Alpha spectrometry is a destructive analytical method that requires chemical purification prior to analysis and can be used to measure most U-series and Pu-series nuclides (Moorthy & Kato 1997, Wallenius et al. 2002, Morgenstern et al. 2002, Chen et al. 2009), although it is most commonly used for analysis of high-specific-activity nuclides that are present at low concentrations in bulk uranium and plutonium materials. In particular, alpha spectrometry is useful for determining concentrations of ^{238}Pu and ^{232}U, which are generally present in extremely low concentrations, and for which it is difficult to completely separate isobars that would otherwise interfere in a mass spectrometric analysis.

Mass spectrometry methods commonly used for radiochronometry analyses include high-resolution single- or multicollector inductively coupled plasma mass spectrometry (ICP-MS), thermal ionization mass spectrometry (TIMS), and secondary ion mass spectrometry (SIMS). These methods are capable of the highest-precision analyses for most uranium and plutonium radiochronometry systems. Because of their higher sensitivity relative to counting methods for most radionuclides, mass spectrometry methods can be used to analyze samples that are comparatively much smaller or younger and therefore have very low total amounts of decay products (e.g., Wallenius & Mayer 2000, Wallenius et al. 2002, Eppich et al. 2013, Gaffney et al. 2015, Kayzar & Williams 2016, Varga et al. 2015). Isotope dilution methods are used for quantification of parent and progeny isotope abundances by TIMS or ICP-MS. For ICP-MS and TIMS, the analyte must be purified from sample matrix, whereas SIMS analysis utilizes bulk sample. Sample requirements may be as low as 1 μg of uranium for TIMS analysis (Pointurier et al. 2013) or plutonium particles on the order of 10 μm for in situ SIMS analysis (Wallenius et al. 2001).

Results of Chronometric Studies

The fundamental assumptions in the model age calculations are that (*a*) no progeny isotopes were present in the material at the time of its production and (*b*) no parent or progeny isotopes have been gained or lost from the material since the time of its production; that is, the material is a closed system. If these assumptions are true, then the sample age and the model age are the same (**Figure 2**).

The model age of a material is reset when it is completely purified of decay products; therefore, a corollary assumption in model age determinations is that the sample was completely purified from decay products at the time that it was produced, so that the sample production age is the same as the purification age (**Figure 2**). Scenarios that will result in a model age older than the production age are (*a*) incomplete purification of decay products from material during production and (*b*) contamination of material with trace decay products during its production, history, or laboratory analysis. Contamination of material with decay products may be purposeful, with the goal of spoofing—that is, intentionally producing a material of a particular apparent age (e.g., Moody et al. 2014)—or it may simply be a byproduct of the environmental conditions under which a material was produced, used, stored, or analyzed.

Perturbation of the model age by loss of decay products from a sample, which would result in a model age younger than the production age, is unlikely when the material is in solid form. However, certain mechanisms may cause decay products to be lost from a liquid or gas sample. For example, hydrolysis of thorium or protactinium may form insoluble species that sorb to the
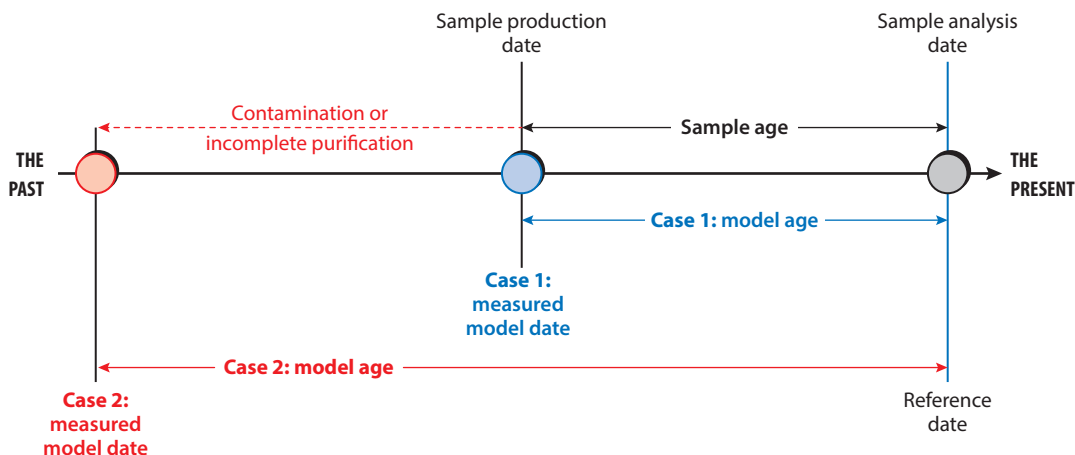
Figure 2

The model age of a sample is calculated from the measured daughter/parent or granddaughter/parent ratio of the sample. The model date for a sample is then calculated by subtracting the model age from the reference date, which typically is the date on which the sample was purified for analysis. In Case 1, the model age is the same as the sample age. In this case, the sample was completely purified from the relevant daughter and/or granddaughter nuclides at the time that the sample was produced, and has remained a closed system since that time. In Case 2, the model age is older than the sample age. In this case, either the sample was incompletely purified from daughter and/or granddaughter nuclides during production, or it was contaminated with daughter and/or granddaughter nuclides after it was produced.

walls of a vessel containing a uranium solution, thereby decreasing the apparent concentration of thorium or protactinium in the sample (Williams & Gaffney 2011).

In the absence of independent information about a sample's history, one does not know whether the assumptions involved in a model age calculation are correct. The analysis of multiple radiochronometers can provide a wider range of data on which to base the interpretation of a material's history than if the analysis is limited to a single isotopic system. If concordant model ages are determined with multiple radiochronometers, then the model age may be interpreted as the production age of the material with a high degree of confidence. Concordant model ages are observed in many uranium and plutonium reference materials that are commonly analyzed for validation of analytical methods (Wallenius & Mayer 2000, Nygren et al. 2007, Shinonaga et al. 2009, Eppich et al. 2013, Sturm et al. 2014). However, reference materials are produced with great care in controlled environments; real world samples produced in industrial facilities may not necessarily be expected to exhibit such ideal behavior.

In cases where multiple radiochronometers yield inconsistent model ages, an understanding of the behavior of parent and progeny elements during the relevant processes involved in material production may aid in inferring the sample history (Sturm et al. 2014, Kayzar & Williams 2016). At present, this understanding is very basic, and the interpretation of inconsistent model ages in a more rigorous manner will require further fundamental research on the behavior of uranium and plutonium and their decay products during nuclear material production processes.

Model ages of highly enriched uranium (HEU) determined for the Nuclear Forensics International Technical Working Group (ITWG) Round Robin 3 illustrate how discordant model ages can be used to constrain the timing of multiple events in the production history of a material (Hanlen 2011). The samples used in this exercise were pieces cut from the middle sections of two hollow cylindrical logs of HEU metal that were cast at known times (May 2003, January 2004)

from scrap uranium material of unknown age. Several participating institutions determined ^{230}Th-^{234}U model ages that were concordant with the known casting ages (Hanlen 2011). The observation that the ^{230}Th-^{234}U model ages were consistent with the casting dates of the uranium metal logs indicates that the uranium metal casting process effectively removes ^{230}Th from molten uranium metal, at least from the center of the casting from which these samples were taken. This chrono-metric observation is consistent with observations from industrial-scale uranium metal casting processes, in which Th diffuses through the molten uranium and is incorporated into the slag (Harrington & Ruehle 1959, Christofano & Harris 1960). For the Round Robin 3 samples, one laboratory reported ^{231}Pa–^{235}U model dates of 1974–1975, which are substantially older than the known casting dates (Hanlen 2011). This indicates that Pa was not removed from the molten uranium as effectively as Th and, further, that the scrap uranium used to produce the uranium metal logs may have been chemically purified as much as several decades prior to the casting of the uranium metal logs.

Kayzar & Williams (2016) measured the ^{226}Ra and ^{227}Ac granddaughters in the Round Robin 3 materials and found an excess of ^{227}Ac present in the samples (**Figure 3**). ^{227}Ac is a decay product of ^{231}Pa, so one possible explanation for this observation is that the excess ^{227}Ac is supported by excess ^{231}Pa. When corrected for the excess ^{231}Pa present in the system at the time of casting (as constrained by the ^{230}Th-^{234}U model age), the ^{227}Ac-^{235}U model age was concordant with the casting age of the material (Kayzar & Williams 2016). The ^{226}Ra-^{238}U model ages were 20–21 months older than the casting ages, indicating that most, but not all, Ra is removed from the
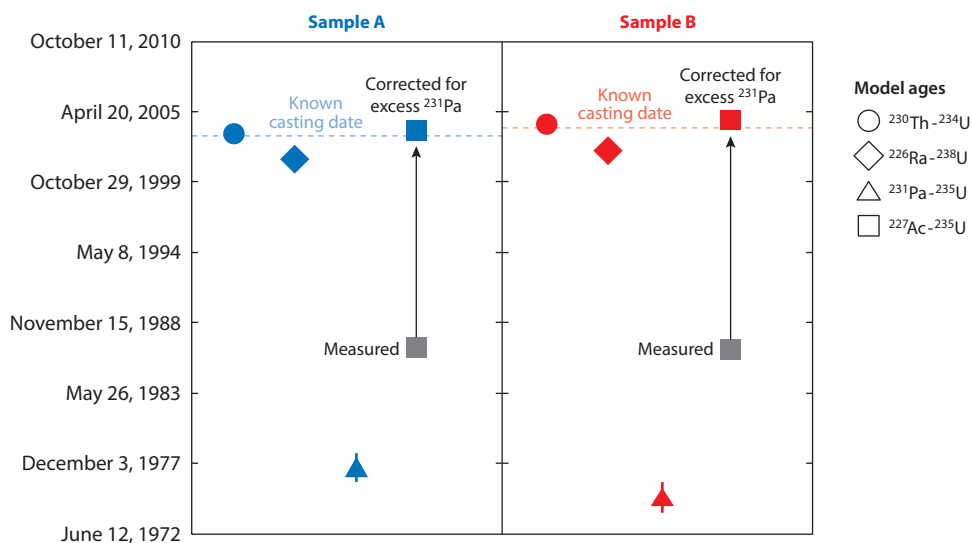

Figure 3

Model ages determined for two highly enriched uranium (HEU) metal samples (Samples A and B) from the Nuclear Forensics International Technical Working Group Round Robin 3; data are from Kayzar & Williams (2016). The dashed horizontal lines are the known casting dates of the two HEU logs analyzed for this collaborative measurement exchange. Analytical uncertainties are shown except when they are smaller than the symbol. The ^{230}Th-^{234}U model ages show good agreement with the known casting dates, indicating that the HEU was free of ^{230}Th at the time of casting. The ^{226}Ra-^{238}U and ^{231}Pa-^{235}U model ages are older, indicating that excess ^{226}Ra and ^{231}Pa were present in the HEU metal at the time of casting. The ^{227}Ac-^{235}U model age is also older than the casting date; however, when corrected for excess ^{231}Pa as determined from the ^{230}Th-^{234}U model age, the ^{227}Ac-^{235}U model age is in good agreement with the known casting date.

system during metal casting (Kayzar & Williams 2016). This example demonstrates that these daughter and granddaughter nuclides are fractionated from U to different extents during U metal casting processes; Th and Ac are essentially completely purified from U, whereas Ra and Pa are purified to a lesser extent. In an unknown forensic sample, the concordance of the ^{230}Th-^{234}U and corrected ^{227}Ac-^{235}U model ages would provide a greater degree of confidence that the model ages represent the production age of the material than if only one model age were determined. This work also illustrates the type of basic research on the behavior of decay products during U (and Pu) production processes that is needed to provide an experimental foundation on which to base interpretation of radiochronometry results of nuclear forensic samples.

Radioactive decay of Pu produces four isotopes of U (^{234}U-^{238}Pu, ^{235}U-^{239}Pu, ^{236}U-^{240}Pu, ^{238}U-^{242}Pu), and these four U-Pu pairs can be used together to constrain the Pu purification date as well as to characterize the isotopic characteristics of uranium contamination, if present, which in turn may be an additional useful signature for a nuclear forensic investigation. The ^{238}U-^{242}Pu system is generally not used in age determinations as the long half-life of ^{242}Pu (375,000 years), combined with the low ^{242}Pu abundance in most bulk plutonium materials and the high abundance of ^{238}U in natural uranium contamination, precludes its usefulness (Sturm et al. 2014). Typically, the ^{236}U-^{240}Pu system is the least likely to be affected by postproduction disturbance or contamination. This is because ^{240}Pu has a relatively short half-life (6,563 years), and the ^{236}U/^{240}Pu ratio therefore changes relatively quickly, but also because ^{236}U is either absent or present in very low abundance in natural and low-enriched uranium (LEU) (Richter et al. 2005, 2008). As a result, contamination of bulk plutonium with natural uranium or LEU will only minimally affect this ratio (Sturm et al. 2014). Therefore, in some cases, it may be assumed that the ^{236}U-^{240}Pu model age represents the production age of the material; a consistent ^{241}Am-^{241}Pu model age provides support for this assumption. From this, excess ^{234}U, ^{235}U, and ^{238}U in the sample may be calculated, and the uranium isotope ratios can then be used to constrain the characteristics of the contaminant (Sturm et al. 2014).

An analogous approach was used in an investigation of Manhattan Project–era plutonium discovered buried in a glass jug in a waste trench at the Hanford site in Washington State (Schwantes et al. 2009). The jug contained hundreds of milligrams of Pu, and radiochronometry analyses were made, among other analyses, in the attempt to identify the origin and history of this material. There are three potential sources for the U present in this sample: (*a*) U produced by radioactive decay of Pu, (*b*) U derived from irradiated reactor fuel that was not completely separated from Pu during reprocessing, and (*c*) natural U derived from the local environment. Historical records indicated that US plutonium production reactors operating at the time were using natural uranium fuel, and reactor modeling indicated that reactor operations would not have substantially modified the isotopic composition of the uranium fuel (Schwantes et al. 2009). Therefore, any uranium present that was not produced by radioactive decay is expected to have a near-natural uranium isotopic composition. Although ^{242}Pu results were not reported for this sample, ^{242}Pu production under these reactor conditions is expected to be negligible. Thus, all ^{238}U present in this material was derived from either the U fuel or the local environment. In contrast, because ^{236}U is generally undetectable in natural U, it can be confidently assumed that all ^{236}U present in this material was formed by in situ radioactive decay of ^{240}Pu. With these constraints, the amounts of ^{234}U and ^{235}U resulting from radioactive decay of ^{238}Pu and ^{239}Pu were calculated, and the ^{234}U-^{238}Pu, ^{235}U-^{239}Pu, and ^{236}U-^{240}Pu isotope systems were used together to determine a production date of 1946 ± 4.5 years (Schwantes et al. 2009). The absence of detectable ^{241}Pu in this sample is consistent with this age. Because of its short half-life (∼14 years), any ^{241}Pu originally present in the sample in ∼1946 would have nearly completely decayed in the intervening ∼60 years. The model age determined for this Pu material, together with its isotopic composition at that time, was compared to

historical records of US reactor operations between 1944 and 1950 to conclude that this plutonium was produced in 1944 at the X-10 reactor in Oak Ridge, Tennessee (Schwantes et al. 2009).

Summary

Because of the predictive ability of radiochronometry, the model age of nuclear material has the potential to yield definitive constraints on the production history of a sample, in terms of when it was produced as well as what processes were used in its production. The model age is best utilized as a predictive signature for nuclear materials that are highly purified, such as U or Pu metals and oxides (e.g., Wallenius & Mayer 2000, Wallenius et al. 2002, Williams & Gaffney 2011). For materials that are less pure, such as UOCs, or samples for which the source material was purified much earlier than the sample production date, the model age is expected to be slightly to significantly older than the production age (Hanlen 2011, Varga et al. 2011b). In this case, the model age can constrain the maximum age of a material and also serve as a comparative signature in establishing a common origin for different materials. This requires that data from comparator samples are available for use in the forensic investigation.

NUCLEAR FORENSIC CASEWORK

Casework provides the ultimate showcase for research and development in nuclear forensics. In the end, if the research and development does not advance our ability to derive conclusions of relevance to law enforcement or nuclear security from our analysis of nuclear material, then it will have been a wasted effort. Unfortunately, many nuclear forensic cases are not publicized due to law enforcement sensitivities or nuclear security concerns. However, enough work has been published to gain suitable insight into the state of practice in nuclear forensics. In this section we review examples of nuclear forensics casework on international seizures, laboratory exercise samples, and historical and geologic materials (**Figure 4**).

International Seizures

The importance of nuclear forensics is, perhaps, best demonstrated by uranium seizures in Rousse, Bulgaria (1999); Paris, France (2001); and Chisinau, Moldova (2011). Niemeyer & Hutcheon
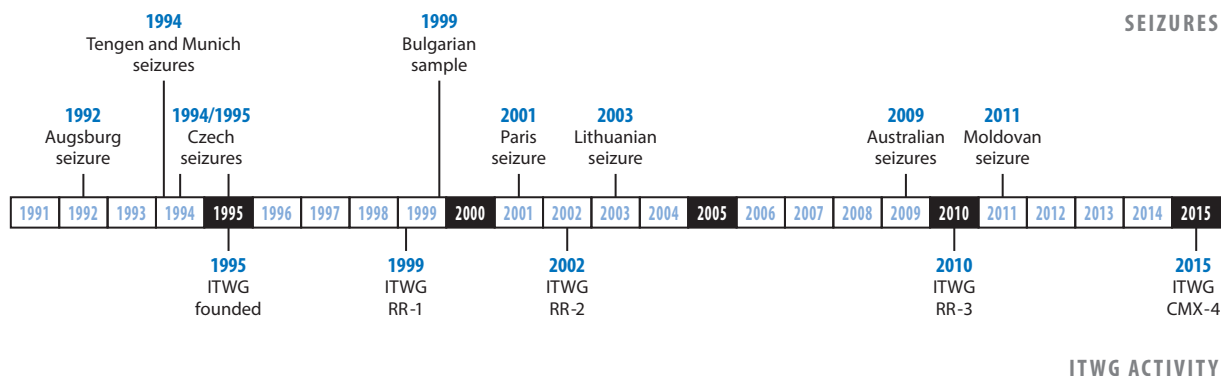

Figure 4

Timeline of international seizures and laboratory exercises mentioned in this review. Actual seizures are listed above the timeline; international events and exercises are listed below the timeline. Abbreviations: ITWG, Nuclear Forensics International Technical Working Group; RR, Round Robin; CMX, Collaborative Materials Exercise.

(2002) and Moody et al. (2014) described the analysis of the Bulgarian seizure material, and Baude (2008) and Baude et al. (2008) described the analysis of the Paris seizure material. Both laboratories in which this work was performed [Commissariat à l'Energie Atomique (CEA) in the Paris case and Lawrence Livermore National Laboratory (LLNL) in the Bulgarian case] determined the stoichiometry of the material (U_3O_8), the isotopic composition of the uranium, the level of trace impurities, the level of residual radionuclides, and the radiochronometric age of the material. Most of the measurements were consistent between the two laboratories and suggested that the source of the material was an HEU-fueled (∼90% enriched) research reactor, whose fuel had been irradiated to ∼300,000 MWd/t then reprocessed and converted to U_3O_8 powder. The radiochronometric model dates of the two materials, however, differed by ∼1 year (October 30, 1993 ± 50 days for the Bulgarian sample versus November 1994 ± 100 days for the Paris sample), well outside the uncertainty of the analyses. This difference in model dates suggests that the same or similar material was reprocessed in batches at two separate times.

In both cases, the laboratories analyzed the lead container, paraffin wax, and borosilicate glass associated with the seizures. In addition, the CEA researchers analyzed polyurethane foam associated with the Paris seizure, which was not found in the Bulgarian seizure, and LLNL researchers analyzed paper associated with the Bulgarian seizure. The analysis of these associated materials suggested an origin in Eastern Europe. In addition, the remarkable similarity of both the nuclear material (U and Pu isotopic composition, trace elemental composition) and the associated packaging (homemade Pb container, yellow waxy interior) between the two cases, despite the fact that the seizures occurred 2 years and over 1,500 miles apart, provided strong evidence of a cache of nuclear material outside of regulatory control (**Figure 5**). Although the material analysis of the Moldovan seizure has not been reported, the similarity of its packaging material to those of the Bulgarian and French seizures is troubling (Zaitseva & Steinhäusler 2014).

Researchers at the Institute for Transuranium Elements (ITU) in Karlsruhe, Germany, have been at the forefront of the development of nuclear forensics and analyzed most of the nuclear material seized in Germany and central Europe in the mid-1990s. Several cases, such as the 1992 Augsburg seizure (Mayer et al. 2007) and 2003 Lithuania seizures (Wallenius et al. 2006), involved the seizure of uranium oxide fuel pellets. In their analysis of the fuel pellets from the Augsburg seizure in 1992, ITU researchers measured the pellet mass and dimensions, determined the U assay with potentiometric titration, measured the U isotopic composition by TIMS, and used optical microscopy for determining macroscopic parameters. In this case, attribution of the source of the pellets was based upon expert interpretation and a search of the open literature, which identified the fuel pellet as intended for a Russian-type RBMK reactor, produced either in Moscow (by the Elektrostal Plant) or in Ust-Kamenogorsk, Kazakhstan (by the Ulba Metallurgial Plant). In their analysis of the fuel pellets from the Lithuanian Seizures in 2003, the ITU researchers added gamma spectrometry for initial measurement of the U isotopic composition, ICP-MS (in addition to TIMS) for measurement of U isotopic composition, hybrid K-edge densitometry and isotope dilution mass spectrometry (in addition to potentiometric titration) for measurement of the U assay, sector field ICP-MS for determination of trace impurities, and measurement of radiochronometric model age (12.6 ± 0.8 years relative to the analysis date of June 16, 2003). At that point, the attribution of the source of the pellets could be referenced to a database of dimensions, U isotopic composition, and impurities for European and Russian reactor fuel (the ITU-Bochvar database on fuel pellets) (Dolgov et al. 1997). The pellets were identified as intended for a Russian-type RBMK-1500 produced at the Elektrostal Plant in Moscow.

The other common form of interdicted nuclear material is oxide powder. Wallenius et al. (2006, 2007) documented analyses of a number of such seizures, including the 1994 Tengen, 1994 Munich, and 2003 Czech seizures. The Tengen and Munich seizures were notable for the

1999 Rousse, Bulgaria, seizure

2001 Paris, France, seizure
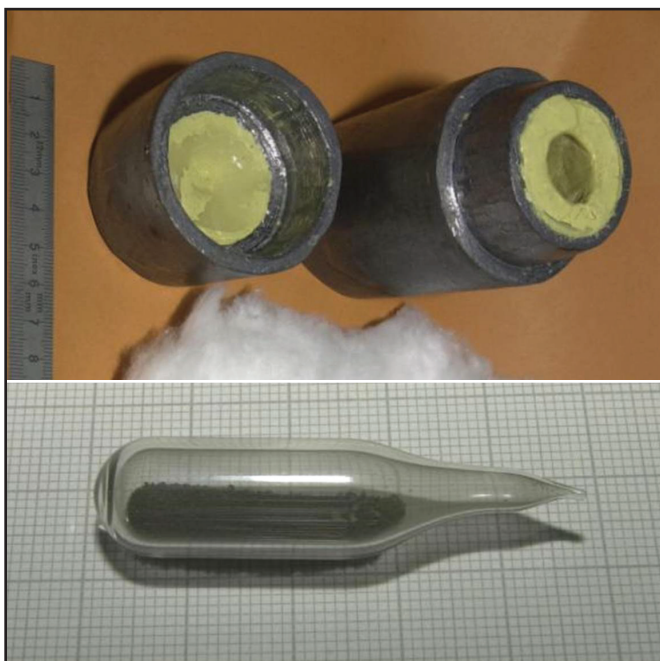
Figure 5

Images of the uranium oxide seizures from Rousse, Bulgaria (1999), and Paris, France (2001). The nuclear material and associated packaging are remarkably similar.

presence of Pu mixed with U and/or other compounds. Work at the ITU revealed that the Tengen material was 10 wt% Pu mixed with Hg, Sb, I, Ga, and O. It also showed that the Pu was 99.75 wt% ^{239}Pu, which is often known as ivory-grade Pu due to its extremely low ^{240}Pu content. The Munich material was 64.9 wt% Pu and 21.7 wt% U. The Pu was determined to be 87.58 $\pm$ 0.16 wt% ^{239}Pu and 10.78 $\pm$ 0.04 wt% ^{240}Pu. The uranium was LEU (1.606 $\pm$ 0.001 wt% ^{235}U). Measurements on individual grains made using SIMS were consistent with a uniform composition from particle to particle. The ITU researchers also performed age dating using a variety of radiochronometers and found a production date around the end of 1979 $\pm$ 0.5 years. Both the Tengen and Munich materials were highly unusual, possibly mixtures of original materials. The materials from each of the Czech seizures were uranium oxide powders, all generally consistent with one another, possibly originating from the same batch of material. The ITU researchers performed gamma spectrometry for initial determination of the enrichment level (89.59 $\pm$ 0.43 wt% ^{235}U), both TIMS and multicollector inductively coupled plasma mass spectrometry (MC-ICP-MS) for more precise determination of the isotopic composition of the U, SIMS for assessment of isotopic homogeneity of the material from particle to particle, potentiometric titration for the U assay, sector field ICP-MS for trace impurity content, scanning electron microscopy for particle morphology, and radiochronometry (August 1976 $\pm$ 3 years). In the cases of U and Pu powders, the ITU researchers were unable to be specific regarding the origin and intended use of the material, primarily because uranium oxide powder normally exists as an intermediate product, and suitable nuclear forensic databases for these types of materials

do not exist. However, such nuclear forensic analyses are useful for excluding a great many possibilities for origin of the material, even if they cannot uniquely identify a certain facility.

In addition to their early work on the Bulgarian sample, researchers at LLNL reported on the analysis of several materials used in nuclear scams or hoaxes. For example, Grant et al. (1998) reported on the analysis of a sample of material purported to be red mercury. Red mercury is a fictional substance at the center of a number of hoaxes. It has been purported to be a poisonous, odorless, tasteless, water-insoluble scarlet red powder that is supposedly of interest for many military systems, including nuclear weapons. X-ray fluorescence analysis showed this material to be predominantly Hg, with minor amounts of Cd, Ag, and Zn. As another example, Grant et al. (1998) analyzed a U metal part offered for sale as nuclear weapon material. Electron microprobe analysis determined that the material was, in fact, a U alloy with 10 wt% Mo. Both gamma spectrometry and X-ray fluorescence analyses indicated that the material also had a thin Ni coating. The LLNL researchers used forensic radiochemistry to determine that it was primarily U, but with a depletion level of $\sim$0.3 wt% ^{235}U. Radiochronometry determined the date of last purification to be 1961 $\pm$ 3 years. They determined that the sample was most likely a counterweight assembly made of depleted uranium. Counterweights are heavy masses used in aerodynamic control systems to maintain an aircraft's center of gravity; the high density of depleted uranium allows a compact size, small in comparison with the steering surfaces.

In addition, Moody & Grant (1999) reported on the analysis of a thorium oxide sample seized in a raid on a drug laboratory. Thorium oxide can be used to catalyze the production of phenyl-acetone from phenylacetic acid and acetic acids. LLNL researchers used a comprehensive radio-chemical isolation procedure, including sample dissolution, chemical separation, and nuclear counting techniques, to analyze a sample of thorium oxide provided by the US Drug Enforcement Agency. They found that the Th derived from an ore with a U/Th ratio consistent with the mineral monazite and that the Th was likely recovered from the ore through an acid leach process. They also determined a date of last chemical purification of May 1, 1978 $\pm$ 0.3 years. These results were consistent with the limited information provided by a possible commercial Th supplier.

In 2011, researchers at the Australian Nuclear Science and Technology Organisation (ANSTO), in collaboration with LLNL, analyzed a set of three samples seized in two separate drug raids. One case occurred in Victoria (Kristo et al. 2015), where two unusual samples with depleted uranium isotopic compositions were seized. The samples were thoroughly analyzed at both ANSTO and LLNL for stoichiometry, trace elemental composition, U isotopic composition, particle morphology, and radiochronometry. Although a specific origin for the samples could not be identified, they clearly originated outside Australia, because Australia has never had a uranium reprocessing capability. The materials were probably imported legitimately into Australia for commercial or scientific purposes but then fell outside regulatory control at some point. The model production date determined by radiochronometry for one of the samples ($\sim$1935) predated the nuclear era (i.e., was anomalously old), indicating that the material had not been completely purified or that contamination of the material with ^{230}Th and ^{231}Pa had occurred. The second sample yielded a model production date of $\sim$1962, unexpectedly old but plausible (within the nuclear era). A second Australian seizure occurred in New South Wales (Keegan et al. 2014), where a small glass jar labeled "Gamma Source" and containing a green powder was obtained. As with the previous seizure, the sample was thoroughly analyzed at both ANSTO and LLNL for stoichiometry, trace elemental composition, U isotopic composition, particle morphology, and radiochronometry. The ANSTO and LLNL researchers were able to identify the material as UOC from the defunct Mary Kathleen mine in Australia. The production date, as determined by ^{230}Th age dating, was January 17, 1964 $\pm$ 233 days.

Laboratory Exercise Samples

In addition to actual casework, which occurs randomly and (hopefully) infrequently, nuclear forensic practitioners around the world have come to rely on the Collaborative Materials Exercises conducted by the ITWG for keeping their skills in good practice. The ITWG is an informal, unaffiliated association of nuclear forensics practitioners that conducts outreach and identifies, develops, and promotes best practices in the field of nuclear forensics. These Collaborative Materials Exercises have been an important activity of the ITWG from its early days.

The first exercise, held in 1999–2000, featured reprocessed plutonium oxide material originating from a batch of three pressurized water reactor fuel elements irradiated in a 1,890-MWth European reactor with an initial enrichment of 3.28 wt% ^{235}U (Dudder et al. 2003b). Six laboratories from the United States and Europe participated in this exercise. A number of analytical techniques were applied in this exercise. One of the important outcomes was a prioritized list of techniques and time frames in which they should be applied in a nuclear forensics case. This prioritized list was incorporated in the IAEA report *Nuclear Forensics Support* (IAEA 2006). Researchers in one of the laboratories were able to specifically identify the origin of the material, because of their access to relevant fuel cycle records. This finding brought home the importance of databases relevant for nuclear forensics.

The second exercise was held in 2000–2002, somewhat delayed in the aftermath of the terrorist attacks of September 11, 2001 (Dudder et al. 2003a,b). The material was an HEU oxide powder (nominally 90 wt% enriched in ^{235}U) provided by the Czech Republic. Nine laboratories from the United States and Europe participated. The techniques and methods applied included radiological (dose rate, surface contamination, radiography), physical (visual, photography, massing, dimensions, optical microscopy, density measurements, scanning electron microscopy, X-ray diffraction, transmission electron microscopy), classical forensics (fingerprints), isotopic analysis (gamma spectrometry, alpha spectrometry, TIMS, MC-ICP-MS), and elemental analysis (ICP-MS, X-ray diffraction, isotope dilution mass spectrometry, ion chromatography). In the absence of a database similar to that utilized in the first exercise, each laboratory's ability to derive specific conclusions as to the origin of the material was limited (Dudder et al. 2003a,b).

The third exercise was a paired-comparison analytical exercise involving two HEU metal pins provided by the Y-12 National Security Complex in the United States. Nine laboratories in the United States, Canada, and Europe participated. The techniques and methods applied were similar to those in the second exercise described above. The key findings were the importance of physical measurements (mass, dimensions) for solid samples, as well as the importance of understanding the assumptions behind radiochronometry, as discussed earlier in this review (Hanlen 2011, Kristo & Tumey 2013). Because the two previous exercises had involved powder samples, the participating researchers had to adjust the prioritization of their techniques to take advantage of the intact fuel pins before aliquoting them for destructive analysis. Through the use of ^{230}Th age dating, researchers in several of the laboratories determined a production date in accordance with the date of metal casting, indicating that the Th in the aged materials had migrated out of the center of the casting, from which the pins were cut, into the so-called hot top, the slag that formed at the top of the molten uranium. However, results from one laboratory indicated that the ^{231}Pa model production dates were earlier, indicating that the U-Pa chronometer had not been reset by casting.

Historical and Geologic Materials

One of the earliest nuclear forensic investigations may be the investigation that resulted in the discovery of the Oklo reactor, a geologic uranium deposit that had naturally undergone fission

(Cowan 1976, Roth 1977). In 1972, processed uranium ores in France were discovered to be deficient in ^{235}U, raising the possibility that large quantities of ^{235}U, estimated to be 200 kg, had been clandestinely diverted. Mass spectrometry was used to characterize the uranium isotope signatures as well as the fission product signatures in these materials. These results, combined with process records, were used to trace the uranium isotopic discrepancy back to a specific set of mines located in the Oklo uranium deposits in Gabon. This investigation led to the conclusion that a remarkable alignment of natural conditions led to the formation of a nuclear reactor nearly two billion years ago.

Nuclear forensic investigations have also been conducted to identify and understand nuclear materials of historical importance. Mayer and coworkers at ITU have performed nuclear forensics analysis of two metal objects reportedly related to early German research into nuclear reactors (Mayer et al. 2011a,b, 2015). The first object was a cube of natural U ($\sim$2.7 kg), suspected to be a residual element from an experimental reactor under development as a part of a secret German program led by Werner Heisenberg to develop nuclear weapons during World War II. The second object was natural U metal plate ($\sim$2 kg) suspected to be a part of another experimental reactor being developed in the German nuclear program by Karl Wirtz. Uranium isotopic analysis by TIMS confirmed that the U metal was of natural isotopic composition. At the time of the German program, there were two likely sources of U ore—Joachimstal (now in the Czech Republic) and the Belgian Congo. Analysis of the REE pattern and Sr isotopic ratio in both the Heisenberg Cube and the Wirtz Plate were consistent with each other and with source material from Joachimstal and not from the Belgian Congo. ^{230}Th radiochronometry resulted in a model production date of September 1943 $\pm$ 0.5 years for the Heisenberg cube and August 1940 $\pm$ 0.2 years for the Wirtz plate, both consistent with the time frame of the German nuclear program.

Researchers at Pacific Northwest National Laboratory (PNNL) applied nuclear forensic techniques in an interesting study of Pu-containing material (determined to be trace Pu in a LaF_3 solid phase in a dilute HNO_3 solution) in an old glass jug found in an abandoned safe at the Hanford site in Washington State (Schwantes et al. 2009). The PNNL researchers applied nuclear counting methods (gamma and alpha spectrometry), inductively coupled plasma optical emission spectrometry, ICP-MS, ion chromatography, and radiochronometry to the residual Pu material. They determined a model production age of 61.6 $\pm$ 4.5 years (relative to an analysis date of July 2007), consistent with Pu from the early days of the US nuclear program. Trace elements found in the materials were consistent with the bismuth phosphate process in use during that time. The trace isotopes in the Pu were consistent with irradiation of natural U in the X-10 reactor in Oak Ridge. They concluded that the material was part of the first batch of Pu separated at the T-Plant at Hanford. PNNL researchers also described how the production of ^{22}Na from ^{19}F in the LaF_3 could be useful in determining the time since sample splitting.

Similarly, Meyers (2013, 2014) explored the model ages and origins of U metal samples taken from an abandoned U processing site used for rolling U rods in the 1940s and 1950s. MC-ICP-MS was used to measure both the isotopic composition of the U and the ^{230}Th radiochronometric age. It was found that the U was of natural isotopic composition and that the production date was July 1950 $\pm$ 1.5 years.

Finally, Tandon et al. (2009) were able to deduce the irradiation history of some historical reactor targets from past Pu production testing. Gamma spectrometry, X-ray diffraction, TIMS, radiochemistry, interstitial case gas analysis, inductively coupled plasma atomic emission spectroscopy, and ICP-MS were performed on the samples. After these analyses, reactor modeling was used to corroborate analytical findings with historical records. It was found that model irradiation dates were consistent with historical records for the material, but that calculated irradiation durations were longer than indicated in those records.

CONCLUSIONS

Nuclear forensic science has undergone significant advances in both the analytical methods that are employed and the interpretation of resulting data in the two decades since research and development began. Despite this progress, no single parameter has yet been identified that is able to discern the identity and origin of unknown UOC samples. Increasingly, combined isotopic fingerprinting approaches are used to constrain the provenance and processing history of samples, and multivariate statistical techniques are used to discriminate between different sources of UOCs (Keegan et al. 2008, 2012, 2014; Bayne et al. 2009; Robel et al. 2009, 2011; Sirven et al. 2009; Varga et al. 2010). Likewise, approaches to chronometry have evolved over time, toward an increasing emphasis on obtaining concordant results from multiple parent, daughter, and granddaughter systems. These efforts continue to improve the accuracy and scope of inferences that can be drawn from isotopic measurements.

Several avenues of productive research are identified in this review. A major limitation of work on UOC forensics to date is that many studies utilize a common set of historic UOC samples. Future work on UOC forensics will likely utilize a wider set of unknown samples, with additional development of more robust isotopic signatures that incorporate new isotopic systems. With respect to chronometry, basic research on the chemical fractionation of decay products during uranium and plutonium production methods is needed in order to provide a more quantitative basis for the interpretation of a sample history from model ages. The examples discussed in this review illustrate that inconsistent model ages determined using multiple radiochronometers do not necessarily mean that one of the results is wrong but rather may indicate that the model age assumptions are not met, either because the material was not completely purified from decay products at the time of material production or because contaminants were added to the material after production. Basic research will provide the ability to understand why an assumption may not be met, and how this can lead to a more detailed interpretation of a sample's history.

Analytical protocols and data analysis methodologies that are developed for geochemical applications are continuously utilized in nuclear forensics research. Although these approaches require unique adaptations to address the specific problems and materials involved in nuclear forensics, they highlight the importance of geochemistry to the development of the field. As new techniques for isotopic fingerprinting and chronometry are developed in geochemical studies and validated for applications to nuclear forensics, it is to be hoped that conclusions of relevance to law enforcement and nuclear security continue to expand.

DISCLOSURE STATEMENT

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